X-RAY STUDIES OF DEFECTS IN
DIAMOND AND GALLIUM ARSENIDE

by

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FRONTISPIECE

COMPUTER GENERATED 'BINARY' IMAGE OF PLATELETS IN DIAMOND (SEE SEC. 6.4.3)
Unusual social stress in South Africa, and the impact. The data collected in this study have been compared using a range of statistical methods. These methods included (but were not limited to) regression analysis, ANOVA, and correlation. The results showed that certain variables were significantly associated with the outcome measures. This suggests that further research is needed to understand the underlying mechanisms.
ABSTRACT

Diamonds from mines in South Africa, and the Argyle Mine in Western Australia, have been compared using synchrotron transmission Laue photography (Laue topography), and the Argyle stones were found to be more variable in quality. By measuring the asterism of the Laue spots, quantitative estimates of lattice distortion have been made. The various types of crystal distortion, and their effects on Laue patterns, have been considered, and it has been determined that distortion in the Argyle diamonds primarily takes the form of mosaic structure.

A modification of the technique of x-ray spike topography, where parts of the specimen were obscured by a tantalum screen, has been used to estimate platelet dimensions at different positions in type Ia diamonds. Direct measurements of the platelets in some of the samples have been made from transmission electron micrographs, and show that the method is reasonably reliable for platelets below about 400 Å in diameter. In the range 1361.3 to 1371.3 wavenumbers, a correlation has been confirmed between 'platelet peak' position in the infrared spectrum and platelet size, in the sense of smaller wavenumbers being associated with larger platelets.
Topographs of gallium arsenide wafers, used for device fabrication, have been taken. A dislocation lineage has been studied in a (100) wafer with field effect transistor arrays fabricated onto it. It has been found to cause a drop of approximately 40 mV in the pinch-off voltage of transistors it touches. The feature has been shown to have an associated Burgers vector of the 211-type, and to be accompanied by a lattice tilt in the wafer of nearly 30".

Previous work in each area of investigation is reviewed, and brief introductions on diamond and gallium arsenide given, together with introductions to the techniques of topography, using both characteristic x-rays and synchrotron radiation.
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CONTENTS

ABSTRACT 3

ACKNOWLEDGEMENTS 5

LIST OF FIGURES 18

LIST OF TABLES 27

CHAPTER 1 INTRODUCTION, X-RAY TOPOGRAPHY AND RADIATION SOURCES 29

1.1 OUTLINE OF THESIS 29

1.2 X-RAY TOPOGRAPHY 32

1.2.1 The Technique 32

1.2.2 Methods of Topography 34

1.2.3 Topography using Conventional Characteristic Radiation 34

1.2.3.1 Characteristic x-rays 34

1.2.3.2 The apparatus 35

1.2.3.3 Reflection projection topography 36

1.2.3.4 Transmission section and projection topography 38

1.2.3.5 Spike topography 40

1.2.4 Synchrotron Radiation Topography 40

1.2.4.1 The source of synchrotron radiation 40

1.2.4.2 The topography stations 43
PART I
AN X-RAY STUDY OF LATTICE DISTORTION IN DIAMOND

CHAPTER 2
DIAMOND - WITH OBSERVATIONS ON STONES FROM THE ARGYLE MINE

2.1 INTRODUCTION

2.2 DIAMOND

2.2.1 Properties, Structure and Morphology

2.2.2 Classification of Diamond

2.2.3 Genesis of Diamond

2.3 DIAMONDS FROM THE ARGYLE MINE, WESTERN AUSTRALIA

2.3.1 The Argyle Mine

2.3.2 Argyle Diamonds

2.3.3 Observations on a Sample of Argyle Stones
CHAPTER 3  THE LAUE METHOD AND THE PERFECTION OF DIAMOND  66

3.1  OUTLINE OF CHAPTER  66

3.2  THE LAUE METHOD  66

3.3  WHOLE CRYSTAL SYNCHROTRON LAUE TOPOGRAPHY  74

3.3.1  Introduction  74

3.3.2  The Diamonds  74

3.3.3  Experimental Details  75

3.3.4  The Laue Categories  76

3.4  ASTERISM  81

3.4.1  The Effect  81

3.4.2  Causes of Asterism  82

3.4.2.1  Elastic lattice bending  82

3.4.2.2  Polygonization  83

3.4.2.3  Bent glide lamellae  85

3.4.2.4  Local curvature  85

3.4.2.5  Deformation and kink bands  86

3.4.2.6  Mosaic spread  87

3.4.3  Other Causes of Laue Spot Streaking  89

3.4.3.1  Crystallite size effect  89

3.4.3.2  Thermal asterism  91

3.4.3.3  Spikes  91

- 9 -
4.1.5 Giant Platelets 124
4.1.6 <111> Spikes 124
4.2 SPIKE TOPOGRAPHY 125
4.3 THE WORK WHICH FOLLOWS 128

CHAPTER 5 X-RAY SPIKE TOPOGRAPHY OF TYPE Ia DIAMOND 129
5.1 INTRODUCTION 129
5.2 THE METHOD FOR TAKING SPIKE TOPOGRAPHS 129
5.2.1 Aim 129
5.2.2 The Basic Set-up 130
5.2.3 Choice of Radiation 130
5.2.4 Direction of Angular Mis-Setting 131
5.2.5 The Images on a Spike Topograph 132
5.2.6 Specimen to Film\Plate Distance 132
5.2.7 The Snare of the 111 Reflexion 135
5.2.8 Cutting the Spike Orthogonally 136
5.2.9 Exposure and Development 136
5.3 DETERMINING PLATELET SIZE FROM SPIKE TOPOGRAPHS 137
5.3.1 The Relationships 137

- 11 -
5.3.2 The Microdensitometry 137
5.4 SHADOWED SPIKE TOPOGRAPHY 140
5.5 DETAILS OF THE PRACTICAL WORK DONE 142
5.5.1 The Specimens 142
5.5.2 The Topography and Results 144
5.6 SYNCHROTRON SPIKE TOPOGRAPHY 149
5.7 CONCLUDING REMARKS 153

CHAPTER 6 TRANSMISSION ELECTRON MICROSCOPY OF TYPE Ia DIAMOND 154
6.1 INTRODUCTION 154
6.2 SPECIMEN PREPARATION 155
6.2.1 Purpose 155
6.2.2 The Initial State of the Specimens 155
6.2.3 Mechanical Thinning 155
6.2.4 The Performance of the Three Specimens 157
6.2.5 Mounting the Specimens for Ion Beam Thinning 158
6.2.6 The Ion-Beam Thinning 159
6.3 THE ELECTRON MICROSCOPY 160
6.3.1 Principles 160
PART III

A TOPOGRAPHIC STUDY OF GALLIUM ARSENIDE USED FOR
DEVICE FABRICATION

CHAPTER 8

FIELD EFFECT TRANSISTORS ON GALLIUM ARSENIDE 204

8.1 INTRODUCTION 204

8.2 GALLIUM ARSENIDE 205

8.2.1 The Material 205

8.2.2 Growth of GaAs for Device Fabrication 207

8.2.3 Electrical Uniformity across GaAs Wafers 208

8.2.4 Dislocations in GaAs Wafers 209

8.3 THE FIELD EFFECT TRANSISTOR 211

8.3.1 The Device 211

8.3.2 Operation and Pinch-off Voltage 211

8.3.3 The GaAs MESFET 214

8.3.4 MESFET Fabrication 216

8.4 RESEARCH ON THE UNIFORMITY OF MESFET
FABRICATION 218

8.4.1 Uniformity of Pinch-off Voltage 218

8.4.2 Effect of Dislocation Density on Pinch-off
Voltage 219

8.4.3 The Proximity Effect 219
8.4.4 Effects near Lineage Features 220
8.4.5 The Proximity Effect Controversy 221
8.4.6 The Dislocation Associated Causes of Pinch-off Voltage Variation 222

CHAPTER 9 X-RAY TOPOGRAPHY OF GALLIUM ARSENIDE WAFERS 224

9.1 INTRODUCTION 224
9.1.1 Synopsis of Chapter 224
9.1.2 The Context of the Current Work - Previous Topography 225

9.2 TOPOGRAPHS OF GALLIUM ARSENIDE WAFERS 227
9.2.1 The 511-Type Reflexion Projection Topograph 227
9.2.2 Descriptions of some Topographs 231
9.2.3 Wafer 5 and Topographs 234
9.2.4 Topographs of Wafer 6 239

9.3 STUDY OF THE LINEAGE FEATURE 242
9.3.1 The Lineage Feature 242
9.3.2 Note on the Condition of Wafer 5 242
9.3.3 Topographs of the Lineage Feature taken in Different Reflexions 243

- 15 -
9.3.4 Reflexion Topographs of the Lineage Feature taken with Synchrotron Radiation 246

9.3.5 Synchrotron Radiation Transmission Topographs of the Lineage Feature 247

9.3.6 The Burgers Vector of the Lineage Feature 249

9.3.7 The Nature of the Lineage Feature 252

9.4 LATTICE MISORIENTATION ACROSS THE LINEAGE FEATURE 253

9.4.1 Topographic Evidence 253

9.4.2 Measurement of the Lattice Tilt 253

9.5 EFFECT OF LINEAGE FEATURE ON FETS FABRICATED ON THE WAFER 260

9.5.1 Measurement of the Pinch-off Voltages 260

9.5.2 Variation in Pinch-off Voltage across the Wafer 261

9.5.3 Pinch-off Voltages in the Proximity of the Lineage Feature 261

9.6 THE LINEAGE FEATURE IN GALLIUM ARSENIDE, AND ITS EFFECTS 268
# LIST OF FIGURES

| Frontispiece | Computer Generated 'Binary' Image of Platelets in Diamond (see sec. 6.4.3) | 2 |
| 1.1 | Berg's Topography Technique | 37 |
| 1.2 | Topographic Arrangement of Barth & Hosemann | 37 |
| 1.3 | The Principle of the Methods of Section and Projection Topography | 39 |
| 2.1 | One Cubic Unit Cell of the Diamond Structure | 54 |
| 2.2 | Morphology and Colour of Argyle Diamonds Obtained by Hall & Smith (1984) | 61 |
| 2.3 | Morphology and Colour of the 'Run of Mine' Sample of Argyle Diamonds | 61 |
| 2.4 | Scanning Electron Micrographs of Argyle Diamonds | 64 |
| 3.1 | Scheme of the Original Set-up of Friedrich and Knipping's Experiment | 67 |
| 3.2 | A Synchrotron Laue Photograph of a Diamond with the Incident Beam Directed along a 4-fold Axis of Rotational Symmetry | 69 |
3.3 A Synchrotron Laue Photograph of a Diamond with the Incident Beam Directed along a 3-fold Axis of Rotational Symmetry

3.4 A Synchrotron Laue Photograph of a Diamond with the Incident Beam Directed along a 2-fold Axis of Rotational Symmetry

3.5 Examples of the Eight Laue Categories

3.6 Scanning Electron Micrographs of Diamonds belonging to some of the different Laue Categories shown in Fig.3.5

3.7 Distribution in Quality of Diamonds from Samples obtained from different Mines, based on the Laue Photograph Classification shown in Fig.3.5

3.8 Reflection of White Radiation by Bent and Polygonized Lattices (Schematic)

3.9 a) Bent Glide Lamellae
   b) Bulk Bending

3.10 Burger’s Suggested Mechanism for Producing Local Curvature

3.11 Sketch Illustrating Local Curvature at a Slip Plane

3.12 Schematic Diagram of a Kinked Crystal
3.13 Extension and Compression of a Crystal produced by Kink Bands

3.14 Geometry of Reflexion from a Finite Size Crystal with Bent Bragg Planes of Radius of Curvature r

3.15 The Measurements to be Taken from the Film

3.16 Diagram showing some of the Parameters which appear in the Equations

3.17 Simulated Laue Patterns of Diamond (reduced 50%) showing 111-type spots only

3.18 Pinhole Laue Picture of a Fairly Undistorted Specimen (Category A)

3.19 Pinhole Laue Picture of a Somewhat Distorted Specimen (Category C)

3.20 Pinhole Laue Picture of a Specimen of Category H - no good for measurement

3.21 Effect of Lattice Distortion on the Shape of a Transmission Laue Spot

3.22 Effect of Lattice Distortion on the Shape of a Back-Reflection Laue Spot

4.1 Representation in Reciprocal Space of Spike-Like Extensions of Reflecting Power along <100> Directions
4.2 A Synchrotron Laue Photograph of a Type Ia Diamond Showing the Spikes Associated with the 111-Type Spots 118

4.3 Lang’s Platelet Model 122

4.4 The Double Nitrogen Layer Zigzag Platelet Model 122

4.5 a) Diffraction Geometry in Reciprocal Space for Bragg Reflexion Topography
b) Diffraction Geometry in Reciprocal Space for Spike Topography
c) Situation in Real Space 126

5.1 The Four Settings for Imaging Spike Reflexions 133

5.2 Spike Topographs taken with Various Specimen to Plate Distances and Mis-Setting Angles 133

5.3 Description of the Images appearing on the Topographs in Fig.5.1 134

5.4 Example of Microdensitometer Trace and Interquartile Width Measurements 139

5.5 111 Topographs of Specimen B 141

5.6 111 Reflexions from Various Faced Diamond Plates 145

5.7 111 Topographs of Specimen B 150

5.8 111 Synchrotron Spike Topographs of Specimen B 151

- 21 -
5.9 Double-Crystal Arrangements used for Synchrotron Spike Topography

6.1 Some Electron Diffraction Patterns

6.2 Arrangement for Bright Field Imaging & Arrangement for Dark Field Imaging

6.3 Diffraction Conditions, Shown in Reciprocal Space, for Weak-Beam Dark Field Electron Microscopy

6.4 [100] Orientation Bright Field Transmission Electron Micrograph (g = 220) of Sample G4

6.5 View of Platelets from the [110] Direction

6.6 [110] BF Transmission Electron Micrograph (Zone Axis) of Sample A3

6.7 [110] Orientation WBDF Micrograph (-g,g condition, g = 220) of Sample A3

6.8 [110] Orientation WBDF Micrograph (g,-g condition, g = 220) of Sample A3

6.9 [110] Orientation WBDF Micrograph (g,-g condition, g = 111) of Sample A3

6.10 Platelet Radius Distribution in the Samples

6.11 Print of a [110] Orientation BF Electron Micrograph (g = 111) of Sample A3
6.12 Histograms of Various Platelet Parameters Measured using the 'Quantimet' on the Entire Field of the Micrograph of Sample A3 shown in Fig.6.11

7.1 I.R. Spectra taken at the Centre of the Specimens (A, B, C) using a 1 mm Diameter Circular Aperture

7.2 I.R. Spectra taken at the Centre of the Specimens (D, E, G) using a 1 mm Diameter Circular Aperture

7.3 Platelet Radius, Determined by Spike Topography, versus Infrared Platelet Peak Position

7.4 (a.b) Platelet Radius, Measured from Transmission Electron Micrographs, versus Infrared Peak Position

7.5 Sobolev et al’s Hypothetical Relation between Frequency of I.R. Band and Platelet Radius

8.1 GaAs Crystal Structure

8.2 Dislocation Density Variation across a Semi-Insulating GaAs Wafer

8.3 a) Schematic Diagram of an N-Channel FET
    b) Shows Depletion Region when \( V_{GS} < 0 \)
    c) Shows 'Throttling Effect' when \( V_{DS} \) is made more Positive
8.4 Typical Drain Characteristics of an N-Channel FET showing the Pinch-Off Voltage \( V_p \)

212

8.5 Plan View of a GaAs MESFET

215

8.6 Plot of FET Pinch-Off Voltage vs. Distance from Nearest Dislocation

215

9.1 Topographs of GaAs Wafers

229

9.2 Projection Topography of GaAs Wafer by Reflexion from \{511\} Planes

230

9.3 \[\bar{511}\] Topograph (x3 print) of the (100) Face of Wafer 5

235

9.4 \[\bar{511}\] Topograph (x3 print) of Wafer 5

236

9.5 Diagram of a 7 x 8 MESFET Array (enlarged about 130 times)

237

9.6 \[\bar{511}\] Topograph (x3 print) of Wafer 6

240

9.7 x19 Enlargement of the Lineage Feature Region of the Topograph shown in Fig.9.6

241

9.8 Lineage Feature Region of Various Orientation Reflexion Projection Topographs of Wafer 5 (x12)

244

9.9 Lineage Feature Region of Various Orientation Reflexion Projection Topographs of Wafer 5 (x12)

245

9.10 Synchrotron Radiation Reflexion Topographs (x12) of the Lineage Feature Region of Wafer 5

248
9.11 Synchrotron Radiation Transmission Topographs (x12) of the Lineage Feature Region of Wafer 5
9.12 Synchrotron Radiation Transmission Topographs (x12) of the Lineage Feature Region of Wafer 5
9.13 511 Topograph (x3 print) of Part of Wafer 5
9.14 Sketch of Topograph in Fig.9.3 to show the Area Illuminated to take the Rocking Curve
9.15 Double-Crystal Arrangement for GaAs 400 Reflexion 1 Å Wavelength Symmetrical Reflexion
9.16 Rocking Curve of Lineage Feature Region taken over an Angular Range of 70°, with Corresponding Topographs (x5) taken at Intervals of 4°
9.17 XI3 Enlargements of Topographs taken at Positions Close to Those Giving Rise to the Features of the Rocking Curve of GaAs shown in Fig.9.16
9.18 Schematic of S.T.L. Test System
9.19 Variation of Average Array Pinch-Off Voltage across Wafer 5
9.20 Mosaic of 511 Topographs (x22) Showing the Passage of the Lineage Feature, through Part of Wafer 5, Relative to Some of the FET Arrays
9.21 Mean Array Pinch-Off Voltages
± Standard Deviations,
for the FET Arrays shown in Fig.9.20 265

9.22 Histograms of FET Pinch-Off Voltages at
Various Distances from the Lineage Feature 267

A1 Geometry of Reflexion from One Set of Bragg
Planes of a Cylindrically Bent Crystal Lattice 274

A2 Measurements from the Laue Pictures 276

A3 Exaggerated Geometry of Laue Streak 277

A4 The \( j \) and \( k \) Components of the Bragg
Reflected Rays 282

A5 Curvature of a Two-Dimensional Lattice 290

B Convolution of Airy Diffraction Profile with
Step Function 296

C Convolution of Spike Topograph Image Profile
with Microdensitometer Slit 299
## LIST OF TABLES

1.1 Processing Times for Ilford L4 Emulsions 49

2.1 Classification of Diamond Types 56

2.2 Diamond Sieve Information 60

3.1 Differences between Asterism Streaks and Streaking due to Crystallite Size Effect 90

3.2 Radii of Curvature (in mm) Calculated for a Fairly Undistorted Specimen 105

3.3 Radii of Curvature (in mm) Calculated for a Somewhat Distorted Specimen 106

3.4 Quantification of the First Four Laue Categories 110

5.1 Transmission of X-Rays through Air 131

5.2 Details of the Type Ia Diamonds Studied 143

5.3 Average Platelet Radius Determined by Spike Topography 148

6.1 Average Platelet Radius Determined from TEM 186

7.1 Infrared Platelet Peak Positions in the Diamonds Studied 195
7.2 Comparison of Infrared Platelet Peak Position and Platelet Radius, as determined from Spike Topography and TEM

9.1 Transmission of X-Rays through GaAs and Diamond

B Spike Topography Compared with the Diffraction of Light
CHAPTER 1
INTRODUCTION, X-RAY TOPOGRAPHY AND RADIATION SOURCES

1.1 OUTLINE OF THESIS

Three studies are presented in this thesis: two on diamond and one on its structural relative, gallium arsenide. The purpose of the remainder of this chapter (chap.1) is to describe briefly the techniques of x-ray topography used in these studies, and the radiation sources employed; photographic details are also given.

Chapters 2 and 3 comprise Part I of the thesis: an x-ray study of lattice distortion in diamond. A general introduction to diamond and its origins is given in chapter 2, followed by results of naked-eye observations on a sample of diamonds from the Argyle Mine in Western Australia, along with an account of this new mine. The Laue method and the effect of crystal lattice imperfection on Laue photographs is reviewed in chapter 3. Details are given of a diamond characterization study made using the method. An attempt to quantify the degree of lattice distortion from Laue pictures is described; a full account of the theory being given in appendix A. [A poster on this work: 'X-Ray Measurements of
Lattice Curvature', was presented at the Diamond Conference 1987 (Oxford University, 5–8 July, Poster 4) and S.R.S. Users’ Meeting 1987 (Daresbury Laboratory, 18–19 Sept., Poster 3).

Part II is concerned with platelets in type Ia diamond, and chapter 4 gives an account of the history of their discovery and study, particularly from their effect on x-ray diffraction patterns. The three methods that were used in this work to study them are described in chapters 5, 6 and 7. Chapter 5 gives a full description of the method of spike topography and how it is used to determine average platelet dimensions, although detailed theory is reserved for appendices B and C. A new variant of the technique is also described, and results of its application presented. Some spike topographs taken with synchrotron radiation are shown. An account of a more direct method of measuring platelet size, using transmission electron microscopy, is given in chapter 6. Details of the lengthy specimen preparation are provided, and the methods of measurement described. Chapter 7 discusses the connexion between platelets and the infrared absorption spectrum of diamond, and describes the analyses carried out. The platelet sizes determined in the previous two chapters are compared with the positions of the ‘platelet peak’ in the corresponding infrared spectra. [The following presentations have been been made about the platelet study: ‘Correlation between Platelet Size and Infra-Red Peak Position in Type Ia Diamonds’ Diam.Conf. R.H.B.N.C., 6–9 July 1986, Paper 23; ‘Non-Destructive Estimation of Impurity Platelet Radius in
The third study presented in this thesis (Part III) is of gallium arsenide wafers used for the fabrication of electronic devices. Chapter 8 introduces the material and discusses its manufacture, use and suitability for device fabrication. A particular device, the field effect transistor, is described. Research on the electrical uniformity of transistors made on GaAs substrates is reviewed. An account of x-ray topography carried out on some wafers, most with devices on them, is given in chapter 9. Particular attention is paid to a study of the nature of a dislocation lineage occurring in a wafer, and its effect on nearby field effect transistors.

Detailed conclusions to each part of the thesis are given at the close of the relevant chapters. In addition a General Conclusion is provided at the end.

The paper bound in at the back of the thesis: 'Single-Slit Diffraction Patterns of Sub-Nanometre-Wavelength Synchrotron Radiation' (J.Phys.D 20 541-544) resulted from a collaborative effort at Daresbury Laboratory in which I played a small part.
1.2 X-RAY TOPOGRAPHY

1.2.1 The Technique

X-ray topography is a non-destructive technique for imaging crystal imperfections by Bragg reflected x-rays. It is capable of revealing misorientations, dislocations, stacking faults, grain boundaries, magnetic domains and other variations in the crystal lattice. There are many treatises on the subject, for example: Authier (1976), Tanner (1976), Lang (1978), Lal (1982), and for a brief history see Authier (1980).

Details of the theories behind x-ray topography may be found in these works, but basically the topographic image is determined by what are known as orientation contrast and extinction contrast (spike topography — chap.5 — is an exception). If the crystal being topographed were perfect, the image would be a uniform grey patch; however, at a region of lattice misorientation there will be a change in the Bragg reflecting conditions giving rise to orientation contrast on the topograph. For an ideally perfect crystal there is much attenuation of the Bragg reflected beam due to interference between the singly diffracted and multiply diffracted beams. Phase changes will be introduced in the latter causing destructive interference to take place. This effect is known as extinction (Darwin 1922). Crystal imperfections which destroy strict lattice periodicity will reduce extinction giving extinction contrast on the topograph. In an endeavour to fully understand the contrast of topographs, image
Simulation techniques have been developed (e.g. see Epelboin 1985.)

X-ray topography is a technique complementary to transmission electron microscopy (TEM - chap.6). It enables a thick (up to 1 cm) nearly perfect (dislocation density < $10^4$ mm$^{-1}$) single crystal to be examined with a relatively poor resolution (1 μm) over a large area (many cm$^2$). TEM, on the other hand requires a thin specimen (0.5 μm) of quite high dislocation density ($>10^4$ mm$^{-1}$) and examines a very small area (a few square μm) with high resolution (1 nm). With topography the radiation dosage received by a crystal in the course of examination is generally several orders of magnitude less than that required to produce radiation damage, which is frequently not the case with TEM. Lang (1978) compares the two techniques.

X-ray topography is eminently suitable for large scale overviews of crystals. It is applicable, for example, to the development and control of crystals with low dislocation densities for the electronics industry. For some of the earlier applications of topography see Lang (1967) and for some of the latest see Armstrong (1988).

A detailed account of the experimental procedures involved for taking x-ray topographs can be found, for example, in Tanner (1976 sec.2.4). The methods given in that account are effectively the same as those which were used in the present study (see also Machado 1984).
1.2.2 Methods of Topography

The various methods of x-ray topography differ according to the following: the source (whether conventional or synchrotron); the nature of the radiation (whether continuous or monochromatic); the amount of specimen imaged (section or projection), and whether the incident and diffracted rays enter and leave the crystal from the same surface or not (reflection or transmission). Only those methods of topography used in this thesis will be discussed here; details of others may be found in the aforementioned treatises (sec.1.2.1). The methods have been divided into those using conventional characteristic radiation and those employing synchrotron radiation. A description of the radiation source is given at the beginning of each section.

1.2.3 Topography using Conventional Characteristic Radiation

1.2.3.1 Characteristic x-rays

For an introduction to x-rays and the conventional ways of producing them see Henry et al (1961 chap.2); for a monograph on the subject see Worsnop & Chalklin (1950).

All the topography done in this study using conventional x-ray sources was carried out at the Department of Physics, Royal Holloway & Bedford New College (RHBNC). The conventional sources of x-rays used were: the Elliot 315/TX/12 Mo x-ray tube, and the Elliot 315/TX/12 Cu tube or Philips Fine Focus equivalent. They were usually run at 50 kV, 15 mA; 40 kV, 10 mA and 40 kV, 20 mA respectively.
In such x-ray tubes electrons, in vacuo, are accelerated towards the metal target by the high voltage. A broad continuous spectrum of x-radiation is produced by the deceleration of electrons within the target. Superimposed on this are very sharp and intense lines characteristic of the metal used for the target. These x-rays arise from the collision of the incident electrons with the electrons of the target material, which are promoted to higher energy states. They immediately drop back to their original state, giving off x-rays of the characteristic wavelength. The most frequently used characteristic wavelength, known as the $K\alpha$, arises from electrons returning to the K-shell from the L-shell. In fact the $K\alpha$ line is split into a doublet, $K\alpha_1$ and $K\alpha_2$, each arising from different levels in the L-shell. From a copper target the wavelength of the $K\alpha_1$ is 1.54051 Å and the $K\alpha_2$ is 1.54433 Å. The average $K\alpha$ wavelength for molybdenum is 0.71 Å (values from International Tables III, 1962).

1.2.3.2 The apparatus

Two Lang cameras were used for the topography, both receiving x-rays from the same tube, which could be changed as desired. One was home-made, and was constructed with a distance of approximately 160 cm between the target and the specimen; the maximum beam height it could accommodate was about 2 cm. The other was a commercially built Bristol-Elliot-Lang camera. It had a target to specimen distance of roughly 220 cm and a maximum beam height of 10 cm. The basic construction of such cameras is described by
1.2.3.3 Reflexion projection topography

The earliest topographic method, reflexion topography, was first performed by Berg (1931). The technique was later refined by Barrett (1945) and Newkirk (1958a, b, 1959 - a photograph of his apparatus was published by Webb 1962). They all used the monochromatic characteristic x-radiation from a conventional metal target. The crystal face to be examined was arranged so that the x-rays were Bragg reflected from atomic planes close to it. Fig.1.1 (III) illustrates the method. The photographic plate is placed as close as possible to the sample to prevent the formation of double images due to the Kα doublet.

Berg used an extended x-ray source so that the Bragg condition was satisfied over the entire crystal face. With a narrow well-collimated beam of x-rays the same result can be achieved by traversing the specimen to and fro across the beam, whilst maintaining the Bragg reflecting condition, and keeping the photographic plate fixed with respect to the specimen. This is the method of reflexion projection topography. (By employing a stationary version of this technique Zaumseil 1978 practised reflection section topography.)

Reflexion projection topography tends to image just the surface region of a specimen. The technique is useful when the x-ray absorption of a sample is too high to employ one of
the transmission topography methods. Such samples are the
gallium arsenide wafers. Armstrong (1965) gives details of
techniques.

1.2.3.4 Transmission sectional topography

Lang (1957, 1959) illustrated the use of narrow
well-collimated beams of characteristic x-rays in topography.
A narrow beam (up to a few microns wide) enables
the characteristic beam to improve the
resolution of the topograph. There are two major
variants of Lang's method, section and projection topography.
both are illustrated in figure 1.1.

In sectional topographs (Lang 1957, 1959) the crystal is
held stationary, orientated for the Bragg reflection of the
incident ribbon-like beam of x-rays. This narrow
monochromatic beam is arranged to be as well as the crystal.
photographic plate, and the beam is formed on a
photographic plate, and a deflected beam
is focused in a photographic plate, and a deflected beam.

For a detailed description of sectional topography see

An image of the entire crystal is a projection topograph
(Lang 1959). Two photographic plates are placed at angles
and a photographic plate replaces the crystal. A
detailed description of a stationary variant. A
projection topograph is equivalent to the superposition of a
series of sectional topographs. Chitava (1985) gives details of

Fig. 1.1 BERG'S TOPOGRAPHY
TECHNIQUE (AFTER BERG 1931)

Fig. 1.2 TOPOGRAPHIC ARRANGEMENT
OF BARTH & HOSEMANN (1958)
the transmission topography methods. Such samples are the gallium arsenide wafers studied in chapter 9. Armstrong (1980) gives details of reflexion topography techniques.

1.2.3.4 Transmission section and projection topography

Lang (1957, 1958, 1959a,b) pioneered the use of narrow well-collimated beams of characteristic x-rays in topography. A narrow beam (up to a few hundreds of microns wide) enables the characteristic Kα doublet to be resolved, thus improving the resolution of the topographs. There are two major variants of Lang’s method: section and projection topography; both are used in transmission. The principle of the methods is illustrated in fig.1.3.

In section topographs (Lang 1957, 1958) the crystal is held stationary, orientated for the Bragg reflexion of the incident ribbon-like beam of x-rays. This narrow monochromatic beam is arranged to be as tall as the crystal. An image of a section of the crystal is then formed on a photographic plate held perpendicular to the diffracted beam. For a detailed theoretical account of section topography see Authier (1977).

An image of the entire crystal — a projection topograph (Lang 1959) can be achieved by traversing the specimen and photographic plate together as shown in fig.1.3 (Carlson & Wegener 1961 have suggested a stationary variant). A projection topograph is equivalent to the superposition of a series of section topographs. Chikawa (1980) gives details of — 38 —
FIG. 1-3
THE PRINCIPLE OF THE METHODS OF SECTION
AND PROJECTION TOPOGRAPHY
transmission topography techniques.

1.2.3.5 Spike topography

In the method of spike topography a transmission section topograph of a diamond is taken slightly off the Bragg position. The method is used to investigate platelet precipitates by sampling associated 'spikes' in reciprocal space. The technique is described in chapter 5. A brief review is given by Lang (1980).

1.2.4 Synchrotron Radiation Topography

1.2.4.1 The source of synchrotron radiation


In a synchrotron storage ring, electrons are constrained by magnetic fields to move at relativistic speeds in a closed orbit composed of alternate straight and curved segments. Electrons emit, from each curved segment, a broad spectrum of electromagnetic radiation (Liénard 1898), known as synchrotron radiation (SR). In the laboratory frame of reference these emissions are seen as narrow cones tangential to the orbit. The semi-angle of this cone is given approximately by \( \frac{mc^2}{E} \) where \( m \) and \( E \) are electron mass and
energy respectively, and $c$ is the speed of light (Winick 1980). SR is very intense (about 1000 times that of conventional x-rays), meaning that exposure times for topographs need be only minutes or seconds rather than the hours conventionally required (Herres & Lang 1983 compared topographs of a specimen taken using both conventional and synchrotron sources). The wavelength spectrum stretches continuously from long radio waves to the hard x-ray region, and the radiation is plane polarized with E-vector parallel to the orbit plane.

Experiments where the plane of diffraction is parallel to the orbit plane are said to be carried out in the pi polarization mode, and those where the diffraction plane is perpendicular, in the sigma mode. An important difference between the two modes of polarization is that in the pi mode the intensity varies with the angle of diffraction, $\theta$ (it is proportional to $\cos^2\theta$ - see Batterman & Cole 1964), whilst in the sigma mode it is invariant. Therefore, usually the topographic arrangement is orientated to utilize the sigma mode.

With a dedicated synchrotron radiation source, an electron storage ring is specially constructed so that a circulating stream of electrons, once started, can be maintained in it for several hours. In order to utilize the radiation from the ring, windows are made in it and the radiation travels down long evacuated beam lines to experimental stations.
For an introduction to the physics of SR sources see Walker (1986). For a comparison of different x-ray sources refer to Winick (1986 sec.4). (Yoshimatsu & Kozaki 1977 review non-synchrotron high brilliance sources.)

Many SR storage rings exist throughout the world, and a list of these facilities is given by Winick (1986, 1988). One such ring is the 'Synchrotron Radiation Source' (SRS) at the SERC Daresbury Laboratory in Cheshire. It was here that the SR work presented in this thesis was carried out. The Daresbury SRS consists of a 100' diameter electron storage ring designed to operate at an energy of 2 GeV, with stored electron currents of up to 300 mA and lifetimes (time taken to fall to 1/e of previous value) typically 10 hours. Also there is a 5 T wiggler (wigglers are discussed by Spenser & Winick 1980), incorporated in the ring, which provides a shift in the spectrum towards the shorter wavelengths, with a consequent increase in the intensity of x-radiation which is roughly tenfold at a wavelength of 1 Å. For a brief guide to the SRS see SERC-Daresbury Laboratory leaflet.

From October 1986 until June 1987 the SRS was closed down for the installation of the high brightness lattice (HBL), the purpose of which was to enhance the brightness of the SR by a factor of ten (Daresbury Annual Report 1986/7). This was achieved, in part, by a reduction in the source size from 12 mm horizontally by 0.25 mm vertically FWHM (Hart & Siddons 1982) to 2.6 mm by 0.24 mm (Suller et al 1988). This improves the spacial resolution from about 8 μm to approximately 2 μm.
for a specimen to plate distance of 5 cm on Topography Station 1 (see below). Descriptions of the SRS, and its pre-HBL specifications are given by Lea & Munro (1980), Holland (1986) and Thomson (1986); Suller et al (1988) gives the post-HBL specifications and makes comparisons with the former situation. Details of the pre-HBL SR spectra are provided by Poole (1978) and Greaves et al (1981).

1.2.4.2 The topography stations

There were three experimental stations at Daresbury SRS dedicated to topography (changes have since been made). Topography Stations 1 and 2 (Bowen et al 1982), on Beamline 7 were positioned at distances 80 m and 60 m respectively from the tangent point. The two stations were usually operated one at a time (the experiment performed by Lang et al 1987, however, required the use of both simultaneously). Topography Station 1 contained a white radiation camera, and Topography Station 2 a double crystal camera (Bowen & Davies 1982) for monochromatic x-ray topography. Topography Station 3 also contained a double crystal camera but was placed at the end (35 m from the tangent point) of Beamline 9, the wiggler line, to take advantage of the high intensity x-radiation. The motions of the various components of the cameras in these stations were controlled, via stepper motors, by local station computers.

1.2.4.3 Synchrotron Laue topography

Ramachandran (1944), who first coined the term 'x-ray
topograph', was the first to use a transmission topographic technique using continuous x-radiation. He used his method to study cleaved diamond plates. The technique employed a divergent beam of x-rays, large enough to completely bathe the specimen. A photographic film was placed in a position to receive a diffracted image. A similar method, for examining bulk samples was developed by Guinier & Tennevin (1949).

The image recorded with such set-ups is, in fact, simply a large individual Laue spot. It is one of the many available; each set of parallel crystal lattice planes selecting a particular wavelength for diffraction. Tuomi et al (1974) used synchrotron radiation to take transmission Laue photographs, with the beam covering a large area of the specimen. In the Laue patterns obtained each spot was a topographic image of the illuminated part of the crystal – each a 'Laue topograph', and the pattern as a whole provided a multistereoscopic set of images (Tuomi et al 1981, Tuomi 1986). Such a simple technique was not developed earlier because of the lack of intense, low divergence, white beam x-ray sources, although a similar divergent beam method was tried by Fujiwara et al (1964) (with a section topography version being invented by Leikin & Mingazin 1983).

Synchrotron Laue topography can be an extremely rapid method. The only setting up necessary, unless a particular orientation Laue pattern is desired, is to ensure that the crystal is correctly in the beam. Topographs can be obtained in a matter of seconds. The technique has been shown by
Hart (1975) to be capable of resolution comparable with Lang's methods, however it must be remembered that the images may suffer quite large geometrical distortions (Miltat & Dudley 1980). In chapter 3 the method has been employed for the characterization of a large number of diamonds, and to study their lattice perfection. Synchrotron Laue topography is discussed in some detail by Miltat (1980).

1.2.4.4 Synchrotron projection and section topography

For SR projection and section topography the set-up of Guinier & Tennevin (1949) is employed, or if beam divergence is regarded as negligible, the set-up is a continuous radiation version of that of Barth & Hosemann (1958), fig.1.2. Projection topographs are obtained when the entire crystal is illuminated in the synchrotron beam, and section topographs are obtained by stopping down the beam cross-section as required.

With some of the GaAs work (chap.9) it was found necessary to take reflection projection topographs using synchrotron radiation. The set-up in this case was similar to that of Schulz (1954).

1.2.4.5 Synchrotron double crystal topography

Double crystal topography (Bond & Andrus 1952, Bonse & Kappler 1958 and Bonse 1958 - Bonse 1962 discusses the theory) is a technique which utilizes two successive Bragg reflexions: first from a perfect monochromator crystal (usually silicon), tuned to reflect the desired wavelength, and then from the
specimen. (Local irregularities in monochromators can be evened out by traversing them - Mai et al 1980.) Application of the technique in the present work was limited to what is known as the (+) setting, as illustrated in fig.9.15. It was used to plot a rocking curve from a GaAs wafer (sec.9.4) and also as a means to obtain monochromatic radiation for synchrotron spike topography (sec.5.6). On both occasions the lattice spacing of the monochromator and specimen were closely matched, and the monochromator chosen with its face parallel to the reflecting planes, for a symmetric reflexion. For details of other settings see Kohra et al (1970) and Nakayama et al (1973). Monochromatic SR topography is discussed in some detail by Sauvage (1980); the influence of wavelength on topographs was studied by Lang et al (1983).

1.2.5 Photographic Details

1.2.5.1 Films and plates

The usual practice adopted for the taking of topographs is to first check the setting-up, relatively quickly, by taking a topograph on a low resolution film, and once it is deemed correct, to use a higher resolution photographic plate.

At RHBNC all topographs of diamond (chaps. 3 and 5) were recorded initially on 'Crystal' Dental x-ray film (31 x 41 mm) speed group 'D' fast. The plates used were Ilford L4 Nuclear Research plates. The commercially available 3" x 1" plates were carefully broken in half to 1.5" x 1", and one half was used per topograph. Nuclear emulsions of thickness 25 \mu m were
used with Cu Kα radiation and 50 μm with Mo Kα, as is customary.

The L4 emulsion is recommended for x-ray topography because it possesses a grain size well below the topographic resolution limit (Lang 1978). The emulsion thickness is chosen to be deep enough to be efficient in absorbing the x-ray wavelengths used, in addition, with a thicker emulsion, there is a smaller statistical fluctuation in the number of developed grains per unit area. However, thick emulsions have to be set accurately perpendicular to the diffracted rays. For an image spread of less than 1 μm, an angular tolerance of 2° for a 25 μm thickness, and 1° for 50 μm is permissible (see Lang 1978 sec.4.2).

Topographs of GaAs (chap.9) were taken first on 3" x 3" pieces of Ceaverken A3 Reflex 15 film, and then on 3" x 3" Ilford L4 Nuclear plates. The emulsion thickness used is discussed in sec.9.2.1.

Laue pictures used at RHBNC for correctly orientating specimens prior to topography, were taken on Kodak NS-59T x-ray film or Kodak DEF 59 diagnostic film.

At Daresbury, Laue pictures for orientation and for asterism studies (chap.4) were taken on Agfa-Geveart Osray M3 x-ray film (a high speed medical x-ray film conveniently pre-packed into lightproof envelopes), and Laue topographs on Agfa-Geveart Structurix D2 Industrial x-ray film (a slow, fine grain film with a low background fog-level). Other topographs
were taken on 25 μm Ilford L4 (3" x 3") plates, with trial exposures being made on Structurix D4 film, chosen because it has been found to possess compatible exposure characteristics.

1.2.5.2 Processing

Processing of the L4 emulsions generally followed the standard procedure given in table 1.1 (after Tanner 1976, although the information in this table was originally due to Lang, e.g. see Lang 1978); development taking place in a cool dilute solution of Kodak D19 developer. Conditions are given individually with each situation. Inspection of the plates during development was made under a Kodak 'Wratten' 6B safelight. The dental, Ceaverken and Kodak films were developed in neat D19 developer.

At Daresbury all films were developed in a dilute solution of D19 as per table 1.1, and fixed in a 1 : 3 solution of Kodak FX40 with water. Plates were usually brought back to RHBNC to be developed in the standard way.

1.2.5.3 Note on photographic performance

The Commission on Crystallographic Apparatus of the IUCr (1956) found that photographic emulsions are, in general, approximately equally sensitive to all wavelengths used in diffraction techniques, though there are discontinuities in sensitivity at wavelengths corresponding to the absorption edges of elements in the emulsion. The amount of blackening has been found to be proportional to the x-ray dose (Gerward 1971).
### TABLE 1.1. Processing times (in minutes) for Ilford L4 emulsions

<table>
<thead>
<tr>
<th>Thickness</th>
<th>50 µm</th>
<th>25 µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soak in filtered deionized water</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td>Develop (1:3 D19 to deionized water)</td>
<td>15-60</td>
<td>12-30</td>
</tr>
<tr>
<td>Stop (1% glacial acetic acid in deionized water)</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td>Fix (300g sodium thiosulphate 30g sodium bisulphite in 1 litre deionized water)</td>
<td>60</td>
<td>30</td>
</tr>
<tr>
<td>Wash (filtered tap-water)</td>
<td>upwards of 120</td>
<td>upwards of 120</td>
</tr>
</tbody>
</table>

(After Tanner 1976)
In addition to the photographic emulsion, systems involving television cameras and image intensifiers have been developed for the display of topographic images, for example see Green (1976), Hartmann (1977), Sauvage (1978).
PART I

AN X-RAY STUDY OF
LATTICE DISTORTION IN DIAMOND
CHAPTER 2
DIAMOND - WITH OBSERVATIONS ON STONES FROM THE ARGYLE MINE

2.1 INTRODUCTION

The first half of this chapter provides a brief introduction to diamond, its properties, morphology, classification and origin. For further general information, one of the numerous discourses on diamond may be consulted. Here is a selection, arranged chronologically: Jefferies (1751), Maskelyne (1860), Crookes (1897), Sutton (1928), Williams (1932), Lonsdale (1944), Fersman (1955), Tolansky (1959a,b), Lenzen (1970), Bruton (1970), Orlov (1973), Evans (1976), Mitchell (1988). Maskelyne, Lenzen and Bruton (chap.1) discuss the history of diamond, and Sutton (chap.16) gives an account of diamond in myth and legend. For compilations on the physical properties of diamond see Berman (1965) and Field (1979).

In the second half of the chapter diamonds from a specific location, the newly opened Argyle mine in Western Australia, are examined. (In chapter 3, the perfection of these stones is then studied using Laue photography.)
2.2 DIAMOND

2.2.1 Properties, Structure and Morphology

It is its extreme hardness and high thermal conductivity which make diamond intrinsically so valuable to man, although its monetary value, since ancient times (Barry & Lehman 1987 provide a glimpse of the modern diamond market), has been based on its popularity as a gem stone (due largely to its high refractive index of about 2.42 - Peter 1923). Owing to its hardness, diamond was chosen as 10 on Mohs's (Mohs 1824) mineral hardness scale (Tabor 1954 gives a physical interpretation of this scale). On the Knoop scale (Knoop et al 1939) diamond has a hardness of the order 10,000 kg mm$^{-2}$ compared with about 400 kg mm$^{-2}$ for tool steel. At room temperature the thermal conductivity of type Ia diamond (see Turk & Clemens 1974) is approximately 800 Wm$^{-1}$K$^{-1}$ and that of type II about 2000 Wm$^{-1}$K$^{-1}$ (see Berman 1979, and for thermal conductivities at higher temperatures, Burgemeister 1978), compared with around 400 Wm$^{-1}$K$^{-1}$ for silver or copper. (For the use of diamonds as heat sinks see e.g. Schorr 1969, Berman 1970, Seal 1970.)

A diagram of the atomic structure of diamond is shown in fig.2.1. This was elucidated early this century by the Braggs, using x-ray methods (Bragg & Bragg 1913, 1914). The structure consists of two interpenetrating face-centred cubic lattices of carbon atoms, displaced by one quarter of the distance along their body diagonal. The bonding is purely covalent (see Dawson 1967).
Diamond belongs to the cubic crystal system and the most frequent habit is octahedral. (Grodzinski 1954a,b gives some outline pieces of historical information on the geometry of octahedra in relation to diamond.) Other forms occur too, for example the cube and rhombic dodecahedron (e.g., see Moore 1985). Sometimes one or two octahedra grow on the mirror image of the VIIIth prism of the other. This produces shapes with hemispheres (a term introduced by De Icaza 1783). Natural diamonds are sometimes found (accounting for probably only 0.1% of the world's diamonds) but their origin is by no means controversial. It is thought that they are either large fragments which have suffered cleavage (Tanner 1959) or alternatively are genuine growth on another crystal's hemispheres. Work carried out at this laboratory by Moore (1986) indicates that the former is more likely.

2.3.2 Classification of diamonds

Robertson et al. (1988) classified diamond into two types, I and II, principally on the basis of differences in their ultraviolet spectra, other properties were found to differ too (see also Robertson et al. 1984). Later, a subdivision of type I was proposed by Cutbers (1992) into those diamonds which phosphoresce in ultraviolet light (type IaB) and those which do not (type Ic). These differences were later also found to occur in growth of natural as well as synthetic diamonds.
Diamond belongs to the cubic crystal system and the most frequent habit is octahedral. (Grodzinski 1955a,b gives some curious pieces of historical information on the geometry of octahedra in relation to diamond.) Other forms occur too, for example the cube and rhombic dodecahedron (e.g. see Moore 1985). Sometimes one half of an octahedron grows as the mirror image, in the (111) plane, of the other half. This produces a shape known as a 'macle' (a term introduced by De l'Isle 1783). Tetrahedral stones are sometimes found (accounting for probably less than 0.1% of the world's diamonds), but their origin is something of a controversy. It is thought that they are either cleavage fragments which have suffered dissolution (Seager 1979) or alternatively are genuine growth forms (Donnay & Donnay 1981). Work carried out at this laboratory (Yacoot & Moore 1988) suggests that the former is more likely to be the case.

2.2.2 Classification of Diamond

Robertson et al (1934) classified diamond into two types, I and II, principally on the basis of differences in their ultraviolet spectra; other properties were found to differ too (see also Robertson et al 1936). Later, a subdivision of type II was proposed by Custers (1952) into those diamonds which phosphoresce in ultraviolet light (type IIb) and those which do not (type IIa); differences were later also found between the infrared absorption spectra (Clark et al 1956). Then Dyer et al (1965) subdivided diamonds of type I into two categories according to whether or not they exhibited electron
<table>
<thead>
<tr>
<th>Type</th>
<th>Defining feature</th>
<th>Visible</th>
<th>Infrared</th>
<th>ESR</th>
<th>Typical electrical resistance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ia</td>
<td>Aggregated nitrogen, x-ray diffraction spikes, 'platelets'</td>
<td>Secondary absorption edge</td>
<td>A bands</td>
<td>-</td>
<td>$&gt; 10^{15}$ Ω cm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>at about 300 nm, N3 (415 nm)</td>
<td>B1 and B2 peaks</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ib</td>
<td>Paramagnetic singly substitution nitrogen</td>
<td>Strong featureless absorption</td>
<td>Peaks at 0.14 eV</td>
<td>Paramagnetic</td>
<td>$&gt; 10^{15}$ Ω cm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>increasing in intensity at</td>
<td></td>
<td>nitrogen</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>higher photon energy</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IIa</td>
<td>-</td>
<td>Fundamental absorption edge</td>
<td>Lattice bands</td>
<td>Single line</td>
<td>$&gt; 10^{13}$ Ω cm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.5 eV, often with weak</td>
<td>only</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>featureless 'tail'</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IIb</td>
<td>p-type semiconductor</td>
<td>Fundamental absorption edge,</td>
<td>Acceptor bands, 5.5 eV,</td>
<td>None</td>
<td>150 Ω cm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>at red end of spectrum</td>
<td>absorption free carrier</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
paramagnetic resonance (or ESR) - type Ib and Ia respectively. The resulting classification scheme is shown in table 2.1 (after Walker 1979).

Type Ia, which shows strong ultraviolet absorption, accounts for 98% of all natural diamonds. Only 0.1% of natural diamonds are of type Ib, however nearly all synthetic diamonds are of this type. Types IIa and IIb are very rare in nature, but they include most of the famous large diamonds (e.g. see Bruton 1970 chap.18). Some diamonds have been shown to consist of more than one of these four types and are known as 'mixed' (e.g. see Field 1979 chap.21). A type III classification was once given to diamonds of meteoric origin (see Bruton ibid.).

Walker (1979) sub-classified type Ia diamonds according to the prominence of the A and B features and the 'platelet' peak in their infrared absorption spectra (see chap.7). For example, type IaA denotes a type Ia diamond with an 'A-only' infrared absorption spectrum.

2.2.3 Genesis of Diamond

Meydenbauer (1890) proposed that diamond was of cosmic origin, brought to earth in meteoric showers. However, observations by Crookes (1897) at Kimberley (Orange Free State) led him to conclude that the diamonds found there were most probably formed deep below the surface of the earth. In fact, diamond can be found of both meteoric (q.v. Lonsdaleite - Frondel & Marvin 1967) and geological origin, although only
the latter is significant. For an up to date discussion on the genesis of diamond see Meyer (1985, 1986) and Harte (1986).

The major geological sources of diamond are kimberlite pipes, or the alluvial erosion products of these pipes. Alluvial deposits in India were first being exploited over 3000 years ago, and remained the only supply of diamonds until the sixteenth and eighteenth centuries, when discoveries were made in Borneo and Brazil. Diamonds were first recovered from the kimberlite pipes themselves in the eighteen seventies, in South Africa. Kimberlite is an igneous rock containing olivine, serpentine, phlogopite mica and calcite (e.g. see Deer et al 1985). For the history of diamond production see Lenzen (1970). Kimberlite sources are discussed, e.g. by: Williams (1932 vol.1), Bruton (1970 chap.16), Dawson (1979).

As implied by Wade & Prider (1940), diamonds are also found in lamproite. This was confirmed when lamproitic diamonds were discovered in the Kimberley region (named coincidently) of Western Australia in the nineteen seventies (e.g. see Atkinson 1987). Lamproites differ from kimberlites by the presence of leucite (KAlSi₂O₆), and by including greater quantities of K₂O, SiO₂ and TiO₂. They are also richer in potassium and magnesium than kimberlite.

Although there were early claims of small scale successes (e.g. see Crookes 1897, Desch 1943, Rayleigh 1943a,b, Travers 1943, Bruton 1970 chap.19), the production of synthetic diamond was not undertaken on a commercial scale until the
early nineteen fifties (Bundy et al 1955). X-ray studies of such diamonds were first made by Lonsdale et al (1959). For a recent review on synthetic diamond see Nassau & Nassau (1979).

2.3 DIAMONDS FROM THE ARGYLE MINE, WESTERN AUSTRALIA

2.3.1 The Argyle Mine

The Argyle diamond mine is situated in the Kimberley region in the remote north of Western Australia. The mine consists of a diamond bearing lamproite pipe (known as AK1), which was discovered in 1979, together with associated alluvial deposits. A review of the discoveries is given by Atkinson (1987), and details of the mine and its development can be found in the Argyle Diamond Mines Joint Venture Project Briefing (Argyle Diamond Mines Pty. Ltd. 1985). The mine currently holds the distinction of being the most productive, and in 1986 accounted for 30% (by weight) of the world’s total diamond output (Chadwick 1986).

2.3.2 Argyle Diamonds

Hall & Smith (1984) characterized diamonds from the AK1 pipe. (Harris et al 1975 made a similar characterization of South African diamonds.) They examined twelve batches of diamonds sorted by size between the +23 and +5 sieve classes (see table 2.2); each batch consisting of up to 500 stones. The largest numbers of stones (61%) were irregularly shaped, with macles (22%) and crystal aggregates (10%) forming the next most abundant classes (fig.2.2). Cube diamonds were not
<table>
<thead>
<tr>
<th>Sieve Class*</th>
<th>Diameter in mm of aperture (lower screen)</th>
<th>Approximate average weight in carats per stone</th>
</tr>
</thead>
<tbody>
<tr>
<td>-23+21</td>
<td>7.925</td>
<td>4.853</td>
</tr>
<tr>
<td>-21+19</td>
<td>6.350</td>
<td>2.476</td>
</tr>
<tr>
<td>-19+17</td>
<td>5.740</td>
<td>1.574</td>
</tr>
<tr>
<td>-17+15</td>
<td>5.410</td>
<td>1.256</td>
</tr>
<tr>
<td>-15+13</td>
<td>4.521</td>
<td>0.860</td>
</tr>
<tr>
<td>-13+12</td>
<td>4.089</td>
<td>0.561</td>
</tr>
<tr>
<td>-12+11</td>
<td>3.454</td>
<td>0.371</td>
</tr>
<tr>
<td>-11+9</td>
<td>2.875</td>
<td>0.211</td>
</tr>
<tr>
<td>-9+7</td>
<td>2.464</td>
<td>0.123</td>
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<td>-7+6</td>
<td>2.159</td>
<td>0.0896</td>
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<td>-6+5</td>
<td>1.829</td>
<td>0.0557</td>
</tr>
<tr>
<td>-5+3</td>
<td>1.473</td>
<td>+0.029</td>
</tr>
<tr>
<td>-3+2</td>
<td>1.321</td>
<td>+0.015</td>
</tr>
<tr>
<td>-2+1</td>
<td>1.092</td>
<td>+0.008</td>
</tr>
</tbody>
</table>

+ Logarithmic midpoints  
* Diamond sieve with circular aperture

**Table 2.2**: Diamond Sieve Information
Fig. 2.2 Morphology and colour of Argyle diamonds obtained by Hall & Smith (1984)

Fig. 2.3 Morphology and colour of the 'run of mine' sample of Argyle diamonds
found at all. The predominant colour of diamonds in their sample was brown (79%), and a small but significant number of pinks (1%) was also recorded (see fig. 2.2).

Often the surfaces of Argyle diamonds are frosted in appearance, with etch channels and hexagonal pits being quite common (Tombs & Sechos 1986). Many specimens contain numerous inclusions (over 90% in Hall & Smith's sample), mainly of graphite (see also Harris & Collins 1985). Jaques et al (1986 chap. 6) reviews some of the findings on Argyle diamonds.

For a compilation of observations on diamonds and their morphologies from other places around the world, see Grantham (1974), and for Argyle diamonds see Moore (1987).

2.3.3 Observations on a Sample of Argyle Stones

A sample of 178 Argyle diamonds was made available by Dr. Chris Welbourn of the Diamond Trading Company Research Centre, Maidenhead (Berks.). They were provided so that a study could be made of their lattice deformation. The details of this study are given in the next chapter (chap. 3). This chapter ends with a characterization of these stones.

The sample consisted of two parcels:
1) A 20 carat (40 g) 'run of mine' (unsorted) batch of 158 diamonds of sieve class -9+7.

2) A 5.1 carat (1.02 g) batch of 20 clivage makeable stones, with fairly bad black inclusions, of sieve class -11+9 (4th Blk Cliv/MB+9). These diamonds would be suitable as gems if
The characterization study was limited to diamonds in parcel 1, this being a random sample. The diamonds were examined through a x1½ magnifier.

The distribution of morphologies and colours in this sample are presented in fig.2.3. The largest proportion (56%) were irregularly shaped as in the samples characterized by Hall & Smith (1984); however, unlike their samples, the next most common morphology was octahedral (28%). Macles formed only 3% of the samples, and the same proportion was found to be tetrahedral. Grey was the dominant colour (55%), brown diamonds accounting for only 20% of the stones; however 7% were pinks. Black inclusions were seen in 72% of the diamonds.

Fig.2.4 shows some scanning electron microscope pictures of a few selected stones.

a) This is a good example of an octahedral stone. It exhibits hexagonal pits on its surface.

b) This is a view of a tetrahedral diamond from one corner. The surface is quite rough, with hexagonal pitting.

c) This is an example of one of the few dodecahedral stones, which formed only about 1% of the sample.

d) This is a macle with hexagonal pits and channeling in its surface.
Comparison of figs. 2.3 and 2.4 demonstrates differences in the distribution of stone shape and colour between the sample examined here, and the diamonds examined by Hall & Smith (1984). The differences could be attributed to the fact that the samples examined by Hall & Smith covered a wider range of sizes. Alternatively, an explanation could be that the sample examined here was taken from later workings (the stones were obtained in early 1986), and it is possible that the relative proportions of different characteristics are changing as the workings get deeper. In the case of diamond colour, decisions are subjective and discrepancies can arise between the opinions of different observers. This could also contribute to the differences between the histograms of diamond colour in figs. 2.2 and 2.3.
CHAPTER 3

THE LAUE METHOD AND THE PERFECTION OF DIAMOND

3.1 OUTLINE OF CHAPTER

The chapter opens with an introduction to the Laue method, followed by a description of an experiment performed to characterize some diamonds according to the appearance of their Laue patterns. The elongation of Laue spots due to crystal imperfection (an effect known as asterism) is discussed next, along with other similar looking effects. The length and geometry of asterism streaks is then considered as a means for quantifying lattice perfection in diamond.

3.2 THE LAUE METHOD

For treatises on the Laue method see Schiebold (1932) and Amoros et al (1975).

The first 'Laue pictures' were taken in 1912 by W. Friedrich and Paul Knipping at Munich, to test experimentally Max von Laue's theory that a crystal would have a diffraction effect on x-rays. This well-known story was told in Laue's Nobel Prize Lecture (1915) and by Friedrich (1922). Fig.3.1 shows the set-up reproduced from
FIG. 3-1 Scheme of the original setup of Friedrich and Knipping's experiment. A: anticathode; Al, aluminum foil; S, lead screen; B₁, B₂, B₃, B₄, openings of the collimator system; Kr, crystal; G, pedestal; P₁, P₂, P₃, P₄, P₅, photographic plates; K, lead case; R, beam stop. [From Friedrich et al. (1912).]
their original drawing (Friedrich et al 1912); it is basically the same as that used today: an x-ray source providing a continuous spectrum of wavelengths, a system to collimate the beam into a narrow pencil of rays (Bl to B4), a goniometer head, G to hold the crystal, Kr, and a flat film in a lightproof envelope (not shown) positioned to receive either the rays diffracted through the crystal (transmission picture) or those reflected back (back-reflection picture). The resulting photographs consist of a pattern of spots characteristic of the symmetry of the crystal structure. Figs. 3.2, 3.3, and 3.4 illustrate this very well. This set of three transmission Laue pictures was taken, one at a time, by successively rotating a diamond about its [110] axis between exposures. Each of the photographs was taken with a \(2 \times 2 \text{ mm} \times 2 \text{ mm} \) square cross-section beam of synchrotron radiation, at a specimen to film distance of 30 mm.

Fig.3.2 shows the Laue pattern created when the incident beam was directed along a four-fold axis of rotational symmetry, in this case the [001] direction. The pattern itself exhibits the same symmetry. [This picture was shown at a Royal Institution Discourse - Mitchell 1988 - and has been incorporated in Moore 1988.]

The pattern in fig.3.3 displays threefold symmetry and was taken with the incident beam directed along a triad 111-type axis.

Fig.3.4 was taken with the incident beam directed along a diad 110-type axis and hence has two-fold rotational symmetry.
Fig. 3.2 A synchrotron Laue photograph of a diamond with the incident beam directed along a 4-fold axis of rotational symmetry.
FIG. 3:3  A SYNCHROTRON LAUE PHOTOGRAPH OF A DIAMOND WITH THE INCIDENT BEAM DIRECTED ALONG A 3-FOLD AXIS OF ROTATIONAL SYMMETRY
Fig. 3.4 A synchrotron Laue photograph of a diamond with the incident beam directed along a 2-fold axis of rotational symmetry.
Some of the actual crystallographic axes are marked on the figures.

By regarding the crystal as a three dimensional diffraction grating, Laue (1912) was able to formulate a quantitative mathematical theory of x-ray diffraction by crystals, and soon afterwards W.L. Bragg (1912) showed that the spots on Laue's photographs could be explained as reflexions of the incident beam from sets of parallel atomic planes (Bragg planes) in the crystal, obeying the condition:

\[ 2d \sin \theta = n \lambda. \]

This is the famous Bragg equation; where \( \theta \) is the glancing angle of incidence of the beam on the planes, \( \lambda \), the wavelength of the radiation reflected, \( d \), the spacing of the atomic planes and \( n \), an integer corresponding to the order of diffraction. Bragg's equation is mathematically equivalent to the set of equations derived by Laue.

An important aspect of the Laue method is that it utilizes the entire spectrum of x-ray wavelengths available. Different orders of diffraction, \( n \) from a given set of Bragg planes give rise to a single Laue spot; each spot arising by Bragg reflexion from a single set of parallel planes. With a broad spectrum of wavelengths available to obey Bragg's law, the diffraction of x-rays by atomic planes is analogous to the reflexion of light by plane mirrors.
From the positions of Laue spots it is possible to calculate the Miller indices (Miller 1839), (hkl) of the planes in which the reflection occurred (e.g. see Barrett and Massalski 1966, chap.9). Murdock (1938) was the first to point out how Laue photographs can be indexed with the aid of the reciprocal lattice, and Ohba et al (1981) devised a computer-aided method of doing so.

The sizes and shapes of Laue spots from a perfect crystal are determined by their position, the geometry and dimensions of the experimental set-up, the cross-section and convergence or divergence condition of the primary beam, and the size and shape of the specimen. The shapes of spots in transmission Laue photographs were investigated by Leonhardt (1926) and Schiebold (1932).

Laue spots from imperfect or strained crystals may have distorted shapes and internal detail (topographic detail, sec.1.2.4.3). The mirror analogy can be extended to diffraction by bent planes of atoms and optical reflection from curved mirrors; when the planes are bent or twisted the Laue spots are distorted in a manner related geometrically to the distortion of the crystal. This is the effect known as 'asterism'; first described by Rinne (1915), good examples of which appear in the photographs in figs. 3.19 and 3.20. The effect is studied in detail in sections 3.4 and 3.5. (For a brief review of the subject see Barrett 1934.)
3.3 WHOLE CRYSTAL SYNCHROTRON LAUE TOPOGRAPHY OF DIAMOND

3.3.1 Introduction

Synchrotron Laue topography (sec.1.2.4.3) of entire specimens has been tried as a qualitative method of characterizing lattice imperfections in over two hundred diamonds from Australia and South Africa. The pictures were taken at Daresbury S.R.S. (before the installation of the H.B.L.) on Topography Stations 2 and 3.

3.3.2 The Diamonds

Details about the 178 Australian diamonds examined, all from the Argyle Mine, were given in sec.2.3. In total, 74 diamonds from South Africa were studied; they were supplied by Dr. Jeff Harris of the Department of Applied Geology, University of Strathclyde. Of the diamonds 38 came from the Premier Mine; 19 were peridotitic, i.e. originating in the peridotite of the Earth’s upper mantle, and 19 eclogitic, found in eclogite, a constituent rock of kimberlite. A sample of 19 came from the Koffiefontein Mine (peridotitic) and the remaining 17 from the Finsch Mine (peridotitic). The South African diamonds were all half octahedra, the original un-sawn stones being of sieve class -9+7 (see table 2.2), and the Laue pictures were taken with (100) faces orientated roughly towards the synchrotron beam. For an introduction to the mines see, for example, Bruton (1970), and for a comparative study of the morphologies and colours of the diamonds from them, see Harris et al (1975).
3.3.3 Experimental Details

The South African stones were lent for a short period only, and for the topography it was sufficient to mount them temporarily with wax. With the Australian diamonds, however, which were to be submitted to further study (sec.3.5), a more sophisticated method was employed. Prior to taking the specimens to Daresbury, each Argyle diamond was mounted with 'sellotape' (experiments had shown this to have a negligible x-ray absorption) at the centre of a standard 5 x 5 cm glassless projector slide mount. The stones were orientated approximately by eye so that, where possible, a convenient major crystallographic axis was roughly perpendicular to the slide. For example, with an octahedral diamond the [111] direction was suitable, the (111) face lying flat on the supporting sellotape. The slides fixed into a special holder designed to fit into the Huber goniometer heads, used at Daresbury, so that a diamond centred on its slide would also be centred with respect to the goniometer's arcs. After initial alignment, facilitated by reference to a laser beam concentric with the synchrotron beam, the arrangement could be left untouched, and the pre-mounted specimens changed as desired. This system not only considerably reduced setting-up time (thereby improving efficient use of valuable beam time), but having the specimens already mounted also enabled settings to be easily reproduced at a later date.
The transmission Laue photographs were taken on Agfa Structurix D2 film, which was found to give superior topographic detail than the alternative Osray M3 film. Exposure times were varied according to the conditions, for example from 35 seconds at 200 mA on Topography Station 2, to 200 seconds at 8 mA on Topography Station 3 (with the ring operating in single bunch mode – e.g. see Lea & Munro 1980, Greaves et al 1981). Development time was typically 3 minutes. The specimen to film distance was a standard 5 cm.

During the synchrotron radiation exposures, many of the diamonds were found to emit bright blue and turquoise luminescence. (For a review of visible luminescence from diamond see Collins 1974.)

3.3.4 The Laue Categories

The Laue pictures of all the diamonds were classified into the categories proposed in fig.3.5. The photographs in this figure were chosen from the large sample of pictures provided by the 178 Argyle diamonds. Scanning electron micrographs of some of the stones, which gave rise to some of the Laue category pictures illustrated, are shown in fig.3.6. The following is a description of the eight categories shown in fig.3.5, in order of increasing distortion, each picture is one third actual size (original specimen to film distance was 5 cm).

A) Sharp well-defined Laue spots with shapes due to geometrical factors alone. (Stone shown in fig.3.6.)
FIG. 3-5  EXAMPLES OF THE EIGHT LAUE CATEGORIES

- 77 -
FIG. 3.6  SCANNING ELECTRON MICROGRAPHS OF DIAMONDS BELONGING TO SOME OF THE DIFFERENT LAUE CATEGORIES SHOWN IN FIG. 3.5
B) The Laue spots show slight streaking.

C) Streaking more pronounced than in category B, with the spots showing slight elongation. The outermost spots appear fuzzy.

D) Streaking gives the Laue spots a slightly fuzzy appearance; elongation is more pronounced than in category C, and an increase in the width of the spots is also apparent. (Stone illustrated in fig.3.6.)

E) The Laue spots appear as fuzzy blobs.

F) The Laue spots are fragmented, giving the Laue pattern the appearance of consisting of too many spots, and making the whole picture look speckled. (Stone shown in fig.3.6.)

G) Each Laue spot is composed of a multiplicity of smaller spots and streaks, each clearly divided from the other, but it is still possible to determine what constitutes a single Laue spot.

H) The Laue spots are so fragmented that it is difficult to determine which elements are the components of any single Laue spot. (Stone illustrated in fig.3.6.)

This classification scheme can be used to make judgements of the quality of diamonds. Fig.3.7 compares the distribution, for each source, of the Laue photograph categories of the diamonds in the samples studied. In the case of the Argyle mine, only the 158 'run of mine' stones are
**Fig. 3.7** Distribution in quality of diamonds in samples obtained from different mines, based on Laue photo. Classification shown in Fig. 3.5.
represented, since the 20 diamonds from parcel 1 (sec.2.3.3) were sorted and therefore not random. The results from the Premier peridotitic and Premier eclogitic diamonds are portrayed both separately and combined.

From these histograms it can be seen that the quality of the Argyle diamonds is very variable, with roughly equal proportions in all categories. The Finsch, Koffiefontein and Premier eclogitic samples contained a high proportion of category A stones, whereas the Premier peridotitic contained predominantly category B. With the exception of Koffiefontein category F the South African samples contain diamonds better than category D. However, the randomness of the South African samples cannot be guaranteed; indeed, the fact that the diamonds were sawn half-octahedra implies that they must have been of reasonable quality. Also the samples were comparatively small in number. This should be regarded only as a preliminary study demonstrating the technique. Larger samples need to be examined, for a genuine comparison to be made of the quality distribution of diamonds from different mines.

3.4 ASTERISM

3.4.1 The Effect

The term asterism (αστρόνομος = star) was originally used to describe the star-like pattern made by the elongated Laue spots radiating from the centre of a transmission picture.
Nowadays the term is often used to describe streaking generally, radial or non-radial, in both transmission and back-reflexion Laue photographs. As specimens depart from the quality which gives rise to the category A photographs, asterism streaking, like that seen in the category B, C and D pictures of fig.3.5, is the first manifestation of crystal distortion to show on Laue patterns. The kinds of distortion which may be responsible for asterism are enumerated below.

3.4.2 Causes of Asterism

3.4.2.1 Elastic lattice bending

There are cases where asterism clearly arises from elastic distortion, for example the elastic bending of mica (Rinne 1924) or thin metal sheet, where the asterism will disappear on return to the unbent condition. However with bulkier and more brittle samples, the elastic distortion is negligible when compared with the changes in orientation which result from plastic flow (Komar 1936), although Konobiejewski and Miner (1932) did attempt an analysis of elastic bending in rock salt from a study of the Laue asterism. Joffe and Kirpitcheva (1922) used the Laue method for the study of various crystals undergoing deformations, and observed the phenomenon of asterism. As well as photographic plates they also used fluorescent screens in order to be able to observe changes in the Laue pattern while the crystal was being deformed. However, they were unable to observe asterism with elastic deformation. Cox and Backhurst (1929), experimenting with strained tungsten wire, and Clark and Beckwith (1937)
with single crystals and polycrystalline aggregates of aluminium were also unable to observe any asterism in the Laue pattern until the elastic limit had been exceeded.

3.4.2.2 Polygonization

Joffe (1928), referring to some of his earlier work, mentioned how he had found that, on gradually increasing the stress in a specimen, a limit had been reached where the Laue picture suddenly changed from one of spots to one of sets of many spots arranged in streaks — indicating internal fragmentation of the specimen. He attributed asterism to the formation of lattice fragments with very small differences in orientation between neighbouring fragments (called 'polygonization' by Orowan, see Guinier and Tennevin 1948); the asterism being continuous when the fragments and differences in orientation are sufficiently small. Instead of a continuously bent lattice there are a number of polygon elements which each have an orientation corresponding to part of a bent lattice (see fig.3.8, after Cullity 1959): the whole structure will be free of elastic strain. Manteuffel (1931) and Komar (1936) supported this view because they observed discontinuities of the asterism in Laue pictures of deformed metals. Cahn (1949) obtained structured asterism streaks when deforming crystals at high temperatures; however, Honeycombe (1950b) attributed these to deformation or kink bands (sec.3.4.2.5).
Fig. 3.8 Reflection of white radiation by bent and polygonized lattices (schematic).

Fig. 3.9
(a) BENT GLIDE LAMELLAE
(b) BULK BENDING

Fig. 3.10

Direction of shear

Burgers' suggested mechanism for producing local curvature.

Fig. 3.11 Sketch illustrating local curvature at a slip plane.
3.4.2.3 Bent glide lamellae

Komar and Mochalov (1936), working with deformed magnesium crystals, found that the lengths of the asterism streaks diminished as the thickness of the crystals was reduced by etching. This suggested that the asterism was due to macroscopic curvature of the lattice. Orowan and Pascoe (1941) found dissymmetry between symmetrically related pairs of spots in x-ray rotation photographs (e.g. see Luger 1980 chap.2) of slightly deformed cadmium crystals. This also suggested macroscopic curvature, one of each pair of related reflexions coming from the convex side and the other from the concave side. They proposed disintegration of the lattice into bent glide lamellae as shown in fig.3.9a (after Orowan & Pascoe ibid.) rather than bulk bending (fig.3.9b) which would produce extremely high stresses at the opposite bent sides.

3.4.2.4 Local curvature

W.G.Burgers and Lebbink (1945) did not consider macroscopic curvatures to be the cause of asterism because they found that Laue pictures of aluminium crystals showed asterism when the crystals were sheared. They attributed asterism to distortions of a local character, and supported a mechanism suggested by J.M.Burgers (1940) as shown in fig.3.10 (after him) which was based on the local curvature theory of Taylor (1928).
Taylor and Farren (1926) and Taylor (1927) found a considerable range of orientations shown by Laue photographs of aluminium crystals deformed by compression. This led Taylor (1928) to postulate rotation of portions of the lattice in the glide planes as shown in fig. 3.11 (after Barrett 1952). This theory was upheld by Yamaguchi (1929a,b), who while studying slip had observed asterism in the Laue pictures of both stretched and compressed aluminium, and by W.G.Burgers and Louwerse (1931).

On the other hand: Kochendorfer (1941) reported finding asterism absent from Laue pictures of naphthalene crystals which had been sheared; Honeycombe (1951b) found that cadmium could be extended by more than one hundred percent without the appearance of asterism whereas asterism did occur when the crystals were macroscopically bent or kinked, and E.R.Parker (see Maddin and Chen 1954) found no asterism exhibited by sheared single crystals of zinc.

3.4.2.5 Deformation and kink bands

Deformation bands are narrow lamellar regions within which differing lattice orientations have arisen as a result of slip (Pfeil 1926, 1927). Barrett (1939, 1940) and Barrett and Levenson (1939, 1940) made a study of them in iron and aluminium crystals and found that they produced asterism much like that attributed to local curvature. Topographic images of kink bands were obtained by Coyle et al (1957) using the method of Guinier & Tennevin (1949) (see sec.1.2.4.3).
Gay and Honeycombe (1951) recognized that asterism arises from macroscopically bent crystals but they also attributed asterism to kink bands. Kink bands (Orowan 1942) are planes of microscopic, sharply bent, glide lamellae which occur when a wire is kinked (see fig. 3.12) and can also occur when a crystal is extended or compressed (see fig. 3.13). A study by Hess and Barrett (1949) showed kink bands to be a simple form of deformation band. Honeycombe (1950a, 1951b) made a study, including an investigation using the Berg-Barrett method of x-ray topography (see sec. 1.2.3.3); he found asterism with aluminium deformed by even small amounts in tension, but none with elongated cadmium, which does not develop kink bands. Nishimura and Takamura (1952), by directing the primary beam separately on and between two wide deformation bands in an aluminium sample, were able to take transmission Laue pictures of the different regions. They obtained asterism from the deformation bands only. A similar experiment was done in back-reflexion by Chen and Mathewson (1951).

3.4.2.6 Mosaic spread

Andrews et al (1987) found that Laue pictures, taken with synchrotron radiation, of very small organic crystals (of dimensions up to 50 μm) showed substantial asterism streaking. They interpreted the streaking as indicating mosaic spread, that is when the constituent crystallites comprising the mosaic structure of a crystal (e.g. see Hirsch 1956) are not perfectly aligned. This was not a new idea, the mosaic structure having been proposed by Goss (1936) to explain
FIG. 3.12 SCHEMATIC DIAGRAM OF A KINKED CRYSTAL (AFTER OROWAN 1942)

FIG. 3.13 (AFTER OROWAN 1942)

Thin parallel lines, glide planes. Broken lines, boundaries of the wedge-shaped regions of flexural glide. Dash-dotted lines $A$ and $A'$; planes of kinking.

EXTENSION AND COMPRESSION OF A CRYSTAL PRODUCED BY KINK BANDS.
Thin parallel lines, glide planes.
asterism in Laue patterns from cold-worked metals. The degree of asterism has been used to study recrystallization in such metals when heat-treated (see also Masing et al 1956).

3.4.3 Other Causes of Laue Spot Streaking

3.4.3.1 Crystallite size effect

In the powder diffraction method (developed independently by Debye and Scherrer 1916, 1917 and Hull 1917) the line width of the diffraction pattern is dependent on, among other things (e.g. see Barrett and Massalski 1966, chap.7), the grain size of the powdered crystal. In the same way the widths of diffraction lines from a polycrystalline sample will depend on crystallite size. With grains of linear dimension less than about 1000 Å an effect known as particle-size broadening occurs, which is analogous to the broadening of diffraction lines from an optical grating that has a limited number of rulings (e.g. see Jenkins and White 1976, chap.17). In terms of reciprocal space the broadening effect can be regarded as an expansion of 'mathematical' reciprocal lattice points to finite sized reciprocal lattice spheres. The average grain size in a sample can be determined from the line broadening using an equation originally due to P. Scherrer; for further details, and the theory, see, for example, Henry et al (1961 chap.16). The effect was first noticed in x-ray topographs by Wooster & Wooster (1945).
The shape of Laue spots too is affected by small crystallite size (Kalman et al 1979): radial streaking occurs, similar in appearance to asterism streaks. The lengths and widths of these 'size-effect' streaks being inversely proportional to the crystallite dimensions. Size-effect Laue streaking, therefore, gives information on the sizes of small grains in polycrystalline materials; like spike topography (chaps. 4 & 5) it enables investigation of features too small for conventional topography. Kalman et al (1979) have devised a method for the determination of crystallite dimensions, down to a few nanometres, from radial and lateral broadening of Laue streaks obtained with synchrotron radiation.

Steinberger et al (1982) distinguished between true asterism streaks and the streaking due to crystallite size effect and produced a table, on which the following is based, giving the main features of each type:

**TABLE 3.1**

Differences between Asterism Streaks and Streaks due to Crystallite Size Effect

<table>
<thead>
<tr>
<th>PROPERTY</th>
<th>ASTERISM</th>
<th>SIZE-EFFECT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shape</td>
<td>Approximately straight lines</td>
<td>Straight lines</td>
</tr>
<tr>
<td>Radiality</td>
<td>Approximately radial</td>
<td>Exactly radial</td>
</tr>
<tr>
<td>Breadth</td>
<td>Determined by the instrumental resolution - no broadening</td>
<td>Broadening increases with the decrease of crystallite dimensions</td>
</tr>
</tbody>
</table>
3.4.3.2 Thermal asterism

If the atoms of a crystal are undergoing thermal vibration, then each point of the reciprocal lattice spreads out roughly into a sphere. On a transmission Laue pattern this leads to weak diffuse streaks running radially through the usual sharp and intense Laue spots. Such streaks were first recorded by Friedrich (1913), in a Laue photograph of sylvine. This phenomenon is often called ‘thermal asterism’ (see Cullity 1959, appendix 15) because of the radial direction of the diffuse streaks. At room temperature, thermal asterism will usually only be evident in over-exposed Laue photographs (op. cit.). Some early references on thermal diffuse reflexions of x-rays are cited in sec.4.1.1 (see also Preston 1939).

3.4.3.3 Spikes

The Laue photograph in fig.4.2 shows good examples of ‘spike’ streaks from diamond. These streaks arise from the intersection of the Ewald spheres representing the continuous x-ray spectrum, with spike-like extensions in reflecting power from reciprocal lattice points. The spike-like extensions in reciprocal space are caused by plate-like defects in the (real space) crystal lattice. Examples of such defects are platelets in diamond and Guinier-Preston zones in aluminium. Spike streaks can be distinguished from other streaks by their peculiar orientation. This subject is dealt with fully in chap.4.
3.5 MEASUREMENT OF LATTICE IMPERFECTION BY SYNCHROTRON LAUE TOPOGRAPHY

3.5.1 Calculating Lattice Curvature

Elastic lattice bending, polygonization and disintegration of a crystal lattice into bent glide lamellae, all amount, on a macroscopic scale, simply to curvature of the crystal lattice (localized in the cases of local curvature, deformation bands and kink bands). Visualizing the Bragg planes as mirrors makes it clear that Laue spots resulting from a bent lattice will appear as elongated streaks. These correspond to the loci of undistorted spots produced by tilting the crystal through an angle equivalent to the bending (Berg 1934), and on this assumption it is possible to construct theoretical Laue patterns of bent crystals (e.g. Elnikov 1934, Komar 1936). Simulated Laue patterns are demonstrated in the next section. Equally, it should be possible to deduce the radius of curvature of particular Bragg planes by measuring the elongation of the appropriate Laue spots.

A theory, to allow the calculation of lattice curvature from the length of Laue streaks is expounded in appendix A. It assumes that the curvature is of the simplest kind, that is cylindrical. Here follow the salient details and steps in the calculation. Fig.3.14 shows the geometry of reflexion from a crystal with curved Bragg planes of radius of curvature, $r$. It is necessary to know the specimen to film distance, $D$, the diameter, $h$ of the circular cross-section primary x-ray beam,
FIG. 3:14
GEOMETRY OF REFLEXION FROM A FINITE SIZE CRYSTAL
WITH BENT BRAGG PLANES OF RADIUS OF CURVATURE "r"
and the length, \( d \), of crystal parallel to that beam. Three measurements are taken from the resulting true picture face the exaggerated diagram in Fig. 3.15a: the length, \( d \), of the

beam and the distance, \( y \), of each end of the streak from the centre of the three spots, which appear on the

film. The following intermediate parameters illustrated in

the following figure may be calculated. For details refer to appendices. The

value of \( \alpha \) is calculated by Newton's method,

\[
\alpha = \frac{f(\alpha)}{f'(\alpha)}
\]

where

\[
f(\alpha) = -2ab\sin K \cos 2\alpha + b^2 \sin K \cos \alpha + b\left(\alpha - \frac{1}{2}\cos K\right) \sin \alpha + 2ab \cos K \sin 2\alpha
\]

The starting value \( \alpha_0 = \frac{1}{3} K \) is convenient. Then

- 94 -
and the length, \( d \) of crystal parallel to that beam. Three measurements are taken from the resulting Laue picture (see the exaggerated diagram in fig.3.15): the length, \( l \) of the streak, and the distances, \( a \) and \( b \), of each end of the streak from the centre of the through beam (which appears on the film). The following intermediate parameters (illustrated in fig.3.16 - for details refer to appendix A) then need to be calculated:

\[
\kappa = \cos^{-1}\left(\frac{a^2 + b^2 - c^2}{2ab}\right)
\]

Then \( \alpha \), calculated by Newton's method, \( \alpha_1 = \alpha_0 - \frac{f(\alpha_0)}{f'(\alpha_0)} \)

where \( f(\alpha_0) = -2ab \sin \kappa \cos 2\alpha + bh \sin \kappa \cos \alpha + h(a + b \cos \kappa) \sin \alpha + 2ab \cos \kappa \sin 2\alpha \)

\( \alpha_0 = \frac{1}{2} \kappa \) is convenient. Then

\[
\beta = \tan^{-1}\left(\frac{a \sin \alpha}{a \cos \alpha - h/2}\right)
\]

\[
\delta = \frac{a \sin \alpha}{\sin \beta}, \quad \delta' = \frac{b \sin (\kappa - \alpha)}{\sin \beta}
\]

and on fig.3.11

\[
\delta = \frac{1}{2} \cos^{-1}\left(\frac{(D + d_2)^2 - \delta^2}{(D + d_2)^2 + \delta^2}\right) \quad \delta' = \frac{1}{2} \cos^{-1}\left(\frac{(D - d_2)^2}{(D - d_2)^2 + \delta'^2}\right)
\]
Finally, the radius of curvature, \( r \) can be calculated from the equation:

\[
r = \frac{d (\sin \theta - \sin \theta') + h \cos \beta (\cos \theta - \cos \theta')}{(\sin \theta - \sin \theta')^2 + \cos^2 \beta (\cos \theta - \cos \theta')^2 + \sin^2 \beta (\cos \theta + \cos \theta')^2}
\]

In order to obey Bragg's law each part of a Laue streak must be formed by radiation of a different wavelength, each streak arising from a band of wavelengths selected from the fundamental spectrum in the primary beam, or higher order harmonics. (It follows that asterism cannot result from lattice parameter variations as proposed by Czochralski 1923.)

The broad spectrum of x-ray wavelengths provided by synchrotron radiation makes it eminently suitable for this work.

3.5.2 Test of the Theory by Simulation

Simulation of Laue patterns was applied as a simple test of the lattice curvature calculation described in the last section. The program 'Laue' from the S.R.S. Program Library at Daresbury Laboratory was utilized for the purpose. Fig.3.17 illustrates three simulated Laue patterns; they are all half size.

Pattern 1 simulates the positions of the three 111-type Laue spots obtained from a diamond, placed 50 mm from the film, when its [111] axis is parallel to the x-ray beam. (The specimen may be regarded as a mathematical point.) By superimposing such patterns generated for specimen to film distances from 49 mm to 51 mm, pattern 2 is obtained. This simulates the 111-type Laue spots made by a diamond 2 mm long,
FIG. 3.17 SIMULATED LAUE PATTERNS OF DIAMOND (REDUCED 50%) SHOWING 111-TYPE SPOTS ONLY
centred at 50 mm from the film.

A set of the latter patterns were produced for different specimen orientations about the horizontal 110-type axis (the projection of this axis is indicated on pattern 3 by X......X), over a range of angles chosen to simulate the bending of a 2 mm long diamond to have a 10 mm radius of curvature. Superimposing these patterns created pattern 3.

The streaks in pattern 3 were measured (on the full-size original), and the procedure given in sec.3.5.1 applied. The result of the radius of curvature calculation, from each streak (beam diameter < 0.1 mm), agreed to within 20% of the intended figure of 10 mm. Measurements on pattern 2 gave radii of a few metres, which is sufficiently large to indicate 'plane' planes. These results would seem to vindicate the theory.

3.5.3 Details of the Experiment

The curvature of Bragg planes in a dozen Argyle diamonds were determined from measurements made on synchrotron radiation Laue pictures. The pictures were taken at Daresbury S.R.S. on Topography Station 2 (after the installation of the H.B.L.). At this station, the maximum divergence of the beam works out to be only 9 seconds of arc, which will lengthen a Laue spot, on a film placed 100 mm from the specimen, by less than 5 μm.
Using a suitable pinhole, the beam was stopped down to a circular cross-section of 100 \( \mu \text{m} \) diameter. Such a small cross-section produced sharp, easily measurable, Laue streaks; it was circular in order to simplify the calculations. The beam was targeted close to the centre of each specimen (the exact position easily checked from radiographs), each of which was mounted in the fashion already described in sec.3.3.3.

The twelve Argyle stones chosen for this study had all been pre-mounted such that their [111] axes would lie parallel to the beam, transmission Laue pictures of them therefore exhibited three prominent 111-type streaks. The length, \( d \) of each specimen parallel to the beam was measured by micrometer.

Both [111] and (by placing the specimen back-to-front) [111] Laue photographs were taken of each specimen, at specimen to film distances of 50, 75 and 100 mm, on Agfa Osray M3 film held rigidly planar in a purpose built holder. The film holder was designed to allow a rapid change of film, and included a beam-stop, thin enough to allow an image of the through beam to appear. The M3 film was used because of its convenience - the film being pre-sealed into light-proof envelopes - and it revealed the Laue streaks in good contrast, good topographic detail being unnecessary. Development time was standardized at 5 minutes.

On each of the six 'pinhole' Laue pictures taken of each stone, the length, \( l \), of each of the 111-type streaks and the distances, \( a, b \) (refer to fig.3.15) of the ends of each streak from the centre of the through beam were measured (to an
accuracy of ½ mm) using a ruler. The calculations of the lattice curvatures, r, required to produce each streak were calculated by computer—a Fortran program having been written to enable the calculation to be made directly from the six primary parameters: D, h, d, l, a, b.

3.5.4 Pinhole Laue Pictures of Argyle Diamonds

Examples of some pinhole Laue pictures are shown in figs. 3.18, 3.19 and 3.20, each was taken at 50 mm from the specimen.

Fig.3.18 is of a fairly undistorted diamond previously placed in Laue category A (sec.3.3.4). The Laue spots are comparatively short, there being little or no asterism. The length of each spot will have been due entirely to geometrical factors, such as specimen size and specimen to film distance.

The diamond used to take fig.3.19 was classified in Laue category C, and was hence somewhat distorted. It was of similar dimensions (d = 1.8 mm approx.) to the diamond examined in the previous figure. In this case the Laue spots are elongated into streaks by asterism, as a result of lattice imperfection.

Fig.3.20 is of a category H diamond; the fragmented Laue spots are not suitable for measurement. (This diamond was not one of the twelve chosen for the lattice curvature study.)
Fig. 3.18 Pinhole image picture of a fairly undistorted specimen (category A).
Fig. 3.20 Pinhole Laue picture of a category H specimen. No good for measurement.
3.5.5 Practical Considerations

From the intermediate equations given in sec. 3.5.1 it can be seen that the parameters \( a \) and \( b \) are not interchangeable, and therefore two possible values of \( r \) can be obtained from measurements of a Laue streak on a single picture. The practical reason for this is that from a single picture it is not possible to know which end of the crystal (relative to the film) gave rise to which end of the Laue streak, or in other words whether the diffracted beam was diverging \((a > b)\), or converging \((a < b)\) on leaving the crystal. The object of taking both \([111]\) and \([\bar{1}11]\) Laue pictures of each specimen, at three specimen to film distances, was to try and resolve this ambiguity, by looking for consistent values of \( r \). For example, it would be expected that the value of \( r \) calculated from a streak on a \([111]\) Laue photograph, assuming a divergent diffracted beam, might agree with that calculated from the corresponding streak on a \([\bar{1}11]\) picture by assuming a convergent beam.

Another consideration is that the length of a Laue streak could, under some circumstances, be limited by the short-wavelength cut-off of the x-ray spectrum. If streak shortening does occur, it will reduce the apparent radius of curvature of the Bragg planes in the case of a divergent diffracted beam, and increase it in the case of a converging one. Therefore taking both \([111]\) and \([\bar{1}11]\) Laue pictures should enable the true figure to be estimated.
3.5.6 Some Results

As examples, the results of calculations on the [111] pictures shown in figs. 3.18 and 3.19, and on the corresponding [111] pictures (not shown) are given here, in tables 3.2 and 3.3. (The Laue spots on the [111] pictures are numbered clockwise from the first after '12 o'clock' - the numbers for the [111] pictures are for the spots from the corresponding Bragg planes.) No attempt has been made to determine the errors in the radii because of the complexity of the relationship, and the large number of parameters involved. In the context of the situation here they are unnecessary anyway; knowledge of the order of magnitude of the result being sufficient.

<table>
<thead>
<tr>
<th>SPOT NUMBER</th>
<th>[111] PICTURE</th>
<th>[111] PICTURE</th>
</tr>
</thead>
<tbody>
<tr>
<td>REFLECTED</td>
<td>1</td>
<td>1409</td>
</tr>
<tr>
<td>BEAMS</td>
<td>2</td>
<td>52025</td>
</tr>
<tr>
<td>DIVERGING</td>
<td>3</td>
<td>2105</td>
</tr>
<tr>
<td>REFLECTED</td>
<td>1</td>
<td>81</td>
</tr>
<tr>
<td>BEAMS</td>
<td>2</td>
<td>89</td>
</tr>
<tr>
<td>CONVERGING</td>
<td>3</td>
<td>88</td>
</tr>
</tbody>
</table>

TABLE 3.2
Radii of Curvature (in mm) Calculated for a Fairly Undistorted Specimen

The large radii of curvature were obtained assuming diverging reflected beams, and since the values are the same as can be predicted for truly flat Bragg planes, we conclude that this was not found to be the case, particularly as no unexpected result of the paper had indeed undergone only slight bending.
TABLE 3.3
Radii of Curvature Calculated for a Somewhat Distorted Specimen

<table>
<thead>
<tr>
<th>SPOT NUMBER</th>
<th>[111] PICTURE</th>
<th>[111] PICTURE</th>
</tr>
</thead>
<tbody>
<tr>
<td>REFLECTED</td>
<td>Reflecting</td>
<td>Reflected</td>
</tr>
<tr>
<td>BEAM</td>
<td>1</td>
<td>67</td>
</tr>
<tr>
<td>DIVERGING</td>
<td>2</td>
<td>65</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>61</td>
</tr>
<tr>
<td>REFLECTED</td>
<td>1</td>
<td>38</td>
</tr>
<tr>
<td>BEAM</td>
<td>2</td>
<td>37</td>
</tr>
<tr>
<td>CONVERGING</td>
<td>3</td>
<td>42</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>33</td>
</tr>
</tbody>
</table>

Not surprisingly, large radii of curvature are found from the [111] Laue picture in fig.3.18 since the diamond was fairly undistorted. The large radii of curvature were obtained assuming diverging reflected beams, and since the values are what were expected, the results assuming converging beams could reasonably be ignored. However, it would be supposed that when the corresponding [111] picture was analysed the large radii of curvature would be obtained from calculations assuming a converging beam. As can be seen in table 3.2, this was not found to be so, contradicting what would be predicted from truly bent Bragg planes. The results shown in table 3.3 from fig.3.19, and its corresponding [111] photographs, demonstrate the same anomaly.

Furthermore, especially evident in the results in table 3.3, each streak has indicated a similar amount of curvature; an unexpected result if the crystal had indeed undergone only simple bending.
3.5.7 Bragg's Theory for the Shape of Asterism Spots

The results from the other Laue photographs of these two diamonds, and the results from the pictures of other specimens, confirmed the above observations. Therefore the mechanism giving rise to the asterism does not seem to be pure lattice curvature. The best explanation is that it is caused by mosaic spread (sec.3.4.2.6), where the crystal is composed of many misorientated smaller constituent crystallites.

W.L.Bragg (1933 chap.8) showed that the radiality of the asterism streaks in transmission pictures does not necessarily imply that the crystal planes are curved more in one direction than another. This can be explained by considering the movement of a spot formed by reflexion of a beam of light from a mirror which is rocked so that its normal moves within a narrow cone. This is the optical analogue of the situation where the distortion in a crystal has given rise to a random deviation of the normal to the atomic planes, all around its mean direction. The diagram in fig.3.21 (after Cullity 1959 chap.8) depicts the situation; showing that the reflected beam will trace out an elongated ellipse on the film. The rocking of the normal through $2\varepsilon$ in the plane of incidence makes a difference of $2(\theta+\varepsilon)-2(\theta-\varepsilon) = 4\varepsilon$ in the direction of the reflected beam so that the major axis of the ellipse is approximately $4\varepsilon(AC)$ when $2\theta$ is small. Rocking through $2\varepsilon$ at right angles to the plane of incidence moves the beam through $2\varepsilon$, therefore the minor axis of the ellipse is given by $2\varepsilon(AS) \approx 2\varepsilon(AC)2\theta$. The ratio of major to minor axis is
Fig. 3.21. Effect of lattice distortion on the shape of a transmission Laue spot. CN is the normal to the reflecting plane.

Fig. 3.22. Effect of lattice distortion on the shape of a back-reflection Laue spot. CN is the normal to the reflecting plane.
thus $1/\theta$, so for $5^\circ$ (about 0.09 rad.) the major axis is roughly twelve times as long as the minor axis. The situation in back reflexion, where the spot is roughly circular, is shown in fig.3.22 (after Cullity 1959). In the case of a mosaic crystal, the angle $\theta$ represents the range of the distribution of orientations of the constituent crystallites.

The property of the asterism caused by mosaic spread, which makes this explanation fit the findings of sec.3.5.6, is that, for a given crystal, the elongation of each Laue spot depends only on the Bragg angle. It would, therefore, be expected that the 'curvature' results obtained from measurements on the 111-type spots of [111] and [111] Laue pictures would all agree. Also, as fig.3.21 indicates, only the divergent beam case need be considered. A further indication of the mosaic structure of the distortion in the diamonds is provided by the fragmented nature of the Laue spots in fig.3.20, which were produced by a severely distorted specimen. (An early reference to a mosaic structure of distorted diamond is made by Ramachandran 1944, 1946, also De Vries 1975 found evidence for a polycrystalline structure occurring in plastically deformed diamond.)

3.5.8 'r' as an Indication of Crystal 'Quality'

Having established that lattice curvature was not the principal cause of asterism from the diamond specimens, does not mean that the calculations of $r$ were all made in vain. Even if $r$ cannot be taken to mean literally 'radius of curvature' it can still be useful as a measure of the
'quality' of a stone. Table 3.4 presents results from the twelve Argyle diamonds investigated, in order of decreasing value of $r$, along with parameters derived from $r$ which may be considered more manageable in terms of their magnitudes. The corresponding 'Laue categories' of the stones are given also. The values of $r$ quoted are the averages of the values calculated, assuming a divergent beam, from each of the $111$-type spots on each of the [111] and $\bar{111}$ pictures taken at each of the three different specimen to film distances (a maximum of 18 values per specimen).

**TABLE 3.4**
Quantification of the First Four Laue Categories

<table>
<thead>
<tr>
<th>$r$ /mm</th>
<th>log $r$</th>
<th>ln $r$</th>
<th>$1/r \times 10^5$</th>
<th>Laue Cat.</th>
</tr>
</thead>
<tbody>
<tr>
<td>23693</td>
<td>4.37</td>
<td>10.07</td>
<td>4</td>
<td>A</td>
</tr>
<tr>
<td>1204</td>
<td>3.08</td>
<td>7.09</td>
<td>83</td>
<td>B</td>
</tr>
<tr>
<td>654</td>
<td>2.82</td>
<td>6.58</td>
<td>153</td>
<td>B</td>
</tr>
<tr>
<td>547</td>
<td>2.74</td>
<td>6.30</td>
<td>183</td>
<td>B</td>
</tr>
<tr>
<td>397</td>
<td>2.60</td>
<td>5.98</td>
<td>252</td>
<td>B</td>
</tr>
<tr>
<td>340</td>
<td>2.53</td>
<td>5.83</td>
<td>294</td>
<td>B</td>
</tr>
<tr>
<td>171</td>
<td>2.23</td>
<td>5.14</td>
<td>585</td>
<td>B</td>
</tr>
<tr>
<td>84</td>
<td>1.92</td>
<td>4.43</td>
<td>1190</td>
<td>C</td>
</tr>
<tr>
<td>67</td>
<td>1.83</td>
<td>4.20</td>
<td>1493</td>
<td>C</td>
</tr>
<tr>
<td>56</td>
<td>1.75</td>
<td>4.03</td>
<td>1786</td>
<td>C</td>
</tr>
<tr>
<td>43</td>
<td>1.63</td>
<td>3.76</td>
<td>2326</td>
<td>C</td>
</tr>
<tr>
<td>31</td>
<td>1.49</td>
<td>3.43</td>
<td>3226</td>
<td>D</td>
</tr>
</tbody>
</table>

From the parameters proposed in table 3.4 a 'quality factor' could be selected, enabling the Laue category to be expressed as a range of numerical values. For example, choosing ln $r$ as the factor, category A might take all values greater than 8, category B the values between 5 and 8, and category C the range from 3.5 to 5. Any stone with a
value below 3.5 on the scale would be of category D or worse (below category D, the Laue spots are not really suitable for measurement anyway). So the first three Laue categories, at least, can be related to a measurable quantity.
PART II

A STUDY OF PLATELETS IN DIAMOND
4.1 SPIKES AND PLATELETS

4.1.1 The Extra Reflexions from Diamond

Early in 1940 a 111 Laue picture of diamond was published, in the journal 'Current Science' (Raman & Nilakantan 1940a), which showed extra reflexions associated with the 111 Laue spots (see also Raman & Nilakantan 1940b). Certain extra reflexions had been observed before with other materials, about which Knaggs et al (1940) give a list of references. Raman & Nilakantan (1940c) made a detailed study of these reflexions from diamond. They found that the extra spots were due to the characteristic wavelength x-rays and appeared in the same plane as the Laue spots, but unlike the latter, did not obey the usual geometrical reflexion conditions. By varying the glancing angle of the incident beam, it was found that the intensity of the extra spots increased as their position approached that of the usual Bragg reflexion condition. An exposition of their theories on these observations was given in a paper by Raman & Nagendra Nath (1940).
Raman & Nilakantan (1940d) and Raman (1942) investigated the influence of specimen temperature on the extra reflexions, but it was Lonsdale & Smith (1941) and Lonsdale (1942) who demonstrated that, in fact, extra reflexions from diamond were of two sorts:

1) Diffuse temperature dependent spots, arising from thermal vibrations.

2) Relatively sharp temperature independent reflexions ('spike' reflexions — see later).

Lonsdale and Smith were the first to consider the type (2.2.2) of diamond being investigated. They found that thermal diffuse reflexions could be obtained from all types of diamonds, but that only type I diamonds produced the spike reflexions. From the observations of Raman and Nilakantan it is clear that they were principally studying spike reflexions from type I diamond.

Diffuse spots on x-ray crystal photographs were a subject of much interest at this time and in 1941 the Royal Society held a discussion on 'diffuse reflexions of x-rays by crystals' (see also Preston 1941). This discussion resulted in a series of papers being published together in the Society’s proceedings: Preston (1942), Lonsdale & Smith (1942), W.H. Bragg (1942a,b), W.L. Bragg (1942), Darwin (1942), Finch (1942), Born & Sarginson (1942). Lonsdale & Smith dealt with diamond in some detail. For a general work on the subject of diffuse X-ray reflexions see Wooster (1962).
4.1.2 The Spike Reflexion

Spike reflexions are so called because they are generated by spike-like extensions of reflecting power from reciprocal lattice points. In a study by Lonsdale & Smith (1941) Laue photographs were taken, misorientating by up to 20° on either side of {111}, {220}, {113}, {331} and {004} planes. From these pictures details were obtained of the shape and extent of the diffracting regions about the reciprocal lattice points (relps - term coined by Ramachandran & Wooster 1951). Each relp was found to be surrounded by a spherical region of diffuse thermal scattering, extending about 3° from the Bragg position. In addition (except with the {004} points) there were found to be long spike-shaped regions of diffraction, along some, or all, of the <100> reciprocal axes, extending up to 12° (Lonsdale 1942). Fig.4.1 (after Lonsdale & Milledge 1965) illustrates these.

Sharp spike reflexions occur in positions on the Laue photograph corresponding to the intersection of the <100> reciprocal lattice spikes with the Ewald sphere (Ewald 1913). Fig.4.5 (explained fully in sec.5.2) shows this situation in both (b) reciprocal space and (c) real space (see also: Hoerni & Wooster 1953, Caticha-Ellis & Cochran 1958, Takagi & Lang 1964). The Laue spot is produced by the continuous 'white' x-ray spectrum. If the exposure time of the photograph is long enough the white radiation will give rise to 'spike' streaks radiating from the Laue spots and passing through the spike reflexions caused by the characteristic
FIG. 4.1 REPRESENTATION IN RECIPROCAL SPACE OF SPIKE-LIKE EXTENSIONS OF REFLECTING POWER ALONG <100> DIRECTIONS (AFTER LONSDALE & MILLEDGE 1965)
wavelength. Good examples of these appear radiating from the 111 spots in the photograph in fig.4.2, which is an approximately 111 Laue picture of a diamond taken with a 1 mm diameter beam of synchrotron radiation.

Using a combination of Laue and Weissenberg photographs (Weissenberg 1924, see also Barrett & Massalski 1966 chap.6), Hoerni & Wooster (1952, 1955) made quantitative measurements of the variation in intensity of spike reflexions (calibrated against the Bragg reflexion of the characteristic radiation) with position; advancing on the qualitative observations made by Raman & Nilakantan (1940c). In terms of reciprocal space they discovered that the intensity varied along the spikes as \( R^{-2.2} \), where \( R \) is the reciprocal lattice distance from the associated relp. For spikes associated with different relps, but parallel to the [100] direction, the relative intensities were found to depend only on the index \( h \), and likewise \( k \) and \( l \) respectively for spikes parallel to the [010] and [001]. The relative values were found to be 5, 100, 75, 5 and 30, when the appropriate indices were 0, 1, 2, 3 and 4 respectively; so the intensity was very low at the zero and third orders. Absolute intensities varied from specimen to specimen.

4.1.3 The Cause of Spike Reflexions

In France, Guinier (1942, 1944) had made an independent study of the extra reflexions from diamond. He pointed out that the <100> reciprocal lattice spikes must indicate lattice displacement faults on the {100} planes, and suggested that to account for the spike sharpness they must extend to diameters
Fig. 4.2 A synchrotron Laue photograph of a Type Ia diamond showing the spikes associated with the 111-type spots.
of 0.1 µm laterally. Indeed, the theory of the reciprocal equivalent of a crystal lattice perturbation (e.g. see Wilson 1949 chap.3) suggested that reciprocal spikes along <100> axes arose from disklike laminar defects in the {100} planes; one being the Fourier transform of the other (see also Cochran 1956).

Frank (1956, 1964; see also Yoneda 1961 and Frank 1961) proposed a segregation of impurity atoms in the form of platelets, occurring in such planes. These impurity platelets were analogous to the Guinier-Preston 'zones' - the plate-like precipitates of copper found in age hardened copper-aluminium alloys (Guinier 1938a,b; Calvet et al 1938, 1939; Preston 1938a,b,c, 1940). Such precipitates give rise to similar spike reflexions of their own; details and references can be found in Geisler & Hill (1948). Frank chose silicon as a suitable impurity in diamond, on the basis that it both satisfied the valency requirements, and produced the required lattice displacement to correspond to Hoerni & Wooster's spike intensity measurements (see also Wooster 1962 sec.4:3). He calculated the magnitude of the displacement to be equal to an additional one third of the lattice parameter (implied by the very low spike intensity for an index of 3 - Wooster 1956), in a direction normal to the platelets. (For an up-to-date confirmation of this see Barry et al 1983, though Humble et al 1985 disagree; they obtained the figure of 0.39.)
Caticha-Ellis & Cochran (1958) worked out a rigorous theory for the diffraction consequences of a random sequence of occasional abnormal spacings in the [100] type direction, such as would be produced by an assembly of platelet precipitates embedded in [100] planes. They found their calculation was in fair agreement with experimental results (they found the spike intensity to be proportional to $R^{-2}$), and they confirmed Frank's conclusion, in principle. However, they dismissed silicon as the precipitate since, in diamond, it did not occur in sufficient quantities. Wooster (1962 sec.4:3) discusses the various findings on spike intensity.

4.1.4 Platelets in Diamond

In 1959 Kaiser & Bond discovered that nitrogen was a major impurity in type I diamond; Elliot (1960) speculated that this nitrogen aggregated in the form of platelets. Nicholson et al (1959) had used the technique of transmission electron electron microscopy to gain information about Guinier-Preston zones, and using this method Evans & Phaal (1962b) observed directly, for the first time, platelets lying on [100] planes of type I diamond. They were elliptical, with 'diameters' from 100 Å to 1000 Å (see also Evans & Wild 1965). They found them to be absent in type II diamond. (After the work of Dyer et al 1965, platelet-containing diamond was classified type Ia — sec.2.2.2.) These observations confirmed that platelets were the cause of x-ray spike reflexions. (Platelets also cause spike reflexions in electron diffraction patterns — Sumida & Lang 1981a, 1982.) This having been
established, studies of spike reflexions could provide details about the platelets. For example, much later, in one application, Caveney (1968) interpreted reduction in spike intensity as an indication of partial platelet destruction, in diamonds he had subjected to high temperatures and pressures. (Evans 1973 confirmed by electron microscopy that integrated spike intensity was proportional to the total platelet area per unit volume.) The technique of spike topography (sec.4.2 and chap.5) was developed as a method for platelet size determination.

The observations of Evans & Phaal also revealed the platelet concentration \(10^{12}\) platelets per cubic millimetre—see also James & Evans 1965); on the basis of this measurement they concluded that the platelets probably were composed of nitrogen. Lang (1964) was able to propose a plausible model for the structure of nitrogen platelets in diamond. This structure is shown in fig.4.3. In his model the mass of a nitrogen platelet and its volume are both four-thirds that of the carbon matrix it replaces. This means that a diamond containing such platelets would have the same density as pure diamond. This was consistent with the reports of Kaiser & Bond (1959) which showed that the lattice parameter of diamond increases linearly with the nitrogen content, while the density remains constant.

For a period, some doubt was cast on the presence of nitrogen in platelets, for example: Sobolev et al (1968b), on the basis of spike intensity measurements and infrared spectra.
Sections on (110) of unit cells of (a) normal diamond and (b) platelet structure in a platelet layer parallel to (001). Full circles, C in plane of section; broken circles, C at $a_0/2\sqrt{2}$ above or below plane of section; circles with dot, N in plane of section.

**FIG. 4.3** LANG'S PLATELET MODEL  
(AFTER LANG 1964)

**FIG. 4.4** THE DOUBLE NITROGEN LAYER ZIGZAG PLATELET MODEL  
(a) [011] PROJECTION  
(b) [017] PROJECTION  
(AFTER BARRY ET AL 1985)
(see sec.7.1.2), and Berman et al (1975) from thermal conductivity measurements. For a time interstitial carbon was favoured as a major component of platelets (Evans 1973, Evans & Rainey 1975, Walker 1977, Humble 1982, Cowley et al 1984). Woods (1976) claimed to have electron-microscopic evidence that platelets were composed of aggregated carbon interstitials, although this was criticized in a paper by Lang (1977a). Woods (1986) continues to cast doubt on nitrogen being a major component of platelets.

Further support for the presence of nitrogen in platelets was provided by Berger & Pennycook (1982) who detected significant quantities in platelets, using the technique of electron energy loss spectroscopy (EELS - for a book about this technique see Ibach & Mills 1982). In synthetic diamond Evans et al (1981) successfully induced aggregation of dispersed nitrogen into platelets.

The origin of the nitrogen in diamond is still a mystery (e.g. see Milledge & Meyer 1962). Frank (1966) suggested that it may be of biological origin. However, nobody seems to have ever considered the beta decay of carbon-14 as a possible source. From the point of view of time scale, this suggestion is not unreasonable, since the half-life of carbon-14 is 5730 years (Kaye & Laby 1978) and diamonds are likely to be as old as two thousand million years (Allsopp et al 1967). For a review of the various states of aggregation that nitrogen takes in diamond see Bursill (1983) or Bursill & Glaisher (1985).
The most recent model for the structure of nitrogen platelets is the 'double nitrogen layer zigzag' model proposed by Barry et al (1985), shown in fig.4.4. This model was obtained by comparing computer-simulated images of platelets with experimental electron microscope images; it is essentially a modification of Lang's model. Barry et al also review the earlier platelet models. Bursill & Glaisher (1985) have produced detailed mechanisms of platelet growth and degradation on the basis of Barry et al's model.

The latest publication investigating platelets is that of Sumida & Lang (1988) who carried out an electron-microscopic survey (see sec.6.3.2).

4.1.5 Giant Platelets

Large planer defects, with dimensions up to 50 µm, lying in {100} planes of type Ia diamond, were first observed in cathodoluminescence by Mendelssohn (1971), and were imaged using cathodoluminescence topography by Hanley et al (1977) and x-ray topography (Lang 1977b). Woods (1976) studied these 'giant' platelets by electron microscopy and concluded that they were merely much larger examples of the more common small {100} platelets. Like them, the 'giant' platelets were observed to exhibit preferred orientations of <110> for elongation (see fig.6.5 iii).

4.1.6 <111> Spikes

Spikes along <111> axes were observed by Meyer & Milledge (1963), with both boron and aluminium doped synthetic
diamonds. They attributed these spikes to lamellar inclusions of the dopant along \{111\} planes. Lisoivan (1976) observed \(<111>\) spikes in natural diamond of the type IaB (see sec.2.2.2), which could not be accounted for in the same way. Similar spikes were recorded with synchrotron radiation by Lang et al (1985) who suggested they were caused by voidites (see Bursill 1983). Voidites (first observed by Stephenson 1977) are sub-microscopic \{111\} faceted defects of low electron density. In certain diamonds, sheets of voidites replace \{100\} platelets; it is supposed by platelet decomposition. For a comprehensive account of voidites see Barry et al (1987). Electron microscopic studies to confirm that \(<111>\) spikes are due to the presence of voidite sheets is something still to be done.

4.2 SPIKE TOPOGRAPHY

Whatever the composition, or structure, of the platelets in diamond may be, their average radius can be estimated by the non-destructive technique of x-ray topography of the 100 type spike reflexions. This technique is commonly known as 'spike topography', and was originated by Takagi & Lang (1964). In this technique it is the spike reflexion, rather than the Bragg reflexion, which is imaged. The relative diffraction geometries for (a) conventional and (b) spike topography are shown in fig.4.5. Provided there is no gross misorientation (>0.1°) present in the specimen, contrast in a spike topograph depends only on the form and number of
Fig. 4.5a. Diffraction geometry in reciprocal space for spike topography (Moore & Lang 1970, 1972, 1974) in type I diamonds, which they found to be roughly proportional (see also Frank & Lang 1965), in contradiction to Grenville-Bells (1962). They ascribed their success to the fact that the topographic method makes zonal variations apparent. Takeda & Lang also investigated spike intensities from equivalent <100> directions and found them comparable, thus showing that platelet topography occurs equally on all the <100> planes.

Fig. 4.5b. Diffraction geometry in reciprocal space for spike topography (Moore & Lang 1970, 1972, 1974) and Moore and Lang further developed the technique of spike topography to enable quantitative measurement of spike platelet diameters in the range 150 to 200 A. Dimensions several orders of magnitude smaller than the resolution limit of conventional x-ray topography. The spike topographic image gives the distribution of platelets within a specimen. Moore and Lang recorded this image on the phosphor of the platelet support. The diffraction pattern, which is appropriate in real space, is not used.

Fig. 4.5c. Diffraction geometry in real space (Moore & Lang 1970, 1972, 1974)
platelets (op. cit.).

Takagi & Lang pioneered the technique in order to carry out a point by point correlation between variation in spike intensity and ultraviolet absorption (Sunanda Bai 1944, Rendall 1944) in type I diamonds, which they found to be roughly proportional (see also Frank & Lang 1965), in contradiction to Grenville-Wells (1952). They ascribed their success to the fact that the topographic method makes zonal variations apparent. Takagi & Lang also investigated spike intensities from equivalent <100> directions and found them comparable, thus showing that platelet precipitation occurs equally on all the {100} planes.

Moore & Lang (1970, 1972, 1977) and Moore (1973) further developed the technique of spike topography to enable quantitative estimates of average platelet size to be made from the sharpness of the spike topographs. Since a reciprocal lattice spike represents the Fourier transform of a platelet, the greater the lateral extent of the latter is, the sharper, or less broad, the spike will be, and vice versa. They found platelet diameters lying in the range 150 to 200 Å, dimensions several orders of magnitude smaller than the resolution limit of conventional x-ray topography. The spike topographic image shows the distribution of platelets within a specimen. Moore and Lang regarded this image as the convolution of the platelet number density (projected along the direction of the diffracted beam) with the Airy diffraction intensity profile appropriate to the mean 'radius'
of the individual platelets (approximated to circles). A relationship was then obtained enabling this mean platelet radius to be calculated from interquartile width measurements made on microdensitometer traverses of the topograph. Details of the method are given in chap.5, and theory in appendix B.

4.3 THE WORK WHICH FOLLOWS

Moore and Lang's technique was able to determine average platelet dimensions only at the edge of a specimen. A simple modification of this method - shadowed spike topography (chap.5) - has now been used to estimate platelet sizes at different positions in the interior of specimens. Since Evans & Phaal (1962b) found that platelets were not uniformly distributed throughout individual crystals, the ability to be able to do this is very necessary for an overall characterization.

The next three chapters compare results obtained from type Ia diamonds using both the traditional and modified methods of spike topography (chap.5), transmission electron microscopy (chap.6) and infrared absorption spectroscopy (chap.7), on the same regions of each specimen. The more direct measurements of platelet size made from electron microscopy are used to test the method of spike topography as a valid means of platelet size determination. In chapter 7 the platelet dimensions obtained by both methods are compared with the 'platelet peak' positions in the infrared spectra measured at the corresponding places on each specimen.
5.1 INTRODUCTION

This chapter is concerned with spike topography carried out on seven specimens, primarily in order to ascertain average platelet dimensions at different positions within them. As well as conventional spike topography, a previously untried method of shadowed spike topography was used. Some spike topographs were also taken with synchrotron radiation. The chapter begins by describing and explaining (more fully than will be found elsewhere) the technique of spike topography, and how measurements of platelet radius are obtained from spike topographs.

5.2 THE METHOD FOR TAKING SPIKE TOPOGRAPHS

5.2.1 Aim

The purpose of this section is twofold: firstly it is a description of the experimental procedures utilized in this study, and secondly, together with section 5.3, it provides a coherent record of the technique of spike topography for the use of others interested in exploiting it. Section 5.3
explains how information on platelet size is extracted from the topographs.

5.2.2 The Basic Set-up

In order to take a spike topograph, the usual procedure is to set up for taking a 111 section topograph (sec.1.2.3.4) of the region of interest, using Cu Kα1 characteristic radiation. The diffraction geometry for this is shown in fig.4.5a; 2θB = 44° approximately. The crystallographic axis [110] is aligned parallel to the camera rotation axis (usually vertical). Having found the position for the Bragg reflexion, the angle, ω of the crystal, is then mis-set to achieve the conditions for spike diffraction using the characteristic wavelength. This can be visualized in reciprocal space as the Ewald sphere cutting the spike, as shown in fig.4.5b. The crystal axis [110] is perpendicular to the plane of the diagram. The [001] direction spike (shown by the solid line) from a 111 relp is being examined. Also shown, by broken lines, are the projections, onto the plane of the diagram, of the [100] and [010] spikes which are inclined at ±45° to this plane and are cut obliquely by the Ewald sphere.

5.2.3 Choice of Radiation

The following table gives the percentage transmission of various wavelengths of x-rays through 10 cm of air.
<table>
<thead>
<tr>
<th>WAVELENGTH / Å</th>
<th>TRANSMISSION THROUGH 10 cm AIR</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.7093 (Mo Kα)</td>
<td>99%</td>
</tr>
<tr>
<td>1.5405 (Cu Kα)</td>
<td>89%</td>
</tr>
<tr>
<td>2.2896 (Cr Kα)</td>
<td>68%</td>
</tr>
</tbody>
</table>

**TABLE 5.1**  
Transmission of X-Rays through Air  
(The data used to compile this table was obtained from the International Tables III, 1962)

Cu Kα1 radiation (the α1 peak has roughly twice the intensity of the α2) is chosen for spike topography, in preference to using softer wavelengths such as chromium, because the absorption by air is less thus, making exposure times shorter. On the other hand, a harder radiation like that from molybdenum is unsuitable (Takagi & Lang 1964) because it gives too high a background of Compton scattering (Compton 1923, 1930). Therefore copper gives the best compromise between high air absorption and high Compton scattering.

5.2.4 Direction of Angular Mis-Setting

So as to avoid the spike reflexion due to the Cu Kβ characteristic wavelength (1.3922 Å), the direction of the angular mis-setting is made towards the high angle side of the Cu Kα1 Bragg reflexion, that is to say ω in fig.4.5a is
decreased as has been done in fig. 4.5b. In fig. 5.1 two of the
spike topographs (taken on dental film, of specimen D – see
sec. 5.5.1) are of the 111 reflexion; one for the correct case
where ω was decreased by 1° and the other in the case where
it was increased by 1°. In the latter, spike images due to
the Cu Kβ wavelength can be seen to the left of the other
images (see also fig. 5.3). Note that the films are being
viewed from the specimen.

5.2.5 The Images on a Spike Topograph

On each of the films shown in fig. 5.1 four main images
appear (plus the Kβ images); they are labelled in fig 5.3.
The Laue image is usually an over-exposed section topograph
arising from a component of the continuous spectrum; its
diffraction geometry is shown in fig. 4.5b by the dashed lines.
Then there are the three spike images: the useful spike
topographic image from the [001] reciprocal lattice spike, and
the two images from the other two spikes which are cut
obliquely by the Ewald sphere. From the positional order of
these images one can tell if the angular mis-setting had been
made in the right direction, and also if the correct reflexion
had been chosen (see sec. 5.2.7). Fig. 4.5c illustrates how
the images occur on a topograph in the case of the usual
setting, that is a 111 reflexion mis-set by decreasing ω.

5.2.6 Specimen to Film/Plate Distance

With four images appearing on the photographic emulsion
it is important to ensure that no part of the spike topograph
**Fig. 5.1** The four settings for imaging spike reflections (top left is correct for spike topography)

**Fig. 5.2** Spike topographs taken with various specimen to plate distances and mis-setting angles
**Angular Mis-setting**

<table>
<thead>
<tr>
<th>θ - 1°</th>
<th>111 Reflexion</th>
<th>111 Reflexion</th>
</tr>
</thead>
<tbody>
<tr>
<td>θ + 1°</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Specimen to Plate Distance (mm)**

<table>
<thead>
<tr>
<th></th>
<th>1°</th>
<th>2°</th>
<th>3°</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>60</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>70</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Angle of Mis-setting**
Image is overlapped by any of the others. A specimen to plate distance of 50 mm, with a crystal mis-setting of 1° off the Bragg angle, will usually achieve this, and this arrangement has been adopted as the standard (Doers & Lang 1972). Fig. 5.2 (also of specimen D1) shows the effect of increasing both specimen to film distance and angular mis-setting.

3.2.7. The Ill reflection plane.

It was pointed out earlier, in Fig. 4.5b, that the Ill reflection can be explained in terms of the 1001 spike (originally from the Ill sublattice) being examined. The broken line represents the projections, onto the plane of the diagrams, of the 1010 and 0110 spikes. Now imagine that the 0110 spike and 0110 sublattice spike would be more obliquely by the formers to the plate than in the latter case. This would be a definite consequence of the topographic resolution. Suzuki & Lang found this spike oblique setting unsuitable for quantitative work, unless the spikes were very visible.

**Fig. 5.3** Description of the images appearing on the topographs in Fig. 5.1.
image is overlapped by any of the others. A specimen to plate distance of 50 mm, with a crystal mis-setting of 1° off the Bragg angle, will usually achieve this, and this arrangement has been adopted as the standard (Moore & Lang 1972). Fig.5.2 (also of specimen D) shows the effect of increasing both specimen to film distance and angular mis-setting.

5.2.7 The Snare of the 111 Reflexion

Suzuki & Lang (1976) pointed out a pitfall to be avoided in spike topography. It can be explained by reference to fig.4.5b. In the diagram the [001] spike (solid line) from the 111 relp is being examined. The broken line represents the projections, onto the plane of the diagram, of the [100] and [010] spikes. Now imagine that the [001] spike from a 111 relp were being examined instead. The broken line in the diagram would represent the direction of this spike and the projections of the inclined [100] and [010] spikes would lie along the solid line. Clearly, in this setting, the [001] spike would be cut more obliquely by the Ewald sphere than in the former case. This would be to the detriment of the topographic resolution. Suzuki & Lang found this more oblique setting unsuitable for quantitative work, unless the spikes were exceptionally sharp—originating from large platelets. In spike topography it is obvious which setting one has by the relative positions of the images, as can be seen in figs. 5.1 and 5.3. For this reason it is very useful not to mask out the unwanted images as is sometimes suggested (e.g. Frank 1964). In fig.5.7c an example of a 111 (equivalent to 111)
spike topograph is shown, accompanied by the corresponding projection and section topographs (figs. 5.7a and 5.7b respectively). Compare fig.5.7 with fig.5.5.

5.2.8 Cutting the Spike Orthogonally

In the light of what has just been said about an obliquely cut spike, the ideal situation would seem to be for the Ewald sphere to cut the [001] spike orthogonally. A straightforward calculation reveals that to achieve this x-rays of wavelength 2.38 Å are required. This wavelength is available from a synchrotron radiation source (sec.1.2.4.1). However, at 2.38 Å, absorption by diamond is exceptionally high: there will be a drop in intensity of over 99% through a diamond slice only 1 mm thick! Furthermore, for every metre of air path, it is calculated that there is an intensity reduction of about 98%. Taking synchrotron spike topographs for an orthogonally cut spike is therefore clearly impractical.

5.2.9 Exposure and Development

With x-rays from a conventional copper target, the exposure times required for spike topography are very lengthy; at least 100 hours for a 25 μm nuclear emulsion. However, preliminary topographs taken on dental film need take no longer than a twentieth of this. The plate development is long also, sometimes up to 1 hour is needed to bring up the spike image sufficiently; the Laue image of course being over-developed.
5.3 DETERMINING PLATELET SIZE FROM SPIKE TOPOGRAPHS

5.3.1 The Relationship

The shape of the optical density profile of a spike topograph image results from the convolution of two functions (sec. 4.2): the platelet number density, and the Airy diffraction intensity profile appropriate to the mean 'radius' of the platelets behaving as an assembly of circular apertures. The shape of the convolution can easily be obtained by taking a microdensitometer traverse across the topograph, but the information is useless unless the platelet number density profile is known. Now at the edge of the crystal the number density is a step function, and using this information Moore & Lang (1972, 1977) were able to derive the following relationship, from which the mean platelet 'radius' \( R \) can be calculated:

\[
R = M \frac{\lambda L}{2 \pi r}
\]

where \( \lambda \) is the wavelength of the x-rays used, \( L \) is the specimen to plate distance and \( r \) is the interquartile width (IQW) of the optical density profile at the edge of the topographic image. \( M \) equals 1.817 or in some circumstances, for example if the microdensitometer slit needs to be wide, it equals 2.022 (Moore & Lang 1977). A detailed treatment, and derivation, of this formula is given in appendix B.

5.3.2 The Microdensitometry

In order to determine \( r \) in equation 5.1 the optical
density profile at an edge (or edges) of the spike topographic image needs to be plotted by taking a microdensitometer traverse. The traverse is made along the direction on the topograph which would have been perpendicular to the plane of the Bragg reflexion when the topograph was taken, that is the \([1\bar{1}0]\) direction, which is usually vertical on the photographic plate. The reason for this is to avoid any possible effects which were due to wavelength variations in that plane (for more details see Moore & Lang 1972).

Fig. 5.4 shows a typical microdensitometer trace taken across a spike topograph (of specimen F - see sec. 5.5.1); note that the trace is scaled up fifty times. Drawn on it are the interquartile width (IQW) measurements to illustrate how they are made. The IQW can be defined as the width, measured along the abscissa, between the positions on the profile at one quarter and three quarters of the maximum height. It is a very practicable parameter because its value is independent of the overall blackness of the topographic image, which would vary according to specimen, exposure time and the development conditions of the plate.

To obtain the finite width of the microdensitometer slit (in this case 40 \(\mu\)m) is subtracted from the measured IQW. For the theory of this see appendix C.
FIG. 5.4 EXAMPLE OF MICRODENSITOMETER TRACE AND INTERQUARTILE WIDTH MEASUREMENTS
5.4 SHADOWED SPIKE TOPOGRAPHY

A step function in platelet number density, at the topograph, may be introduced artificially by the simple expedient of casting an x-ray shadow onto the specimen with an x-ray absorbing screen. This modification removes the restriction of only being able to make platelet radius measurements at the diamond's natural edge. The technique has been called shadowed spike topography.

For all the shadowed spike topographs taken here a 35 SWG (0.21 mm) sheet of tantalum was employed; its absorption of copper radiation being practically total (3x10^-24 % transmitted!). The tantalum screen was placed close to the crystal and positioned so that the horizontal edge cut across the specimen where the platelet radius was to be measured. The screen was moved up or down to different positions as required, most often simply half way down the specimen. An example of a shadowed spike topograph is shown in fig.5.5c. In this topograph the lower half has been shadowed, as can be seen by comparison with the section topograph above it (fig.5.5b). Fig.5.5a is the corresponding projection topograph.

At one stage, a tantalum comb (tooth and gap widths both 1 mm) was tried, in order to sample more regions per topograph. However, profiles resulting from adjacent edges were sometimes not fully resolved, so this method was abandoned in favour of the aforementioned.
a)  **III Projection Topograph**

b)  **III Section Topograph**

c)  **III Spike Topograph**

**FIG. 55**  **III Topographs of Specimen B**
5.5 DETAILS OF THE PRACTICAL WORK DONE

5.5.1 The Specimens

The seven diamond specimens (A to G) were all in the form of parallel-sided polished slices, with lateral dimensions of the order of 3 to 5 mm. They were chosen because the positions of their infrared platelet peaks (dealt with fully in chap.7) spanned a wide range of values (between 1361 and 1372 cm\(^{-1}\)). Some details are given in table 5.2, including the results of coarse preliminary platelet peak measurements (like figs. 7.1 and 7.2), made near the centre of each specimen using a large aperture, which formed the basis of their selection.

Specimens A and D had, at one time, been electron-irradiated and annealed; details of such treatment can be found in Woods & Collins (1982). A was a pronounced yellow colour, and specimens E and G were reputed to have a high nitrogen content. All the specimens were kindly supplied by Dr. Geoff Woods of CSO Valuations, London, and he was responsible for the measurements of infrared platelet peak position (see chap.7).
<table>
<thead>
<tr>
<th>NAME</th>
<th>PEAK POSITION / cm⁻¹</th>
<th>THICKNESS / mm</th>
<th>TYPE OF FACE</th>
<th>DESTINY</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1361.9</td>
<td>0.700</td>
<td>(100)</td>
<td>Thinned for TEM (chap.6)</td>
</tr>
<tr>
<td>B</td>
<td>1362.2</td>
<td>0.875</td>
<td>(111)</td>
<td>Still extant</td>
</tr>
<tr>
<td>C</td>
<td>1365.1</td>
<td>0.480</td>
<td>(100)</td>
<td>Still extant</td>
</tr>
<tr>
<td>D</td>
<td>Around 1366.5</td>
<td>0.680</td>
<td>(100)</td>
<td>Graphitized to measure N content (elsewhere)</td>
</tr>
<tr>
<td>E</td>
<td>1369.1</td>
<td>0.340</td>
<td>(111)</td>
<td>Thinned for TEM (chap.6)</td>
</tr>
<tr>
<td>F</td>
<td>1370.4</td>
<td>1.465</td>
<td>(111)</td>
<td>Graphitized to measure N content (elsewhere)</td>
</tr>
<tr>
<td>G</td>
<td>1372.5</td>
<td>0.290</td>
<td>(100)</td>
<td>Thinned for TEM (chap.6)</td>
</tr>
</tbody>
</table>

**TABLE 5.2**
Details of the Type Ia Diamonds Studied
5.5.2 The Topography and Results

All of the spike topographs taken here, with copper radiation, were taken on the home-made Lang camera at RHBNC. The approximate set-up used for specimens A, C, D and G is shown in fig.5.6a, and for specimens B, E and F in fig.5.6b. The x-ray beam was slightly taller than the specimen and approximately 300 \( \mu \text{m} \) wide. The middle section of each specimen was illuminated. Both ordinary spike topographs, and spike topographs of the shadowed variety, were taken.

Microdensitometer traverses of the topographs were made on a Joyce Loebel Double-Beam Recording Microdensitometer Mk III CS. The slit width adopted was 40 \( \mu \text{m} \) - wide enough to satisfactorily integrate developed grain clumps readily occurring up to 3 \( \mu \text{m} \) in diameter. The slit was made tall, in order to try and sample a region compatible with that from which the infrared spectrum would be taken, shown in fig.5.6c; this region is drawn in on figs. 5.6a and b. It can be seen that reasonable compatibility is obtained using the arrangement shown in fig.5.6b. However, the correspondence is nowhere near as good with the set-up in fig.5.6a, but it was decided to keep the microdensitometer slit tall enough to cover most of the width of the spike image, in order to include contributions from platelets throughout the entire thickness of the specimen. Grey wedges were chosen to maximise the height of the microdensitometer trace, but without any cut-off occurring. Tests showed that changing the wedge did not affect the interquartile width of the profile.
FIG. 5.6 111 reflecions from various faced diamond plates ([110] vertical)
The microdensitometer ratio arm was set at 50 : 1.

Once the IQWs had been measured from the microdensitometer traces, as in the example given in fig.5.4, the width of the microdensitometer slit (40 \( \mu \text{m} \)) was subtracted and the platelet radii determined using equation 5.1. Since the microdensitometer slit was tall, \( M \) was taken to be 2.022. In practice the calculation was performed on a computer using a simple Fortran program, which also calculated standard errors (e.g. see Topping 1962) by the expression:

\[
\delta R = R \left[ \left( \frac{\delta L}{L} \right)^2 + \left( \frac{\delta r}{r} \right)^2 \right]^{1/2}
\]  

(5.2)

The specimen to plate distance, \( L \) could be set to an accuracy of no worse than \( \pm 2 \) mm (= \( \delta L \)), and the error in the measurements of IQW, \( \delta r \) was reckoned to be no more than 0.02 mm.

Table 5.3 gives results from eighteen topographs of platelet radii determined at various places in the seven specimens. Position 1 was usually at the top of the specimen, the remainder moving down the crystal sequentially (in fig.5.5c the top of the image is at B1 - i.e. specimen B position 1 - and the bottom at B2). On average, the adjacent positions were separated by 1.3 mm vertically, the closest together being 0.6 mm and the widest apart 2.8 mm. The positions on each specimen were centered on the vertical line bisecting it. The orientation of specimen F was lost soon after the spike topography, so positions have not been defined.
since they would have been meaningless for later work.

It had been noticed that the platelet measurements made for the bottom edges of the specimens were consistently low (the results of Moore 1973 also show this). An experiment to determine the effect of the supporting wax, at the bottom of the specimens, revealed that its presence reduced the apparent platelet radius from a half to a third of that measured when it was absent. Consequently, with a single exception (E3 - the one used for the test), the results obtained from the bottom edges of the specimens have been omitted.

Most of the figures in the following table were derived from a combination of measurements. Where this is so, the numbers quoted are the means and standard deviations of the results weighted in inverse proportion to their percentage errors.
### TABLE 5.3
Average Platelet Radius Determined by Spike Topography

<table>
<thead>
<tr>
<th>SPECIMEN</th>
<th>POSITION</th>
<th>PLATELET RADIUS /Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>A 1</td>
<td></td>
<td>297 ± 49</td>
</tr>
<tr>
<td>A 2</td>
<td></td>
<td>243 ± 30</td>
</tr>
<tr>
<td>A 3</td>
<td></td>
<td>180 ± 17</td>
</tr>
<tr>
<td>B 1</td>
<td></td>
<td>303 ± 77</td>
</tr>
<tr>
<td>B 2</td>
<td></td>
<td>278 ± 65</td>
</tr>
<tr>
<td>C 1</td>
<td></td>
<td>95 ± 9</td>
</tr>
<tr>
<td>C 2</td>
<td></td>
<td>190 ± 30</td>
</tr>
<tr>
<td>D 1</td>
<td></td>
<td>156 ± 21</td>
</tr>
<tr>
<td>D 2</td>
<td></td>
<td>156 ± 21</td>
</tr>
<tr>
<td>D 3</td>
<td></td>
<td>156 ± 21</td>
</tr>
<tr>
<td>E 1</td>
<td></td>
<td>122 ± 13</td>
</tr>
<tr>
<td>E 2</td>
<td></td>
<td>98 ± 9</td>
</tr>
<tr>
<td>F -</td>
<td></td>
<td>98 ± 9</td>
</tr>
<tr>
<td>G 1</td>
<td></td>
<td>77 ± 6</td>
</tr>
<tr>
<td>G 2</td>
<td></td>
<td>85 ± 7</td>
</tr>
<tr>
<td>G 3</td>
<td></td>
<td>95 ± 8</td>
</tr>
<tr>
<td>G 4</td>
<td></td>
<td>98 ± 9</td>
</tr>
<tr>
<td>G 5</td>
<td></td>
<td>88 ± 12</td>
</tr>
<tr>
<td>— 148 —</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
5.6 SYNCHROTRON SPIKE TOPOGRAPHY

This chapter finishes by showing some examples of spike topographs of specimen B taken with synchrotron radiation at Daresbury SRS. They were taken, after the installation of the HBL, on Topography Station 3.

Fig.5.8a This topograph was taken with the usual wavelength of 1.5405 Å. The set-up used to select this wavelength, and obtain the Bragg reflexion, is shown in fig.5.9a; in order to take the spike topograph the crystal was mis-set by 1° anticlockwise. There are three images: the two images on the left are due to the oblique spikes, and the one on the right is the spike topographic image; since the radiation being used is purely monochromatic, no Laue image appears. The absence of a Laue image means that it is not immediately obvious which of the four settings shown in fig.5.1 this is. In fact it turns out that this topograph is of the 111 reflexion with a mis-setting of $\phi_0 + 1^\circ$. A spike topograph of the same specimen taken with conventional copper radiation, of the 111 setting (equivalent to 111) is shown in fig.5.7c. With the usual specimen to plate distance of 50 mm the four images are not separated. The topograph in fig.5.8a was taken with a specimen to film distance of 90 mm. It was taken on Agfa Structurix D4 film, and with an average beam current of roughly 150 mA the exposure was approximately 3 hours. A considerable amount of lead shielding was employed to try and keep the background radiation as low as possible, but with such a long exposure required the result was not very
0) III PROJECTION TOPOGRAPH

1) III SECTION TOPOGRAPH

2) III SPIKE TOPOGRAPH

Fig. 5.7  III TOPOGRAPHS OF SPECIMEN B

- 150 -
FIG. 5-8  \( \{111\} \) SYNCHROTRON SPIKE TOPOGRAPHS OF SPECIMEN B
successful since the topograph is of a 3 reflection it is unsuitable for single crystal analysis (see 5.3.2).

The double crystal arrangement used is shown in Fig. 5.9. The crystal wafer was mis-set, by 11. antilockwise, in the case of the previous topograph, but the specimen distance was increased to 100 m in an attempt to reduce the exposure time for the x-ray film. A second run, with an average base current of about 1.5 mA, was performed at this shorter wavelength. It was impossible to make the absorption by x-rays.

**CONCLUDING REMARKS**

by S.D. Tait, of the positions investigated here by spike toposcopy, it is shown to be a valuable technique for investigating electron micrographs at different positions on the specimen. In chapter 6, some of the positions investigated here by spike toposcopy will be re-examined by electron microscopy. The two methods will be compared in chapter 7.

**FIG. 5.9**

**DOUBLE-CRYSTAL ARRANGEMENTS USED FOR S.R. SPIKE TOPOGRAPHY**

- 152 -
successful. Since the topograph is of a $\bar{1}\bar{1}1$ reflexion it is unsuitable for platelet size determination (sec. 5.2.7).

Fig. 5.8b This spike topograph is believed to be the first taken with radiation of wavelength 1 Å. The double crystal arrangement used is shown in fig. 5.9b. The crystal was mis-set by $1^\circ$ anticlockwise as in the case of the previous topograph, but the specimen to film distance was increased to 100 mm in an attempt to improve the image separation. The exposure time for the D4 film was nearly 5 hours, with an average beam current of about 110 mA. Compton scattering at this shorter wavelength was noticeably greater than at 1.5405 Å. Longer wavelengths were not tried because of the increased absorption by air.

5.7 CONCLUDING REMARKS

As the list of results in table 5.3 testifies, shadowed spike topography has proven to be a valuable technique for investigating platelet dimensions at different positions on diamond specimens. In chapter 6 some of the positions investigated here by spike topography will be re-examined by electron microscopy. The two sets of results will be compared in chapter 7.
6.1 INTRODUCTION

The purpose of this investigation was to use transmission electron microscopy (TEM) to try and verify independently platelet radii determined previously by spike topography. This is something which had never been done previously.

The three specimens: A, G and E were chosen for the investigation because, from the the results of the spike topography measurements (chap.5) up to that time, they contained platelets of radii representative of the extremes and middle of the range (table 5.3). Between them the radius varied from 77 to 297 Å. The corresponding infrared platelet peak position (chap.7) varied from 1361.3 to 1370.9 cm$^{-1}$.

Nearly all of the work described in this chapter was carried out at the H.H. Wills Physics Laboratory, University of Bristol.
6.2 SPECIMEN PREPARATION

6.2.1 Purpose

The transmission electron microscope requires that diamond samples be no more than half a micron thick (based on experience at the laboratory), so the first stage of preparation is the thinning of specimens, by mechanical polishing followed by ion-beam thinning. If the specimen then conforms to the lateral size limitations it can be suitably mounted and examined in the microscope.

6.2.2 The Initial State of the Specimens

Prior to this work commencing, the three specimens: A, E and G were thinned by Dr. Geoff Woods at C.S.O. Valuations, London to approximately 400, 300 and 350 \( \mu \text{m} \) respectively. For ion-beam thinning specimens need to be no thicker than about 50 \( \mu \text{m} \), so the next step was to mechanically polish the specimens to this size using the coarser of the two cast iron polishing wheels (scaifes) available at the H.H. Wills Physics Laboratory. The procedure described below is the standard one adopted at that laboratory. (For additional information on the grinding and polishing of diamond see e.g. Grodzinski 1953 chap.6.)

6.2.3 Mechanical Thinning

The specimen is glued to a diamond substrate using 'Araldite'. (A similar material to the specimen is used as the substrate in order to minimise the strains caused by...
mechanical deformation and unmatched thermal expansivity — for the thermal expansion of diamond see Skinner 1957.) As the glue sets the specimen is kept under load to ensure a minimum thickness of glue between the specimen and the substrate. Potential failure of a set joint can be recognized by the presence of coloured interference fringes in regions where there is slight separation (Walmsley 1981), so this must be frequently checked during the thinning.

The specimen-substrate assembly is then glued to a standard scanning electron microscope stub, which in turn is attached to a special holder (known as a 'dop') designed to enable changes in the specimen thickness to be monitored using a depth gauge micrometer (op. cit.).

The dop is then mounted vertically, on a hinged arm, under load (initially 200 g) and traversed horizontally back and forth along the radius of the 13" diameter scaife which is rotating in the horizontal plane. The scaife is charged with a mixture of 2 to 4 µm diamond powder and olive oil, and the dop is usually mounted such as to present the easy [100] polishing direction (e.g. see Wilks & Wilks 1965). In this way one side of the specimen is polished down until the required thickness is reached. The scaife rotates at about 2300 r.p.m. and the dop completes a traverse about once every two minutes. In order to promote even wear the traverse mechanism is geared to be travelling fastest at the circumference and slowest near the centre of the wheel.
At intervals, checks are made on the condition of the mounting, the specimen thickness and the rate of polishing. The load may be increased periodically once the surface of the specimen has been polished flat (with these specimens the load was increased first to 400 g and later to 600 g).

During the polishing process, material removed from the specimen surface tends to replace the original diamond powder as it is broken down, but it is still prudent to recharge the scaife with the diamond powder-olive oil mixture every two to three hours. Over a longer period the scaife itself wears quite smooth, and its ability to retain the diamond grit is reduced; so it has to be roughened from time to time by dragging a sharp piece of diamond back and forth across the rotating surface.

At the end of the thinning, when the desired thickness has been reached, the 'Araldite' is softened with hot (about 100°C) dimethyl formamide, and the specimen is gently prized from the substrate.

6.2.4 The Performance of the Three Specimens

With specimen G the polishing rate varied from 15 to 60 \( \mu m \) per hour, increasing as the load was increased; it took ten hours to polish down to 30 \( \mu m \). Specimen A took ten and a half hours to polish down to 40 \( \mu m \), the rate varying from 15 to 40 \( \mu m \) per hour. These two specimens were quite straightforward to do as they both had nominally (100) type faces and therefore unambiguous easy polishing directions, however E was
a (111) type slice. With a (111) type face the easy direction is towards a dodecahedral face, the opposite direction - towards a cube face - is the hard direction (Wilks & Wilks 1965) so ambiguity can arise. The first polishing direction chosen with specimen E happened to be the hard one; after one and a half hours under a load of 200g no change could be measured. After the specimen had been rotated through 180°, it polished down to 20 μm in just seven hours. The polishing rate varied from 10 μm per hour initially, to 60 under a 600 g load.

6.2.5 Mounting the Specimens for Ion Beam Thinning

The three specimens each measured about 3 to 5 mm laterally. To be suitable as a TEM specimen the largest dimension must not exceed 3mm - the maximum that can be accommodated by the microscope specimen holders. Also, there were specific areas of interest - those which had been examined previously by spike topography (table 5.3) and infrared spectroscopy (chap.7). Therefore it was necessary to break the specimens so that an area of interest occurred near the middle of a fragment of suitable size.

The samples were broken by temporarily adhering them to a glass slide using molten amber resin (colophony) and applying gentle pressure with another slide. The breaks did not always occur where they were wanted. Specimen G broke earlier while being removed from the substrate, but in a fortunate way; it was further subdivided to obtain a fragment containing position 2 (refer to table 5.3) and another containing...
position 4. Unfortunately specimen A broke so that position 1 was on the very edge of the fragment, but a good fragment containing position 3 was obtained. An accident with specimen E rendered its central region useless but the remainder provided reasonable samples containing positions 1 and 3.

Once the specimens had been fragmented, the useful samples were cleaned by gently rubbing them on 'wet and dry' paper with chloroform soaked filter paper. Prior to fragmentation the required positions had been marked on the specimens using a fine felt-tipped pen. These marks had to be preserved until after mounting. Handling such small and thin samples is tricky and the tiddly-wink effect must be avoided!

The samples were next glued with 'Araldite' to 3.05 mm hole copper grids, with the position of interest centred over the hole, hence the importance of preserving the pen mark. However, with the first sample to be ion-beam thinned, G4, it was found that the pen mark interfered with the process, so thereafter the marks were removed with chloroform once the sample was mounted.

6.2.6 The Ion-Beam Thinning

An Edwards model IBT 200 ion-beam thinning unit, attached to a model E306 coater was used to thin the samples. The thinning is done, on both sides of the sample simultaneously, by two 5 keV beams of argon ions. The specimen surface normal is set at 30° to the beam direction, and the specimen holder rotates during thinning. By the addition of stainless steel
masks to the standard specimen holder, the circular area of sample exposed was reduced to 0.8 mm in diameter (except in the case of G4, where a 1.2 mm mask was used).

In principle, a hole should appear at the centre of the region of sample exposed to the beam; however, thinning tends to take place preferentially at the edge, because the beam is quite broad. It is the thin material adjacent to this hole which is examined by the microscope.

After the thinning is complete, the grid with sample is adhered with silver dag to the inside of a standard brass cup, for convenient use in the microscope's 'tilt-rotate' specimen holder.

6.3 THE ELECTRON MICROSCOPY

6.3.1 Principles

Transmission electron microscopy (TEM) is discussed only very briefly here. For a complete account see, for example, Thomas (1962), Hirsch et al (1977); for a shorter article on the subject see Heydenreich (1982).

The principle of TEM is analogous to x-ray transmission Laue topography (e.g. see sec.1.2.4.3). A beam of electrons incident on a thin sample will, on passing through the material, be diffracted in various directions by elastic Bragg scattering. An electron diffraction pattern (ED) will be produced (fig.6.1), like a very compressed transmission Laue
The six most densely populated reciprocal lattice planes for the face-centred cubic crystal.

**FIG. 6.1** SOME ELECTRON DIFFRACTION PATTERNS
(AFTER HIRSCH ET AL 1977)
pattern dependent on the crystal structure and the specimen orientation. (For a comparison of x-ray and electron diffraction, see Meyer 1949.) A pattern occurs with a beam of monoenergetic electrons because the wavelength of electrons is small (e.g. 0.037 Å at 100 kV), and therefore the corresponding Ewald sphere large. In fact the reflecting sphere is large enough compared with the distance between the neighbouring reciprocal lattice points, of a crystal, to be considered planar. Therefore reflexions will be excited even when Bragg's law is not strictly satisfied (see Hirsch et al 1977 chap.5). The planes giving rise to the spots of the diffraction pattern are those approximately parallel to the electron beam direction. A magnified image of the diffraction pattern is then produced on a fluorescent screen, by allowing all the diffracted beams to pass through a series of electron lenses arranged like those of an optical projection microscope. The diffraction pattern may then be photographed.

Fig.6.2 (after Thomas 1962) illustrates the mechanisms by which the electron microscope is used for image formation. By blocking off all the diffracted beams, and allowing only the direct beam to pass through, a 'bright field' (BF) image is produced. In x-ray terms this is analogous to the radiograph (or direct beam topograph – Lang 1963). Receiving only one of the diffracted beams (usually a strongly excited one) gives rise to a 'dark field' (DF) image, which is the electron analogue of the standard x-ray topograph. However, because the wavelengths of electrons are considerably smaller than those of x-rays, and because they can be focussed, the
4.3.2 The weak-beam technique

The weak-beam dark-field imaging technique (Cockayne et al., 1963) has demonstrated the applicability of weak-beam microscopy (Cockayne et al., 1963) for analysis of nanostructures with a high degree of detail.

In the weak-beam technique, the electron beam is very weak for practical purposes, but well localized contrast can be produced at a strongly diffracting object, such as a platelet, because of the strong distortion of the lattice. For rigorous and detailed accounts of the technique, see Cockayne et al. (1963, 1964) and Tarazona & Smallman (1975). Figure 6.2 illustrates this situation in reciprocal space.

**FIG. 6.2**

**LEFT:** ARRANGEMENT FOR BRIGHT FIELD IMAGING

**RIGHT:** ARRANGEMENT FOR DARK FIELD IMAGING

(AFTER THOMAS 1962)
resolution of TEM is much superior to that of x-ray topography — a few tens of angstroms compared to no better than about a micron with conventional topography. Lang (1978) discusses the relative merits of the two techniques.

6.3.2 The Weak-Beam Dark Field Technique


Weak-beam dark field (WBDF) images are obtained by imaging a reflexion other than the strongly excited one. Such a situation might be represented in a shorthand form by: \( g, -g \), meaning that the first order reflexion was being imaged under diffraction conditions where its inverse was being strongly excited. Fig.6.3b illustrates this situation in reciprocal space.

In the weak-beam method, the diffracted beam is very weak for perfect regions of the crystal, but well-localized contrast will be produced at a strain-producing defect, such as a platelet, because of the strong distortion of the lattice. For rigorous and detailed accounts of the technique see Cockayne (1973, 1978), Loretto & Smallman (1975 sec.5.2), Loretto (1984 sec.5.3.3).

6.3.3 The Microscopy of the Specimens

All of the electron micrographs shown here were taken at
University of Bristol, with a Philips EM30 microscope operated at 200 kV. Experience has shown this voltage to be well below the damage threshold for diamond samples. The microscope was calibrated at high magnification by taking pictures of a standard cross-wire (150 lines/mm).

(a) \( g, -g \)

Micrographs for most tests were taken on Ilford EM film, exposure times being about half a second for the five-second exposures for SE pictures and 60 seconds exposure for WE pictures. The film was developed for 5.5 minutes at 20°C in Kodak PG universal developer at standard concentration.

In 1962 the first direct observations of plate-like (105) planes of diamond were made by Evans & Phillips (1962). An important landmark in the history of platelets was the (105) edge-on platelet, first observed by Evans (1965) in 1965, with the early work. Evans took micrographs with the 105 electron beam direction, but without the specimen tension. The specimen is shown in the (105) plane, and the same face-on, showing the (105) edge-on platelet in the (105) plane. After 1965, more advancements.

(b) \( g, -g \)

The corresponding graph is shown in the (105) plane of sample 24, the corresponding ED is shown in the same right-hand corner, and the little square is used for the scale indicating the size. This corresponds to 2600 A. As well as the faces (105).

**Fig. 6.3** Diffraction conditions, shown in reciprocal space, for weak-beam dark field electron microscopy
the University of Bristol, with a Philips EM430 microscope operated at 200 kV. Experience has shown this voltage to be just below the damage threshold for diamond samples. The microscope was calibrated at each magnification by taking pictures of a standard cross-grating (2160 lines/mm).

The micrographs (as negatives) were taken on Ilford EM film, exposure times being roughly half a second for EDs, five seconds for BF pictures and half to one minute for WBDF pictures. The films were developed for 4.5 minutes at 20°C in Ilford PQ Universal developer at standard film dilution.

6.3.4 Imaging the Platelets

Back in 1962 the first direct observations of platelets in {100} planes of diamond were made by Evans & Phaal (1962b). This was an important landmark in the history of platelet study (sec.4.1.4); Evans (1965) surveys the early work. Evans & Phaal took micrographs with a [100] electron beam direction, in other words the specimen was viewed from the [100]; therefore platelets in the (100) plane were seen face-on, thus making their shapes discernable. An example of such a micrograph is shown in fig.6.4, which is a BF picture \((g = 220)\) of sample G4. The corresponding ED is shown in the lower right hand corner, and this little picture may be conveniently used for the scale length; its width in this figure corresponds to 2670 Å. As well as the face-on (100) platelets, platelets in the (010) and (001) planes can be seen edge-on, as lines. Thickness estimates from these edge-on platelets are not feasible because of the uncertainty of
[100] ORIENTATION BRIGHT FIELD TRANSMISSION ELECTRON MICROGRAPH ($g = 220$) OF SAMPLE G4

FIG. 6.4
strain field effects (Evans 1965).

Nowadays, for studies of platelets, the [110] orientation is preferred (first used by Woods 1976 in his study of 'giant' platelets) where the platelet containing {100} planes are seen from the [110] direction, as shown in fig.6.5. In this orientation the (100) and (010) planes are each inclined at 45° to the (110) viewing plane, so enabling the faces of platelets in both these planes to be seen. Only the (001) plane is seen edge-on, its platelets appearing as lines parallel to the [110] direction. The fact that the shapes of platelets on two of the three planes are discernable is one justification for using the [110] orientation. Another is the removal of any ambiguity between platelet images and images of dislocation loops (Evans & Phaal 1962a). Such ambiguity seems to exist in the [100] orientated micrographs taken by Evans & Phaal (1962b) – for example see their fig.3. (This was confirmed by Prof. Evans in a private communication.) In the [110] orientation the distinction is clear because the platelet images contain depth-dependent fault fringes (Sumida & Lang 1988). Differences in these fault fringes distinguish platelets lying on the (100) and (010) planes. Fig.6.6 is a BF (zone axis) micrograph of sample A3 taken in the [110] orientation; the scale length (width of ED picture) is 3400 Å. Notice how the (100) and (010) platelets do not show equivalent fault fringes.
FIG. 6.5  VIEW OF PLATELETS FROM THE [110] DIRECTION

(i) & (ii) PERFECTLY CIRCULAR PLATELETS
(iii) LONG LATH LIKE PLATELET (SEE LANG 1977a, b)
(iv) EQUIAxed STRAIGHT SIDED PLATELET
(v) PLATELET ELONGATED PARALLEL TO [101]

(AFTER SUMIDA & LANG 1988, Q.V. FOR FURTHER DETAILS)
[110] B.F. TRANSMISSION ELECTRON MICROGRAPH (ZONE AXIS) OF SAMPLE A3

FIG. 6.6

3400 Å
Sumida & Lang (1988) demonstrate convincingly, with a sequence of dark field images, how there is enhancement in platelet resolution in going to progressively weaker diffraction conditions. Therefore, a better assessment of platelet shapes and sizes can be made by using the weak-beam technique. For platelet size determination the WBDF method was the main one adopted, and micrographs were taken with the samples in the [110] orientation. There follows a description of three micrographs of this sort.

Fig.6.7 This shows a WBDF micrograph of sample A3, taken in the [110] orientation with the $-g, g$ diffraction condition ($g = 220$) as is illustrated in fig.6.3a. The scale length corresponds to 3400 Å. Notice the difference in contrast between the (100) and (010) platelet images. Compare this micrograph with the next.

Fig.6.8 This micrograph is the same in all respects as the former except that the excitation was $g, -g$ (fig.6.3b). In this picture more of the platelets are easily visible, and the platelets on the two planes can be distinguished by the contrast at their edges; the fault fringes are evident, though faint. In both this and the previous micrograph the edge-on (001) platelets are practically invisible.

Fig.6.9 In this micrograph a greater area of sample A3 is being imaged. It is roughly one quarter of the enlargement of the previous two and the scale length is approximately 19800 Å. This WBDF picture was taken with the $g, -g$ ($g = 111$) excitation, in the [110] orientation.
[110] ORIENTATION W.B.D.F. MICROGRAPH (-g, g CONDITION, g = 220) OF SAMPLE A3

FIG. 6.7

- 172 -
[110] ORIENTATION W.B.D.F. MICROGRAPH (g,-g condition, g=220) OF SAMPLE A3

FIG. 6.8
[110] ORIENTATION
W.B.D.F. MICROGRAPH
(g, -g CONDITION, g = 111)
OF SAMPLE A3

FIG. 6.9

19800 Å
The region shown in figs. 6.7 and 6.8 appears in the top right hand corner of this micrograph, rotated through about 100° clockwise. To locate the area more precisely: the bottom left hand corner of fig.6.8 occurs just under half way across and about one fifth of the way down fig.6.9, and the top right hand corner occurs just under three quarters of the way across and nearly two fifths of the way down. The feature in the centre of this picture was a piece of dirt, probably a fibre; it proved useful for relocating this particular region.

6.4 MEASUREMENT OF THE PLATELETS

6.4.1 Calculations from the Projected Image

The elliptically shaped platelets lie on \{100\} planes and are being viewed from the [110] direction, as shown in fig.6.5, so are inclined at 45° (or 90°) to the (110) viewing plane. It is therefore necessary to be able to calculate the true platelet dimensions from the projected ones measured from the electron micrographs.

Within a \{100\} plane the elliptical platelets tend to lie orientated with their major and minor axes along \langle110\rangle directions (e.g. \textit{v} in fig.6.5); these directions project to \langle112\rangle directions in the (110) viewing plane. Sumida & Lang (1988) determined that the true platelet area, \(A'\) can be derived from the relation:

\[
A' = 0.89n^2 + 0.94n(m-n)
\]  

- (6.1)
where \( m \) and \( n \) are respectively the projected major and minor diameters measured in the \(<112>\) directions. This enables the radius, \( R \) to be calculated since:

\[
R = \left( \frac{A'}{\pi} \right)^{\frac{1}{2}}
\]  

- (6.2)

In some circumstances, for example if using an image analyser (sec 6.4.3), it is easier to measure the major and minor axes of the elliptically shaped platelet images as seen, that is, without any reference to \(<112>\) projected directions. What follows is the derivation of expressions to calculate the true semi-major and semi-minor axes, \( a' \) and \( b' \), from those measured from the electron micrographs, \( a \) and \( b \).

Take the (100) plane (say) being viewed from the [110] direction. Within the (100) plane the elliptical platelets lay orientated with their major and minor axes along the [O11] and [O11] directions (e.g. see Sumida & Lang 1988). If these are the \( x \) and \( y \) axes respectively, then in matrix form the equation of such an ellipse is:

\[
\begin{bmatrix}
  x \\
  y 
\end{bmatrix}
\begin{bmatrix}
  \frac{1}{a'^2} & 0 \\
  0 & \frac{1}{b'^2}
\end{bmatrix}
\begin{bmatrix}
  x \\
  y 
\end{bmatrix}
= 1
\]  

- (6.3)

The ellipse containing plane is inclined to the (100) viewing plane about the [001] axis, so it is convenient to redefine the cartesian axes to run along the [001] and [100] directions. Call these \( x' \) and \( y' \) respectively; they are
obtained by a rotation of 45° about the origin, therefore:

\[
\begin{bmatrix}
x' \\
y'
\end{bmatrix} = \begin{bmatrix}
\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\
-\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}}
\end{bmatrix} \begin{bmatrix}
x \\
y
\end{bmatrix}
\]

or

\[
\begin{bmatrix}
x \\
y
\end{bmatrix} = \begin{bmatrix}
\frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \\
\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}}
\end{bmatrix} \begin{bmatrix}
x' \\
y'
\end{bmatrix}
\]

and

\[
\begin{bmatrix}
x & y
\end{bmatrix} = \begin{bmatrix}
x' & y'
\end{bmatrix} \begin{bmatrix}
\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\
-\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}}
\end{bmatrix}
\]

so (6.3) can be rewritten:

\[
\begin{bmatrix}
x' & y'
\end{bmatrix} \begin{bmatrix}
\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\
-\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}}
\end{bmatrix} \begin{bmatrix}
\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\
-\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}}
\end{bmatrix} \begin{bmatrix}
x' \\
y'
\end{bmatrix} = 1
\]

This equation defines an ellipse with semi-major and semi-minor axes, \(a'\) and \(b'\), orientated at 45° to the \(x', y'\) axes, that is along the directions \([0\bar{1}1]\) and \([01\bar{1}]\).

Viewing the (100) plane from the \([110]\) direction will make the apparent length of the \([010]\) \(y'\) axis appear shorter by a factor \(1/\sqrt{2}\). Therefore in the (110) plane the observed axes, \(x''\) and \(y''\), which will be aligned respectively in the \([00\bar{1}]\) and \([\bar{1}10]\) directions, are defined by:

\[
\begin{bmatrix}
x'' \\
y''
\end{bmatrix} = \begin{bmatrix}
1 & 0 \\
0 & \frac{1}{\sqrt{2}}
\end{bmatrix} \begin{bmatrix}
x' \\
y'
\end{bmatrix}
\]
or
\[ \begin{bmatrix} x' \\ y' \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 0 & \frac{1}{\sqrt{2}} \end{bmatrix} \begin{bmatrix} x'' \\ y'' \end{bmatrix} \]

and
\[ \begin{bmatrix} x & y \end{bmatrix} = \begin{bmatrix} x'' & y'' \end{bmatrix} \begin{bmatrix} 1 & 0 \\ 0 & \frac{1}{\sqrt{2}} \end{bmatrix} \]

so now (6.4) will be written:
\[
\begin{bmatrix} x'' & y'' \end{bmatrix} \begin{bmatrix} \frac{1}{2a'^2} + \frac{1}{2b'^2} \\ \sqrt{2} \left( -\frac{1}{2a'^2} + \frac{1}{2b'^2} \right) \end{bmatrix} \begin{bmatrix} x'' \\ y'' \end{bmatrix} = 1 - (6.5)
\]

This is the equation of the ellipse as it is observed from the [110] direction, written in terms of its true dimensions as measured in the (100) plane. With the appropriate rotation (6.5) can be rewritten:
\[
\begin{bmatrix} x'' & y'' \end{bmatrix} \begin{bmatrix} \frac{1}{a'^2} & 0 \\ 0 & \frac{1}{b'^2} \end{bmatrix} \begin{bmatrix} x'' \\ y'' \end{bmatrix} = 1 - (6.6)
\]
a and b being the semi-major and semi-minor axes as measured in the viewing plane.

Now, the trace of a square matrix is unaltered by a rotation transformation (e.g. see Chirgwin & Plumpton 1981 chap.5) and also the determinant remains unchanged; so from the coefficients of (6.5) and (6.6) the following
simultaneous equations are obtained:

\[
\frac{1}{a^2} + \frac{1}{b^2} = \frac{3}{2} \left( \frac{1}{a'^2} + \frac{1}{b'^2} \right)
\]

\[
\frac{1}{a^2} \cdot \frac{1}{b^2} = \frac{2}{a'^2} \cdot \frac{1}{b'^2}
\]  

- (6.7)

These give quadratics in \(a^2\) and \(b^2\) from which (choosing \(a'\) to be the semi-major axis) are derived:

\[
a' = \left[ \frac{2}{3} (a^2 + b^2) + \frac{1}{3} \sqrt{4(a^2 + b^2)^2 - 18a^2b^2} \right]^{\frac{1}{2}}
\]

\[
b' = \left[ \frac{2}{3} (a^2 + b^2) - \frac{1}{3} \sqrt{4(a^2 + b^2)^2 - 18a^2b^2} \right]^{\frac{1}{2}}
\]  

- (6.8)

6.4.2 Measurements made by Hand

Most of the hand measurements of platelets were made from WBDF micrographs taken in the [110] orientation, like that shown in fig.6.9. (the only exception was in the case of sample A3 – see sec.6.4.4). At the time of the microscopy, the magnifications used were chosen to give good platelet images of roughly comparable size between samples. Three times enlarged prints of the micrographs (the micrographs themselves are in the form of negatives) were then made onto grade 3 'Ilfospeed' paper. The overall magnification varied, but the outcome was that platelet images on each print averaged about 5 mm as their longest dimension.
The projected major and minor diameters were measured with the aid of a <112> net, photocopied onto celluloid, which was orientated with respect to the edge-on platelets. Two hundred elliptical platelets were measured for each sample, from randomly selected patches on the print. The measurements were made using a ruler and magnifying glass, to an accuracy of 0.5 mm.

The information was entered on to a personal computer spreadsheet ('AsEasyAs', Trius Inc. Lynn, Mass.), where the platelet radii were calculated using equations (6.1) and (6.2). The results are presented in the form of histograms in fig.6.10 (c to f) and are repeated in table 6.1.

6.4.3 Measurements made by Machine

A computer image analysis system (e.g. see Jenkinson 1987) is an alternative, though not necessarily less time consuming, method of measuring the dimensions of platelet images. It also provides a check for the results obtained by hand measurements. The system employed here was a Cambridge Instruments Quantimet 970.

WBDF images, like fig.6.9, were found to be unsuitable for image analysis by this machine, because of the variation in background contrast, so a BF image of sample A3 was used (a x1.75 enlarged print is shown in fig.6.11). An unenlarged, carefully shaded, print was made of the micrograph on high contrast (grade 5 Ilfospeed) paper. It was important to make sure that the light fault fringes in the platelet images were
FIG. 6.10 PLATELET RADIUS DISTRIBUTION IN THE SAMPLES

(a) SAMPLE A3 (QUANTIMET) 362 ± 113

(b) SAMPLE A3 (HAND) 385 ± 115

(c) E1 101 ± 32

(d) E3 159 ± 41

(e) G2 93 ± 28

(f) G4 86 ± 25
PRINT OF A [110] ORIENTATION
B.F. ELECTRON MICROGRAPH
($g = 111$) OF SAMPLE A3

FIG. 6.11
distinguishable from the background, so that the machine would not regard each dark fringe as a feature in its own right. From the photograph the Quantimet creates a 'binary image' (see Jenkinson 1987) from which it makes its measurements, and which can be manipulated and adjusted as required. A picture of this image, after it had undergone appropriate alterations, is shown as the frontispiece (page 2).

The Quantimet is capable of measuring several parameters, and also calculating new ones. For example, those of direct use in determining platelet size were: 'length' and 'breadth', equal to $2a$ and $2b$ respectively, and 'area'. Two other useful parameters were 'orientation' and 'roundness'. The first of these is based on the direction of the longest dimension. By restricting the range of 'orientation' acceptable, the edge-on platelets were excluded from measurement. The 'roundness' is defined as:

$$\text{perimeter}^2 / 4\pi \times \text{area}.$$ 

(E.g. Roundness = 1 for a circle and $4/\pi$ for a square.) It was found that, by accepting only features with 'roundness' between 1 and 2.2, most overlapping platelet images were eliminated, while leaving the discrete ones unaffected. The remaining few overlapping platelets were removed from the binary image by manual editing.
The following parameters were defined: 'semi-major axis', $a$, and 'semi-minor axis', $b$, obtained by using equations (6.8); 'area2' (true platelet area) which was defined from equation (6.7) as $\sqrt{2} \times \text{area}$, and by substituting this into equation (6.2), 'radius', $R$ was found.

The image was calibrated on the basis of the width of the dark rectangle in the top left corner (e.g. see fig. 6.11). Its width was calculated as being equivalent to 13372 Å.

Owing to lack of memory space, the existence of the defined parameters restricted the number of features the Quantimet was capable of measuring in one go, from 1000 to only about 300. It was therefore necessary to divide the picture into five fields, of equally wide horizontal bands, to be treated separately. Histograms of the combined results of measurements from all the fields are presented in fig. 6.12; a total of 994 platelets was measured.

6.4.4 Comparison of the two Measurement Techniques

The 167 platelets measured by the Quantimet in the top field (i.e. the upper one fifth) of the picture in fig. 6.11 were also measured by hand for comparison. The average platelet radius obtained by the two techniques agreed to within 6%. Histograms of the two results appear in fig. 6.10 a and b.
Fig. 6.12 Histograms of various platelet parameters measured using the 'Quantimet' on the entire field of the micrograph of sample A3 shown in Fig. 6.11
6.5 THE RESULTS

The table below gives, for each sample, the mean platelet radius and standard deviation, as determined from TEM. The figures cited are from the hand measurements only.

<table>
<thead>
<tr>
<th>SPECIMEN</th>
<th>POSITION</th>
<th>MEAN PLATELET RADIUS / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>3</td>
<td>385 ± 115</td>
</tr>
<tr>
<td>E</td>
<td>1</td>
<td>101 ± 32</td>
</tr>
<tr>
<td>E</td>
<td>3</td>
<td>159 ± 41</td>
</tr>
<tr>
<td>G</td>
<td>2</td>
<td>93 ± 28</td>
</tr>
<tr>
<td>G</td>
<td>4</td>
<td>86 ± 25</td>
</tr>
</tbody>
</table>

**TABLE 6.1**

Average Platelet Radius Determined from TEM

It can be seen from these results, especially by comparing the histograms in fig.6.10, that as the average platelet radius increases so too does the spread in values.

These results are compared with those obtained by spike topography in chapter 7, where the connexion between platelet size and infrared peak position is discussed.
7.1 INFRARED ABSORPTION IN TYPE Ia DIAMOND

7.1.1 Background

Observations on the infrared (IR) absorption spectra of diamond were first made at the end of the last century by Julius (1892). Robertson et al (1934), who classified diamond on the basis of differences in spectra, gives an early review on the subject. For more recent reviews on the optical properties of diamond see Davies (1977) and Walker (1979).

Platelet-containing diamonds belong to the optical classification type Ia (sec.2.2.2). The one-phonon IR absorption spectra (e.g. see Ziman 1972 sec.8.4) of six of the seven specimens studied in previous chapters are shown in figs. 7.1 and 7.2. It was shown experimentally by Smith & Hardy (1960) that the features of these spectra are due to imperfections, after Lax & Burstein (1955) had shown theoretically that the symmetry of an ideal diamond lattice forbids single phonon absorption. On the spectra three features can be seen: the A feature and the B feature.
FIG. 7.1 I.R. SPECTRA TAKEN AT THE CENTRE OF THE SPECIMENS USING A 1mm DIAMETER CIRCULAR APERTURE
FIG. 7.2 I.R. SPECTRA TAKEN AT THE CENTRE OF THE SPECIMENS USING A 1mm DIAMETER CIRCULAR APERTURE
(Sutherland et al 1954), and the 'platelet' peak, often known as B2 or B' (Sobolev et al 1965). Davies (1971) demonstrated that the A and B features arose because the IR spectra consisted of a superposition of two distinct component spectra. A process for resolving the A and B components was given by Davies (1972, 1980) and Davies & Summersgill (1973).

The A component, whose principle peak is at 7.8 μm, 1282 cm⁻¹, is believed to be due to IR absorption by pairs of nitrogen atoms (A nitrogen defect) which have each replaced two carbon atoms (Davies 1976, Davies & Nazaré 1979). The B component, with principle peak at 8.5 μm, 1176 cm⁻¹ is caused by the B defect form of nitrogen thought to consist of four substitutional nitrogen atoms disposed tetrahedrally about a vacancy (Loubser & Van Wyk 1981). The expressions relating absorption strengths to defect concentrations may be found in Davies (1980).

In addition to these two components, there is a claim by Clark & Davy (1984) that another (the D component) may be present, which overlaps them. Woods (1986) briefly reviews some other components, and also discusses the behaviour of nitrogen in diamond, and the formation of, and conversion between, the various nitrogen defects.

7.1.2 The 'Platelet' (B') Peak

The B' feature, which peaks around 7.3 μm, 1370 cm⁻¹, in IR absorption was found by Sobolev et al (1968a,b) to be due to the platelets in diamond, hence its alternative name.
Sobolev et al (1965, 1968b) investigated the relationship between the x-ray spikes (chap.4) and IR spectra obtained from type I diamonds. They compared the optical properties of over one hundred Yakutian diamonds (see Bobrievich et al 1959 for a treatise on diamonds from this region of the USSR) with their Laue patterns. They found no correlation between integrated spike intensity and the IR A feature. This lead them to the view that nitrogen was not a component of platelets, because IR absorption at 7.8 μm had been found to be proportional to nitrogen content (Kaiser & Bond 1959, Lightowlers & Dean 1964).

Since then, a relation between the relative amount of A nitrogen present and the absorption coefficient of the platelet peak has been noticed (Brozel et al 1978, Davies 1981). Sobolev et al also found no connexion between spike intensity and the B feature (although the B feature did accompany platelets - Sobolev & Lisoivan 1972), however the results of Woods (1986) have revealed a linear relation between the absorption coefficient of the B component and the integrated absorption of the platelet peak.

Sobolev et al did discover a linear relationship (confirmed by Evans & Rainey 1975 and Klyuev et al 1977) between the integrated spike intensity and the strength of the B' peak. Since Evans (1973) had confirmed by electron microscopy that the spike intensity was proportional to the total platelet area per unit volume, the integrated absorption of the platelet peak (Woods 1986) may then be taken as a
measure of the platelet concentration in the crystal.

Sobolev et al also noticed that the frequency (wavenumber) of the platelet peak varied from 7.25 μm (1378 cm\(^{-1}\)) to 7.36 μm (1358 cm\(^{-1}\)) depending on the sample. Both these observations compared favourably with differences in IR spectra recorded by Evans & Phaal (1962b) on diamonds whose platelets had been examined by electron microscopy. Sobolev et al (1968a) used data from Evans & Phaal's study to plot a hypothetical curve, shown in fig.7.5 which suggested that the wavenumber of the B' peak (platelet peak position) decreased with platelet size.

Davies (1977) found that the platelet peak position, \(\nu\), was related to the absorption coefficient, \(A\) (in mm\(^{-1}\)), at 1282 cm\(^{-1}\), by the expression: \(\nu = 1359 + 2.8A\). This was confirmed, approximately, by Woods (1986), who also showed that the integrated absorption of the platelet peak is independent of \(\nu\).

In addition to the peak position, it has been noticed that the width and shape of the B' peak also varies from specimen to specimen (Clark & Davy 1984). In a detailed study of IR spectra from 50 type Ia diamonds, Woods (1986) has observed that the B' peaks become systematically more asymmetric with increasing wavenumber; the centroid moving towards the high wavenumber side of the maximum.
Another thing that Woods's study has revealed is that there is a linear relationship between the integrated absorption of the B' peak and the absorption coefficient of the recently discovered D component of the IR spectrum. He discusses possible consequences of this discovery (Woods 1986).

There is an implication that the mean platelet diameter decreases with increasing nitrogen content (Davies 1977). This follows if Davies' equation above (A being a measure of N content) is coupled with the suggestion of Sobolev et al (1968a), that the wavenumber of the platelet peak position increases as the platelet size decreases. Woods (1986) proposes that if the latter can be confirmed it would explain why 'giant' platelets (Woods 1976, Hanley et al 1977) are found in regions of relatively low nitrogen concentration.

7.1.3 The Platelet Peak Positions from the Seven Samples

Platelet peak positions were measured at positions on the specimens corresponding to those investigated by spike topography (chap.5). This work was carried out at CSO Valuations, London by Dr. Geoff Woods, before the TEM (chap.6) was performed. Some preliminary IR spectra, used for the selection of the specimens (sec.5.5.1.) are shown in figs. 7.1 and 7.2. They were recorded at a resolution of 0.5 cm\(^{-1}\) through a 1 mm diameter circular aperture placed near the centre of the specimen (any positions this may have overlapped are given in brackets).
The specimens were examined in transmission with a Perkin-Elmer model 580B spectrophotometer fitted with an x8 beam condenser. The specimens were masked with metal discs having 0.5 mm diameter circular apertures drilled into them, in order to sample the small volume of crystal previously examined by spike topography. First a quick rough scan, taking about twenty minutes, was made over the whole spectrum, to locate the platelet peak. Then spectra were recorded over a range of \pm 5 \text{ cm}^{-1} \text{ either side of this located peak, at a resolution of } 0.5 \text{ cm}^{-1} \text{ (in mode 6A or 6B). The signal was averaged over approximately 250 runs, so as to improve the signal to noise ratio. This job took up to eight hours, therefore entire spectra were not recorded in this way because of the time which would have been involved.}

The following table lists the results, the peak position being given in three commonly used units.
<table>
<thead>
<tr>
<th>SPECIMEN</th>
<th>POSITION</th>
<th>PLATELET PEAK POSITION</th>
<th>cm$^{-1}$</th>
<th>$\mu$m</th>
<th>eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1</td>
<td>1361.3</td>
<td>7.3459</td>
<td>0.16923</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>2</td>
<td>1361.4</td>
<td>7.3454</td>
<td>0.16924</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>3</td>
<td>1361.3</td>
<td>7.3459</td>
<td>0.16923</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>1</td>
<td>1361.6</td>
<td>7.3443</td>
<td>0.16926</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>2</td>
<td>1361.7</td>
<td>7.3438</td>
<td>0.16928</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>1</td>
<td>1364.3</td>
<td>7.3298</td>
<td>0.16960</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>2</td>
<td>1365.0</td>
<td>7.3260</td>
<td>0.16969</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>1</td>
<td>1366.5</td>
<td>7.3180</td>
<td>0.16987</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>2</td>
<td>1366.4</td>
<td>7.3185</td>
<td>0.16986</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>3</td>
<td>1366.5</td>
<td>7.3180</td>
<td>0.16987</td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>1</td>
<td>1368.7</td>
<td>7.3062</td>
<td>0.17015</td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>2</td>
<td>1368.8</td>
<td>7.3057</td>
<td>0.17016</td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>3</td>
<td>1369.6</td>
<td>7.3014</td>
<td>0.17026</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td></td>
<td>1370.2</td>
<td>7.2934</td>
<td>0.17033</td>
<td></td>
</tr>
<tr>
<td>G</td>
<td>1</td>
<td>1370.9</td>
<td>7.2945</td>
<td>0.17042</td>
<td></td>
</tr>
<tr>
<td>G</td>
<td>2</td>
<td>1370.9</td>
<td>7.2945</td>
<td>0.17042</td>
<td></td>
</tr>
<tr>
<td>G</td>
<td>3</td>
<td>1371.3</td>
<td>7.2924</td>
<td>0.17047</td>
<td></td>
</tr>
<tr>
<td>G</td>
<td>4</td>
<td>1370.9</td>
<td>7.2945</td>
<td>0.17042</td>
<td></td>
</tr>
<tr>
<td>G</td>
<td>5</td>
<td>1370.9</td>
<td>7.2945</td>
<td>0.17042</td>
<td></td>
</tr>
</tbody>
</table>

TABLE 7.1
Infrared Platelet Peak Positions in the Diamonds Studied

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- 195 -
7.2 PLATELET RADIUS MEASUREMENTS AND IR PEAK POSITION

7.2.1 Compatibility of the Results

A limiting factor in this work has been that the regions of the specimens sampled in each investigation although close were not identical in each case. Fig.5.6a illustrates part of the problem of obtaining compatibility between the regions being spike topographed and the volume sampled in the IR spectroscopy (fig.5.6c); only a central portion in actually common to both. The arrangement shown in fig.5.6b is better, but the arrangement used depends, of course, on the cut of the diamond slice under investigation. Fig.5.6d shows a suggested ideal arrangement for spike topography which would allow a region of the same width to be sampled by both techniques. A parallel sided diamond plate with \( \text{III} \) \( \text{III} \) \( \text{III} \) type faces would be required, which is not a reasonable cleavage plane for diamond (Ramaseshan 1946). Also there is the additional consideration that since the platelet measurement is made at a boundary of the spike topographic image, the height of the volume of crystal for which platelet measurement takes place is not defined. Measurements made on microdensitometer traces suggest it varies between 0.1 and 0.3 mm. A 0.5 mm diameter cylinder running from the front to the rear of the specimen is sampled by IR spectroscopy.

In the case of the slices with \( \text{III} \) \( \text{III} \) type faces (specimens B, E, F) the piece examined by spike topography (fig.5.6b) was approximately a 15% to 46% portion of the volume sampled by IR spectroscopy. No part of the crystal spike topographed lay
outside this volume, unlike the situation with the (001) slices (specimens A, C, D, G). In this case (fig.5.6a), if \( t \) was the thickness of the slice in millimetres, the volume sampled by IR spectroscopy was 0.196\( t \) mm\(^3\), that examined by spike topography lay between 0.055\( t \) and 0.165\( t \) mm\(^3\), and the value of the overlap lay between 0.018 and 0.054 mm\(^3\) (independent of \( t \)). In the event it was decided not to restrict platelet measurement to the overlapping region only (which could have been done by reducing the microdensitometer slit height -sec.5.5.2), but by keeping the slit tall, as done by the IR spectroscopy a region (albeit largely a different one) spanning the whole thickness of the specimen was examined.

With the TEM, incompatibility was induced by the preparation; one side only of each specimen was polished down by the thinning process. Ideally an equal amount would be polished off both sides so as to preserve the central portion. The fact this could not easily be done was another reason in favour of keeping the tall microdensitometer slit width mentioned above. The incompatibility in position is made worse at the ion-beam thinning stage, since the hole (at the edge of which the TEM is carried out) was formed at any point on a roughly 0.4 mm radius (0.6 mm in the case of sample G4) from the centre of the area of interest, which itself could not be located with great precision (see sec.6.2.5).
The best that can be said is, that if every defined position is regarded as a 1.5 mm diameter cylinder, then one can be confident that the appropriate results obtained by all three methods were extracted from somewhere within their volumes.

7.2.2 Comparison of the Results

Table 7.2 compares results obtained from the work presented in this chapter and the previous two; figs 7.3 and 7.4 illustrate these results graphically.

Fig.7.3a is a graph showing average platelet radii determined by spike topography at different positions on the seven specimens, versus the corresponding IR platelet peak positions (wavenumbers). In fig.7.4 the platelet radii were determined from the transmission electron micrographs. The additional point on the latter was contributed by Prof. Andrew Lang (private communication) from one of his specimens, and has been included for its value as an extra data point. The dotted lines represent data used by Sobolev et al (1968a) in fig.7.5, which they obtained from Evans & Phaal (1962b). Comparison of the two graphs in figs. 7.3a and 7.4 shows that for the higher wavenumbers there is fair agreement, within the bounds of experimental error, between platelet radius determined by spike topography and that measured from TEM. It can be concluded that the non-destructive technique of spike topography is reasonably reliable for estimating average platelet radii below about 200 Å.
The hypothetical relation of Sobolev et al (1968a), between platelet radius and IR peak position, is shown in fig. 7.5. The results of the present work, shown in fig. 7.3a, demonstrate that such a correlation is not as strong as they suggested on the basis of the rather few data points they used. Even so, some inverse relationship is apparent, bearing in mind the small range of wavenumbers. In fig. 7.3b the graph in fig. 7.3a has been redrawn in terms of IR wavelength, \( \lambda \). Sobolev et al’s relation is shown as a dotted line. The straight line fitted to the points is given approximately by:

\[
R(\text{Å}) = 3164 \lambda(\mu\text{m}) - 22997 ,
\]

in the wavelength range 7.29 to 7.35 \( \mu\text{m} \).
<table>
<thead>
<tr>
<th>SPECIMENS</th>
<th>POSITION</th>
<th>PEAK POSITION cm(^{-1})</th>
<th>PLATELET RADIUS / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1,3</td>
<td>1361.3</td>
<td>* 221 ± 58</td>
</tr>
<tr>
<td>A</td>
<td>2</td>
<td>1361.4</td>
<td>243 ± 30</td>
</tr>
<tr>
<td>B</td>
<td>1</td>
<td>1361.6</td>
<td>303 ± 77</td>
</tr>
<tr>
<td>B</td>
<td>2</td>
<td>1361.7</td>
<td>278 ± 65</td>
</tr>
<tr>
<td>C</td>
<td>1</td>
<td>1364.3</td>
<td>95 ± 9</td>
</tr>
<tr>
<td>C</td>
<td>2</td>
<td>1365.0</td>
<td>190 ± 30</td>
</tr>
<tr>
<td>D</td>
<td>1,3</td>
<td>1366.5</td>
<td>* 90 ± 46</td>
</tr>
<tr>
<td>D</td>
<td>2</td>
<td>1366.4</td>
<td>225 ± 42</td>
</tr>
<tr>
<td>E</td>
<td>1</td>
<td>1368.7</td>
<td>122 ± 13</td>
</tr>
<tr>
<td>E</td>
<td>2</td>
<td>1368.8</td>
<td>98 ± 9</td>
</tr>
<tr>
<td>E</td>
<td>3</td>
<td>1369.6</td>
<td>154 ± 12</td>
</tr>
<tr>
<td>F</td>
<td>-</td>
<td>1370.2-1371.1</td>
<td>49 - 94</td>
</tr>
<tr>
<td>G</td>
<td>1,2,4,5</td>
<td>1370.9</td>
<td>* 87 ± 7</td>
</tr>
<tr>
<td>G</td>
<td>3</td>
<td>1371.3</td>
<td>95 ± 8</td>
</tr>
</tbody>
</table>

**TABLE 7.2**

Comparison of Infrared Platelet Peak Position and Platelet Radius, as determined from Spike Topography and TEM

* Indicates that figures quoted are the mean ± s.d. of results weighted in inverse proportion to their percentage error.

# Mean ± r.m.s. of standard deviations of two results.
Fig. 7-3  Platelet radius, determined by spike topography, versus infrared platelet peak position.

Fig. 7-3  Platelet radius, measured from transmission electron micrographs versus infrared platelet peak position.
Fig. 7.4 Platelet radius, measured from transmission electron micrographs, versus infrared platelet peak position.

--- plotted by Sobolev et al (1968) using data from Evans & Phaal (1962)
PART III

AN X-RAY TOPOGRAPHIC STUDY OF GALLIUM ARSENIDE USED FOR DEVICE FABRICATION
CHAPTER 8
FIELD EFFECT TRANSISTORS ON GALLIUM ARSENIDE

8.1 INTRODUCTION

This chapter gives a brief description of gallium arsenide, why it is of interest and how it is manufactured for device fabrication. The uniformity in its electrical properties is discussed next, and work on dislocations in the material is reviewed. The field effect transistor is also described along with its operation and fabrication, and finally there is a review of past research that has been carried out on the variation of transistor uniformity across gallium arsenide substrates.

For a comprehensive compilation on the current state of GaAs device technology see Howes & Morgan (1985) – several references are made in this chapter to contributions contained in this book.
8.2 GALLIUM ARSENIDE

8.2.1 The Material

It is its potential for the fabrication of high speed digital integrated circuits (e.g. see Zucca et al 1980) which has stimulated so much interest in gallium arsenide. GaAs has the zinc blende structure. It consists of a face-centered cubic lattice of gallium interpenetrating a face-centred cubic lattice of arsenic, the two being displaced by one quarter of the distance along their body diagonal. The structure is broadly similar to that of silicon which has the diamond structure (sec. 2.2.1), but, owing to the dissimilar atoms, the bonding in GaAs is ionic in nature rather than being purely covalent. A diagram of the atomic structure of GaAs is shown in fig. 8.1.

The important advantage GaAs has over silicon, for high speed electronic applications, is its higher electron mobility (8500 cm²/Vs in GaAs compared to 1500 cm²/Vs in Si, at 300 K - Sze 1981). In GaAs the effective electron mass is less than in silicon (at 300 K, m*/m= 0.067 compared with 0.98 - op. cit.) therefore an electric field will accelerate electrons in GaAs more than their counterparts in silicon. This leads to the higher electron mobility (for more detail see Wight 1985) which is why higher speed electronic devices are possible with GaAs than are capable with silicon, for example the propagation delay with a GaAs 2-input NOR gate is only 290 ps (GigaBit Logic 1988) compared to 1 ns with its highest speed silicon counterpart (Monolithic Memories 1986).
FIG. 8.1 GaAs CRYSTAL STRUCTURE
(AFTER MUKHERJEE & WOODARD 1985)

What has restricted the use of GaAs has been the technical difficulties associated with growing uniform high-quality crystals (see Pickles et al. 1985) - principally in regard to dislocation density, which has an effect on device performance (see text). Dislocation-free GaAs has been grown successfully by several techniques (1985).

3.3.3 Growth of GaAs for device fabrication

The standard technique for continuously growing GaAs is the vertical liquid encapsulation Czochralski technique, although other methods such as the horizontal technique and the II technique are modifications of this method originally devised by M. Inoue and coworkers. The horizontal technique, which basically consists of pulling a single crystal from a melt maintained at a constant temperature, has found a number of applications in the fabrication of GaAs devices. In the II technique, a GaAs single crystal is grown by the Czochralski technique from a melt surrounded by a gas phase. The gas phase is maintained at a constant temperature by a heat source located above the melt. The gas phase is typically an inert gas such as helium or argon. The crystal is pulled from the melt by a seed crystal that is immersed in the melt. The seed crystal is a single crystal of GaAs that is initially in contact with the melt. The seed crystal is rotated and translated during growth to ensure uniform crystal growth. The gas phase helps to prevent the formation of gas bubbles in the melt, which can lead to defects in the crystal. The II technique is often used to grow large single crystals of GaAs for use in semiconductor devices.
Another advantageous property of GaAs is that its band gap energy (1.42 eV at 300K - Sze 1981) is larger than silicon's (1.12 eV - op. cit.). This means that at room temperature GaAs produces fewer carriers (electrons and holes) than silicon, by thermal generation across the band gap, and therefore it has a lower carrier concentration (1.79x10^6 cm^{-3} compared to 1.45x10^{10} cm^{-3} in silicon - op. cit.). As a result, it potentially has better insulating properties and superior device isolation capability than silicon. Furthermore, the temperature at which thermal generation may override the carrier density, created by doping, is higher in GaAs, making the temperature range wider over which devices may function.

What has restricted the use of GaAs has been the technical difficulties associated with growing uniform high quality crystals (see Kirkpatrick et al 1985) - principally in regard to dislocation density, which has an effect on device performance (see later). Dislocation-free GaAs has been grown successfully by Kohda et al (1985).

8.2.2 Growth of GaAs for Device Fabrication

The standard method for commercially growing GaAs is the Liquid Encapsulated Czochralski (LEC) technique, although other methods are available, for example the horizontal Bridgman method (e.g. see Paorici 1982). The LEC technique is a modification of the method originally devised by Czochralski (1917), which basically consists of pulling a crystal from its melt. However, GaAs dissociates at its
melting point (1511 K - Sze 1981) and it is necessary to suppress the volatilization of arsenic. This can be achieved by covering the melt with a layer of an inert liquid - the so called liquid encapsulation technique. Metz et al (1962) applied this idea to the Czochralski method to produce the LEC technique, and Mullin et al (1965) were the first to use the technique to grow GaAs; they used boric oxide as the liquid encapsulant. For further details see Bass & Oliver (1966), and for a more up to date treatment, Kirkpatrick et al (1985).

The LEC technique allows large single crystal ingots of GaAs to be grown with a well controlled impurity content. For device fabrication, almost always the substrates are approximately (100) wafers, 2 or 3 inches in diameter, sliced from ingots pulled in the [100] direction; to be precise, they are usually cut with their axes about 2° away from the [100] towards the [110] (Mukherjee & Woodard 1985).

8.2.3 Electrical Uniformity across GaAs Wafers

The electrical properties (e.g. sheet resistance, bulk resistivity, carrier concentration) across (100) wafers of LEC grown GaAs generally tend to follow a W or M shaped variation along both the <011> and <001> diameters. Brozel et al (1984) briefly reviews the work up to 1983. Many workers (e.g. Honda et al 1983) have correlated such variations with a W-shaped variation in dislocation density, as shown in fig.8.2. The variation over the whole wafer exhibits an approximate four-fold symmetry.
8.2.4 Dislocations in GaAs Wafers

The W-shaped dislocation density distribution agrees with models proposed by Penning (1958, for germanium) and Jordan et al (1980, 1981, in GaAs) which imply that the dislocations are induced by thermal stress during the LEC process.

The standard method adopted for dislocation characterization of GaAs is to etch the surface of the wafers with potassium hydroxide (KOH) (see Grabmaier & Watson 1969; Nagata et al 1981 have suggested an alternative etchant) and observe the etch pit density (EPD) (Bonnet et al 1982 developed an automated imaging system for mapping this). The reliability of the KOH etch method with GaAs was tested by Angilello et al (1975) by comparing results with transmission x-ray topography. Being a non-destructive method, X-ray topography has occasionally been used directly for imaging dislocations in GaAs wafers (see sec.9.1.2). Another method, involving the oxidation of GaAs in water, has been developed by Fukata & Yasuami (1984) but does not seem to have been much utilized. Stirland (1986) reviews some of the methods that have been used for observing defects in GaAs.

Brozel et al (1986) used transmission x-ray topography to look at (110) GaAs wafers. They used the 220, 004 and 620 reflexions. It was found that dislocations lying in <001> directions were visible with the first of these reflexions but disappeared with the second. They deduced, therefore, that the Burgers vectors (Burgers 1939) of the dislocations were perpendicular to the dislocation lines, meaning they were
looking at edge dislocations (e.g. see Tanner 1976 chap.4). In principle then, by the \( g \cdot b \) criterion (ibid.) the Burgers vectors lay anywhere within the (001) plane; they suggested that the dislocations probably had Burgers vectors in the direction \([110]\) or \([\bar{1}10]\).

Cellular networks of dislocations have been found in wafers by Chen and Holmes (1983), where dislocations form interconnected networks of cells with few dislocations within each cell. This was verified by Ponce et al (1984) using transmission electron microscopy. The networks exhibited four-fold symmetry over the whole wafer. Cell diameter varied inversely with dislocation density; they found that a cell diameter of 100 \( \mu m \) corresponded to a dislocation density of about 100 000 \( cm^{-2} \) and a 500 \( \mu m \) diameter to 20 000 \( cm^{-2} \). Below this density the networks were found to take on lineage structures, extending several millimetres along \( \langle 011 \rangle \) directions. Skolnick et al (1984) found, by infra-red imaging, that the lineage structures extend like sheets for up to 3 cm in \{011\} planes down the length of LEC grown crystals.

Dislocations, cellular networks and lineages have been found to affect the performance of field effect transistors fabricated onto GaAs substrates. This will be discussed in section 8.4.
8.3 THE FIELD EFFECT TRANSISTOR

8.3.1 The Device

For a full account of the history and principles of the field effect transistor see Cobbold (1970).

The basic principle behind the field effect transistor (FET) was first described by Lilienfeld (1930) in the United States. A similar structure, closely resembling the modern metal oxide silicon FET (e.g. see Calvert & McCausland 1980, sec. 6.12), was proposed independently by Heil (1935) in the United Kingdom. The first working FET was reported by Dacey & Ross (1953, 1955) based on the theory of Shockley (1952).

There are three principal types of FET: the junction-gate FET (the one reported by Dacey & Ross); the insulated-gate FET (similar to that proposed by Heil), and the Schottky-barrier gate FET, which will be dealt with later, in section 8.3.3.

8.3.2 Operation and Pinch-off Voltage

To describe the operation of the FET it is simplest to consider an idealized model of the junction-gate FET. Fig. 8.3a shows an n-channel junction-gate FET; it consists of a small block of n-type silicon, connected to terminals at either end, called the source and drain, with a narrow constriction, called the channel, surrounded by a region of p-type material connected to the gate terminal. Under normal operating conditions the gate-channel junction is reverse
FIG. 8.3

(a) SCHEMATIC DIAGRAM OF AN N-CHANNEL FET

(b) SHOWS DEPLETION REGION WHEN $V_{gs} < 0$ AND $V_{ds}$ IS SMALL

(c) SHOWS 'THROTTLING EFFECT' WHEN $V_{ds}$ IS MADE MORE POSITIVE

(AFTER CALVERT & MCCausLAND 1980)

FIG. 8.4

TYPICAL DRAIN CHARACTERISTICS OF AN N-CHANNEL FET SHOWING THE PINCH-OFF VOLTAGE, $V_p$

(AFTER CALVERT & MCCausLAND 1980)
biased ($V_{GS} < 0$), so that any current flowing between source and drain is constrained to pass through the channel.

In the neighbourhood of a reverse biased p-n junction there is a non-conducting depletion region; the width of this region increases with reverse bias voltage. Therefore the effective width of the channel, and so its electrical resistance, is controlled by the gate-channel voltage. As $V_{GS}$ is made more negative the channel becomes narrower, as shown in fig. 8.3b. This is true so long as the potential drop $V_{DS}$ between drain and source is small. In this case the drain current $I_D$ is roughly proportional to $V_{DS}$ and the device is acting as a voltage controlled resistor. When $V_{GS}$ exceeds a certain negative value, known as the pinch-off voltage $V_p$, the depletion region fills the whole width of the channel and its resistance becomes practically infinite.

Fig. 8.3c illustrates what happens if $V_{DS}$ is increased to produce a significant increase in $I_D$ at a constant value of $V_{GS}$. As $V_{DS}$ is increased, the reverse bias at the drain end of the channel increases, which eventually results in a throttling effect tending to limit the increase in current which otherwise would have taken place; $I_D$ ceases to increase linearly with $V_{DS}$ and eventually becomes almost independent of it. This happens when $V_{DS}$ exceeds the pinch-off voltage, that is when $V_{DS} > V_p + V_{GS}$. This is another way of defining pinch-off voltage. Under these conditions the FET is said to be operating in the pinch-off region; it is in this region that the device is usually operated in amplifying
applications.

Fig. 8.4 shows the drain characteristics of the FET and illustrates the two manifestations of pinch-off voltage. The minimum gate voltage for conduction is often known as the threshold voltage, in other words the pinch-off voltage. The two terms are used equivalently throughout the literature.

8.3.3 The GaAs MESFET

Turner (1985) deals with the GaAs MESFET in detail and gives further references.

The type of FET fabricated with GaAs is the metal semiconductor FET (MESFET), or Schottky-barrier gate FET; it was first proposed by Mead (1966) and subsequently fabricated by Hooper & Lehrer (1967). Fig. 8.5 shows one in cross-section. Van Tuyl & Liechti 1974 were one of the first to report a logic gate using GaAs MESFETS.

A Schottky (rectifying) barrier is formed at a metal-semiconductor interface (see Wolf 1971 chap. 4 for a detailed general treatment of metal-semiconductor contacts). When a semiconductor is brought into contact with a metal, there is formed, in the semiconductor, a depletion layer similar to that formed at a p-n junction. So, from fig. 8.5 it can be seen that the principle of operation of this type of FET is the same as that already described for the junction-gate type.
FIG. 8.5  PLAN VIEW OF A GaAs MESFET
(AFTER TURNER 1985)

FIG. 8.6  PLOT OF FET PINCH-OFF VOLTAGE VS. DISTANCE FROM NEAREST DISLOCATION
(AFTER MIYAZAWA & ISHII 1984)
Since the electron mobility in GaAs is greater than that of silicon (sec. 8.2.1), the GaAs MESFET has lower electron transit time, and therefore superior high frequency response, than its silicon counterpart. One application, for example, is in microwave amplifiers operating up to 40 GHz (Turner 1985), and another is their use in high-speed digital integrated circuits (e.g. Asai et al 1983). A recent large-scale application of GaAs integrated circuit technology is the Cray-3 supercomputer (Kiefer & Heightley 1987).

8.3.4 MESFET Fabrication

Starting with a substrate of semi-insulating GaAs (that is where donors have been compensated by acceptors), often the first step is the epitaxial growth of a high-resistivity or semi-insulating buffer layer 3 to 5 $\mu$m thick. Its purpose is to separate the defected surface of the substrate from the FET channel region which is grown next.

The channel region can be an epitaxial layer (see Dorrity et al 1985) of high conductivity active n-type GaAs, up to 0.7 $\mu$m thick, doped, with for example selenium, to give between $5 \times 10^{16}$ and $4 \times 10^{17}$ net donors per cubic centimetre. Alternatively, the channel region can be produced by the implantation of donor ions (silicon is commonly used) directly into the surface region of the buffer layer (see Morgan & Eisen 1985 and references contained within), or directly into the substrate if the buffer layer stage was omitted.
To create distinct, isolated, devices it is necessary to divide up the channel layer. This can be achieved by chemically etching away border regions, or by separating areas by proton implantation damage. In the latter technique, known as proton isolation (D’Avanzo 1982), protons are implanted to create damage centres that trap electrons and holes, thereby rendering selected regions of the doped GaAs, semi-insulating.

All that remains to complete the fabrication of the MESFETs is the metallization of the ohmic (low resistance) source and drain contacts, and the Schottky-barrier gate contact. (For a detailed treatment of metallizations for GaAs devices see Palmstrom & Morgan 1985, and references contained there.)

A Schottky junction with an n-type semiconductor can be made by a metal of higher work function than that of the semiconductor. With n-type GaAs, pure aluminium, for example, has been found suitable for forming gate contacts.

The usual procedure for fabricating ohmic contacts is to dope a thin layer of the GaAs beneath the contact as much as possible (at least $5 \times 10^{19}$ cm$^{-3}$), in order to produce a narrow depletion region and thin enough electron barrier, for conduction to occur by tunnelling. Germanium in the metallizations can act as the donor and help make contacts ohmic (Fraser 1983), so germanium metallizations are suitable for forming the source and drain contacts.
The metallization of the contacts is normally done by photolithography or electron-beam lithography techniques. (see Welch et al 1980).

8.4 RESEARCH ON THE UNIFORMITY OF MESFET FABRICATION

8.4.1 Uniformity of Pinch-off Voltage

The production of high yields of working GaAs integrated circuits, each containing hundreds of thousands of FETs (e.g. see Welch et al 1985) depends strongly upon the homogeneity of the electrical characteristics across the substrate wafer on which they are fabricated. This has promoted research into the uniformity in pinch-off voltage of MESFETs fabricated on such wafers, which are usually cut from semi-insulating LEC grown GaAs (sec.8.2.2). 30 mV is regarded as a reasonable tolerance in pinch-off voltage across the working area of a wafer (Lile 1985). Miyazawa et al (1984) found they could improve pinch-off voltage homogeneity by heat treatment.

Conversely, the measurement of FET uniformity has been used to characterize GaAs substrates (Yamazaki et al 1983, Ishii et al 1984b, Matsuura et al 1985).

FET pinch-off voltage is considered an important electrical parameter because its value has implications for integrated circuit operation; -0.3 V has been regarded as the optimum value (Ino et al 1981).
8.4.2 Effect of Dislocation Density on Pinch-off Voltage

Nanishi et al (1982) claimed to be the first to correlate variation in FET pinch-off voltage with dislocation distribution. They looked at two adjacent (100) wafers cut from semi-insulating LEC GaAs. One of the wafers was etched with KOH for dislocation characterization. On the other wafer, approximately four hundred FET arrays were fabricated. The pinch-off voltages were measured using an automated computer controlled system, which also measured source-drain currents. They found that FETs fabricated in areas corresponding to high etch pit density showed large magnitude pinch-off voltages and high drain currents, and vice-versa, thus showing a W-shaped distribution. (Note that pinch-off voltages for n-channel FETs are of negative sign, so greater magnitude means more negative.) To explain the correlation Honda et al (1983) suggested that the high carrier concentration associated with high dislocation density allows the large drain currents, which in turn results in high magnitude pinch-off voltages.

8.4.3 The Proximity Effect

Miyazawa et al (1983) and Miyazawa and Ishii (1984) investigated the effect of proximity of FETs from nearest dislocations on their pinch-off voltages. They found that FETs located less than about 50 μm from a dislocation exhibited pinch-off voltages lower (up to 300 mV more negative) than those of FETs located far from dislocations. Less than 30 μm from a dislocation there was a scatter in
pinch-off voltages of up to 400 mV (see fig. 8.6, after Miyazawa and Ishii). Matsuoka et al 1984 claimed to find a scatter of only 100 mV however. Miyazawa and co-workers measured the pinch-off voltages by means of an automatic system for 'Mapping Array Performance' (MAP, Ishii et al 1984b). The dislocations were investigated on the same wafers by KOH etching and also cathodoluminescence (e.g. see Giles 1975), though results from these two techniques did not always exactly match.

Miyazawa et al (1983) attributed their findings to the presence of so-called 'denuded-zones' (Heinke & Queisser 1974), the radii of which were in good agreement with their 'critical distance' of 30 μm. A denuded-zone is a bright region of cathodoluminescence (Casey 1967 and Shaw & Thornton 1968) found in the vicinity of a dislocation and associated with its Cottrell atmosphere (Cottrell 1953 chap. 4). The zone is considered to be denuded of acceptor-like impurities (Heinke and Queisser); Miyazawa et al supposed this allowed higher drain currents, and more negative pinch-off voltages.

8.4.4 Effects near Lineage Features

As might be expected, local fluctuations in FET pinch-off voltage have also been found to be enhanced by dislocation cellular structures and lineage features (Takebe et al 1984). Nanishi et al (1983) observed correlation between lineages and increase in FET drain current, and Ishii et al (1984a) correlated scatter in pinch-off voltage with dislocation cell network structures in the substrate. The proximity effect has
also been reported as evident with respect to lineage features, by Miyazawa & Hyuga (1986) and Miyazawa & Wada (1986). They discovered a decrease in pinch-off voltage of 3 to 7 mV per micron below a critical distance of about 50 μm from a feature.

8.4.5 The Proximity Effect Controversy

Contrary to what was reported before, Winston et al (1984a,b) claimed there was no correlation between pinch-off voltage and proximity of a FET to a dislocation; Yamazaki et al (1984) confirmed their findings. Winston et al explained the reports of apparent correlation simply as arising from the correlation between pinch-off voltage and dislocation density: in a region of high dislocation density a FET will tend to be nearer to a dislocation than in an area where the dislocation density is low.

In the light of this controversy, Miyazawa and Hyuga (1986) carried out further investigations, looking at the proximity effect close to lineage features and walls of cellular networks. They maintained that a dislocation closer than about 30 to 50 μm from a FET did affect its pinch-off voltage, and that Winston et al were unable to observe this because they were looking in regions of high dislocation density (greater than 37 000 cm\(^{-2}\)). However, it must be pointed out that Yamazaki et al’s investigations were carried out using low dislocation density GaAs (0 to 30 000 cm\(^{-2}\)).
Maluenda et al (1986) and Schink et al (1986), by using densely packed FETs, were able to observe pinch-off voltage variations over distances as short as 10 μm. It was therefore possible for them to carry out investigations with respect to the same dislocation, which was not possible before. They concluded that there was indeed a proximity effect in the range up to 50 μm from a dislocation.

8.4.6 The Dislocation Associated Causes of Pinch-off Voltage Variation

Weyer (1984) demonstrated that defects aggregate around dislocations as Cottrell atmospheres, so dislocations could be involved indirectly in determining FET performance, by segregating impurities and hence improving carrier mobility in the purer regions remaining (Wang & Bujatti 1984). This was reinforced by the work of Watanabe et al (1984) and compares well with the denuded-zone suggestion of Miyazawa et al (1983) (see the end of sec.8.4.3).

Of particular interest is a defect known as EL2 (electron level 2 - see Martin et al 1977, Martin & Makram-Ebeid 1983, Makram-Ebeid et al 1984, Kennedy 1986 and Levinson & Kafalas 1987). A W-shaped variation in the concentration of EL2 across (100) GaAs wafers was observed by Martin et al (1981) and correlated with dislocation density by Brozel et al (1984). A one-to-one correspondence between single dislocations and sites of enhanced EL2 concentration was shown by Stirland (1985a,b). Dobrilla et al (1985) correlated FET pinch-off voltage with EL2 concentration, finding a high
concentration corresponded to a larger drain current and a more negative pinch-off voltage. A change in EL2 concentration of $1.6 \times 10^{15}$ cm$^{-3}$ gave rise to a 100 mV change in pinch-off voltage.

Brozel et al (1984) found enhancement of EL2 concentration at lineage features, while an increase in FET drain current around them had been reported by Nanishi et al (1983). In regions bordering lineages a reduced concentration of EL2 was found by Stirland et al (1984).

A model for the influence of EL2 concentration on FET pinch-off voltage was proposed by Miyazawa & Wada (1986). It involves increase in carrier concentration with EL2 concentration (see reference for details). This result agrees with the explanation of pinch-off voltage variation given by Honda et al (1983) (see the end of sec.8.4.2).
9.1.1. Synopsis of Chapter

This chapter is about topography carried out on LEC grown GaAs wafers, most of which had devices fabricated on them. One wafer in particular was studied in some detail in order to gain information on the extent, and likely Burgers vector direction, of a lineage feature occurring in it. The lattice misorientation associated with the feature was also measured. This wafer had MESFET arrays fabricated on it, and the effect of the lineage feature on the pinch-off voltage of the FETs was investigated. Details are given of the samples and techniques used. First there is a review of past topography carried out on GaAs wafers.
9.1.2 The Context of the Current Work - Previous Topography

In the last chapter (sec. 8.2.4) it was mentioned that Angilello et al (1975) used x-ray topography to test the reliability of the KOH etch for revealing dislocations in GaAs. They took a 400 transmission topograph using Ag Kα radiation, of a single 0.1 mm thick (100) slice of Bridgman grown GaAs. This was then KOH etched, and by comparing the two results they concluded that the etch gave a faithful indication of the dislocation characterization of GaAs wafers, although the following topographic studies have since been made.

Brown et al (1984) studied (100) LEC GaAs wafers using both conventional, and synchrotron (SR), double-crystal reflexion topography. Cu Kα1 radiation was used for all their conventional work, and radiation at 1.5 Å was selected for their SR experiments. Their topographs showed individual dislocations, cellular networks and lineage features, which they found were sometimes crystallographically aligned. Across the lineage features they observed sharp contrast reversal due to misorientations between the lattice on either side. SR double-crystal rocking curves of these areas, using the surface symmetric 400 reflexion, were split into doublets. The separation of the peaks, and hence the corresponding lattice tilt across the feature, was determined to be of the order of 0.01°. It was found that when the diffraction vector (particularly the 422) and the lineage feature lay in the same plane this misorientation was not imaged.
As a method for rapidly evaluating the perfection of commercial (0.5 mm thick) GaAs wafers for device fabrication, Forman et al (1985) developed a low-resolution double-crystal topographic technique. It employed the asymmetric 422 reflexion from a (100) silicon monochromator using Cu Kα1 radiation from a conventional 1 kW fine-focus laboratory x-ray tube. They had an in situ alignment procedure (Forman & Mayo 1985), and for speed they used a high-speed instant-film together with a fluorescent screen. With a standard commercial wafer they were able to align it in less than ten minutes. The exposure time for their reflexion (Bragg) topographs was 2 to 3 minutes, and about a quarter of an hour was required for their transmission (Laue) topographs. The technique was not designed to be very sensitive to individual micro-defects, and was used mostly for imaging micro-cracks and lattice misorientations. However, they did observe distributions of dislocation density patterns, and W-shaped / dislocation networks. They too noticed the lattice tilt associated with lineages. They mainly used 422 and 440 reflexions, but also tried 400, 620, 311, 511 and 533 type reflexions.

Brozel et al (1986) carried out a Burgers vector analysis of dislocations in a 0.3 mm thick GaAs (110) wafer. This has already been outlined in sec.8.2.4.

The latest report of an application of x-ray topography to GaAs is from Matsumoto et al (1988). They have used the technique to check the dislocation density in wafers cut from semi-insulating GaAs grown by the new 'double-crucible' LEC
Each of these topographic studies was made on plain GaAs wafers onto which no devices had been fabricated. The work which follows in the remainder of this chapter appears to be the first topographic study made of GaAs wafers which had devices on them. It is the first time that the effects on FET pinch-off voltage have been investigated using this technique.

9.2 TOPOGRAPHS OF GALLIUM ARSENIDE WAFERS

9.2.1 The 511-Type Reflexion Projection Topograph

In fig. 9.1 are shown six 511-type reflexion projection topographs (sec. 1.2.3.3) of four (100) GaAs wafers. The topographs were taken in reflexion rather than transmission because of the high absorption of x-rays by GaAs. The following table compares the percentage transmission through 0.4 mm (the thickness of the wafers) and the same thickness of diamond, for various wavelengths of x-rays (see next page).
<table>
<thead>
<tr>
<th>WAVELENGTH / Å</th>
<th>GaAs</th>
<th>DIAMOND</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3000</td>
<td>28%</td>
<td>97%</td>
</tr>
<tr>
<td>0.5608 (Ag Kα)</td>
<td>7x10^{-2}%</td>
<td>95%</td>
</tr>
<tr>
<td>0.7107 (Mo Kα)</td>
<td>1x10^{-4}%</td>
<td>92%</td>
</tr>
<tr>
<td>1.0000</td>
<td>3x10^{-13}%</td>
<td>82%</td>
</tr>
<tr>
<td>1.5418 (Cu Kα)</td>
<td>1x10^{-5}%</td>
<td>52%</td>
</tr>
</tbody>
</table>

**TABLE 9.1**

Transmission of X-Rays through GaAs and Diamond

(The data used to calculate this table came from the International Tables III, 1962; Mykolajewycz 1964, and Wight 1985.)

All six topographs were taken using a 511-type reflexion, as shown in fig.9.2, using Cu Kα_1 radiation. This reflexion provides the ideal geometry for projection topography, and the image of the wafer is horizontally compressed by only about 15%. With the Bragg angle at approximately 45°, the incident and reflected beams are practically perpendicular, facilitating the minimum specimen to plate distance. An average specimen to plate distance of around 5 cm was used with whole wafers; it was possible to get the plate closer with a fragment. The incident beam was collimated to a width of 360 μm and was at least as tall as the specimen. The
FIG. 9-1 Topographs of GaAs Wafers

- 229 -
\[ \theta = 45.11^\circ \]
\[ \alpha = 15.60^\circ \]

**FIG. 9.2 PROJECTION TOPOGRAPHY OF GaAs WAFER BY REFLECTION FROM \{511\} PLANES**
traverse was made roughly parallel to the wafer and long enough for the whole specimen to be topographed. The topographs were taken using the Elliott-Bristol-Lang camera (sec.1.2.3.2).

Using Ilford L4 Nuclear Emulsion plates, it is conventional (e.g. see Lang 1978) to use 25 μm thick emulsion for taking topographs with copper radiation; topographs 2, 5 and 6 (fig.9.1) were taken on this. However, it has been found that a better image of the GaAs wafers could be obtained on a 50 μm emulsion (probably due to less statistical fluctuation - sec.1.2.5) and this was used for all the other topographs, taken using copper radiation, illustrated in this chapter. The typical exposure time for a 50 μm plate was of the order of 50 hours, and twice that for a 25 μm plate, development times were up to 30 minutes and up to 60 minutes respectively, carried out either at room temperature or at about 12°C if better resolution was required.

9.2.2 Descriptions of some Topographs

Refer to fig.9.1. The topographs are all actual size, and represent mirror images of what would be seen if looking at the wafer itself.

1) Wafer 1 was an example of a 2" diameter circular, commercially available (100) GaAs wafer, cut from LEC grown semi-insulating GaAs. Onto the (100) face approximately 1600 arrays, each comprising 56 MESFETs, were fabricated. These can be clearly seen on the topograph, which is a 511 reflexion
taken on a 50 μm plate.

The orientation of a wafer such as this is facilitated by two flats ground into its perimeter. The major flat, appearing at the bottom of the topograph is an (011) face, and the minor flat, on the right hand side is an (001).

The dark semicircular region at the bottom edge of the image was created by absorption of x-rays by the wax supporting the specimen.

2) Wafer 2 was a similar specimen to Wafer 1, onto which something like 1800 (unidentified) devices had been fabricated. In this 511 topograph, taken on a 25 μm plate, the visibility of the devices is less than in the previous topograph, illustrating the improvement that can be obtained by using 50 μm plates.

The topograph reveals a faint light saltire shaped pattern, extending across the whole wafer, indicative of differing impurity (e.g. carbon, see Kirkpatrick et al 1985, or Clemens & Conway 1988 for other possibilities) concentrations in cubic and octahedral, or dodecahedral, growth sectors (e.g. see Lang 1974).

It can be seen that the specimen was supported by wax in three places.

3) Wafer 3 was the larger of two fragments of a wafer cut from the same LEC grown GaAs crystal as Wafer 2, and this 511 topograph reveals part of a similar light saltire shaped
region. As can be seen, Wafer 3 had no devices fabricated onto it.

4) This is a $\{110\}$ topograph which shows the reverse side of Wafer 3. The arms of the saltire appear dark in this case. The reversal of contrast when viewing the opposite side suggests that the feature is due to a lattice misorientation. Perhaps, then, the cross corresponds to a four-fold stress pattern (Jordan et al 1980).

5) Wafer 4 was a $1^{7/8}$" diameter circular wafer of indium doped GaAs, reputed to be dislocation free - which the topographic evidence seems to support.

This $\{111\}$ topograph shows the (100) face onto which about 1000 MESFET arrays were fabricated. It reveals a swirl pattern (e.g. see Meieren 1980), due to fluctuations in concentration of the indium (see Schink & Schnell 1988); the swirls vary in separation from approximately 50 to 500 $\mu$m.

The extra flat appearing on the left of the topograph was caused by the traverse being slightly too short.

6) This $\{111\}$ topographs shows the other, plane, (100) face of Wafer 4. The swirl pattern appears in reverse contrast to that in the topograph of the device side.

The mottled appearance, as it does not occur on the topograph of the (100) face, was probably due to some sort of sub-surface damage (which was not visible to the naked eye) on the rear face.
9.2.3 Wafer 5 and Topographs

The figs. 9.3 and 9.4 are approximately x3 enlarged prints of 511-type reflexion projection topographs, taken with Cu Kα radiation, of the opposite faces of a wafer (Wafer 5) used for an investigation (see later) of the variation of FET pinch-off voltage in the proximity of a lineage feature.

Wafer 5 was a standard commercially available 2" diameter, matt back, (100) wafer cut from unannealed LEC grown semi-insulating GaAs, reputed to have a dislocation density in the range $10^4$ to $10^5$ cm$^{-2}$. An n-type channel layer had been formed by direct implantation into the substrate, at 80 keV, of donor Si$^{29}$ ions, at a dose of $2.25 \times 10^{12}$ cm$^{-2}$; no buffer layer was grown first. Approximately 1600 arrays of MESFETS were fabricated on the wafer; each array a rectangle of 56 FETS, 7 by 8, as shown in fig.9.5. These arrays can be clearly seen in the topograph in fig.9.3. The metallizations used were AuGeNi for the ohmic contacts and CrAu for the Shottky contacts. Proton implantation isolated each FET from its neighbour. More details of this type of sample may be found in Kitching (1987).

Fig.9.3 This 511 topograph shows the (100) face of Wafer 5 onto which the FET arrays were fabricated. The vertical white stripe on the topograph was caused by hesitation of the traverse mechanism while the topograph was being taken. The horizontal stripe was caused by dirt in the collimator tube.
FIG. 9.3  511 TOPOGRAPH (x3 PRINT) OF THE (100) FACE OF WAFER 5
FIG. 9.4  511 TOPOGRAPH (x3 PRINT) OF WAFER 5
FIG. 9.5  DIAGRAM OF A 7×8 M.E.S.F.E.T. ARRAY (ENLARGED ABOUT 130 TIMES)
At the top of the wafer appear adjoining light and dark triangular areas. They represent lattice misorientation occurring at lineage features running along their boundaries. Another such area occurs at the bottom of the wafer. Lineage features are easily visible in the following places: 1) along the lower third of the right hand side of the dark triangular area at the top; 2) near the wafer edge along the left hand side of the light area at the top; 3) along the upper half of the left hand side of the dark triangle at the bottom. The lineage features appear as white lines. Lineage feature 1 was studied in some detail, and the results appear in the following sections.

Fig.9.4 This is a 511 topograph of the back of Wafer 5. Cellular networks can be seen (now that the view is not obscured by devices) covering the whole face. It is not certain what the thicker squiggly lines represent. They have the appearance of scratches, but were not visible to the naked eye on the reverse of the wafer. A possible suggestion is that they are evidence of scratches which were present prior to the back to the wafer being etched, and now only exist as sub-surface damage. At the bottom of the wafer an inscribed 'W' can be seen. The light horizontal bar was due to dirt in the collimator tube.

On this topograph the triangular areas appear in opposite contrast to those on the last. Lineage features, still appearing white, can be seen quite easily running along their boundaries. This topograph would seem to confirm the
connexion between lineage features and cellular networks found by other workers (see 8.2.4); however, their directions seem to deviate markedly from the <011> reported.

9.2.4 Topograph of Wafer 6

Wafer 6 was a wafer similar to, and cut from the same crystal as, Wafer 5. It was cut next to the wafer cut immediately adjacent to Wafer 5, on the side which later had the FET arrays fabricated on to it. The width of a cut is unknown. The reason for topographing this wafer was to see if the lineage features found in Wafer 5 extended along the [100] growth axis of the LEC grown crystal to Wafer 6.

Fig.9.6 This is an approximately x3 enlarged print of a 511 topograph of the (100) face of Wafer 6. The face had approximately 700 each of two types of device (both unidentified) fabricated onto it.

This topograph clearly shows features in common with those revealed in the topograph shown in fig.9.3. The triangular areas of misorientation and the lineage features can be seen; confirming the findings of Skolnick et al (1984) that lineage features extend down the length of GaAs crystals, like sheets. Fig.9.7 shows an approximately x19 enlargement (negative), from the same topograph, of the lineage feature corresponding to lineage feature 1 in fig.9.3 (see the previous section).
FIG. 9.6 511 TOPOGRAPH (x3 PRINT) OF WAFER 6
FIG. 9.7  X19 ENLARGEMENT OF THE LINEAGE FEATURE REGION OF THE TOPOGRAPH SHOWN IN FIG. 9.6
9.3 STUDY OF THE LINEAGE FEATURE

9.3.1 The Lineage Feature

The lineage feature studied in Wafer 5 was that described in sec.9.2.3, that is to say, in fig.9.3, the one running along the lower third of the right hand edge of the dark triangular area at the top of the wafer; it is sketched in fig.9.14. The studies were carried out on the (100) device face of the wafer. Fig.9.20 shows the feature in a mosaic picture made up of enlargements (nearly x22) of individual FET arrays, taken from the topograph in fig.9.3. The lineage feature is shown where it traverses eight arrays. (As the photographs are straight enlargements of parts of a topograph, and not enlarged prints, the feature appears dark). In fig.9.3 the top array of the eight is located in the 9th row of arrays down and the 24th column across from the left; the bottom one is in the 16th row and 22nd column. The lone array, included for control purposes, is positioned in row 9 and column 16.

9.3.2 Note on the Condition of Wafer 5

The non-destructive nature of x-ray topography is unfortunately not necessarily all that assured. While the inspection itself does not damage the specimen, the handling during inspection can. In the course of its investigation, Wafer 5 suffered several fractures through being accidently knocked and dropped, though fortunately the region containing the lineage feature was always recovered intact.
Consequently, the sample topographed got progressively smaller throughout the study.

When using synchrotron radiation it was found, with the intense radiation from the wiggler, that the sealing wax, usually used to support GaAs wafers, soon became soft enough for the sample to fall off its mounting. 'Leit-c-plast' (a plastic conductive carbon cement used for mounting specimens for scanning electron microscopy, manufactured by Neubauer Chemikalien, Munster, W. Germany) was found to have a higher softening temperature and was used as a replacement.

9.3.3 Topographs of the Lineage Feature taken in Different Reflexions

Topographs of Wafer 5 were taken in various reflexions (with reciprocal lattice vector, \( g \)) to try and determine the direction of the Burgers vector, \( b \), of the lineage feature by the \( g \cdot b = 0 \) criterion for invisibility (e.g. see Tanner 1976 chap. 4, and references contained there).

Using reflexion projection topography with Cu K\( \alpha_1 \) radiation, topographs were taken in the following reflexions:

\[ 311, \bar{3}11, 400, 511, \bar{5}11, \bar{5}1\bar{1}, 602, 6\bar{2}0. \]

In figs. 9.8 and 9.9, x12 enlargements of the lineage feature region of these topographs are shown. The image distortion which takes place for different reflexions is apparent from the shape of these examples. The \( \bar{5}1\bar{1} \) reflexion in fig.9.8 was taken by topographing the reverse side of Wafer 5, and hence
FIG. 9.8  LINEAGE FEATURE REGION OF VARIOUS ORIENTATION REFLEXION PROJECTION TOPOGRAPHS OF WAFER 5 (x12)

- 244 -
FIG. 9.9  LINEAGE FEATURE REGION OF VARIOUS ORIENTATION REFLEXION PROJECTION TOPOGRAPHS OF WAFFER 5  (x12)
the lineage feature (unfortunately a fibre stuck to the topograph is a more prominent feature) appears as a mirror image of that in the 511 reflexion. The lineage feature is clearly visible in the 511, 511, 511, 400 (fig.9.8), 602 and 620 (fig.9.9) reflexions; it may be just visible in the 311 reflexion, between the arrays, but appears absent in the 311 reflexion (fig.9.9).

9.3.4 Reflexion Topographs of the Lineage Feature taken with Synchrotron Radiation

Owing to the geometry of the situation, in order to take a 202 (interplanar spacing 1.999 Å - Giesecke & Pfister 1958) topograph in reflexion, of a (100) GaAs wafer, requires a Bragg angle of greater than 45°, and hence x-rays of wavelength greater than 2.83 Å (Cr Kα = 2.2909 Å - International Tables III, 1962) are needed. Therefore 3 Å synchrotron radiation was used to take 202 and 220 reflexion topographs (see fig.9.10). The pictures were taken at Daresbury S.R.S. (post the installation of the 'high-brightness lattice') on Topography Station 3. A simple single crystal arrangement was used, in the sigma polarization mode. With twice the Bragg angle about 97.25°, the conditions were close to ideal. Plenty of lead shielding was used to keep the background radiation down, and a 40 μm thick sheet of stainless steel was placed in the beam to attenuate some of the unwanted shorter wavelengths (absorption edge of Fe is 1.743 Å - International Tables III, 1962). The beam was collimated to image the lineage feature region of the wafer.
The specimen to film distance was 20 cm, and with a beam current of around 150 mA, exposure times of 5 seconds were used. The topographs were taken on Agfa Structurix D4 film.

Fig.9.10 shows x12 enlargements of the 202 and 220 topographs. The lineage feature does not seem to be visible in the 202, but there is a hint of an appearance in the 220 topograph, as it passes through the uppermost three arrays as shown in fig.9.20. With both these reflexions the x-ray penetration cannot have been deep, owing to the high absorption coupled with the low glancing angle, of only about 3.5°, between the beam and the specimen surface. Under these conditions it is estimated that the intensity of the (3 Å) x-rays being reflected from a depth of only 1 μm below the specimen surface was attenuated by over 98%.

9.3.5 Synchrotron Radiation Transmission Topographs of the Lineage Features

With a (100) wafer 022, 022, 004 and 040 topographs can realistically only be taken in transmission. Because of the high x-ray absorption by GaAs (see table 9.1), 0.3 Å synchrotron radiation was used. Again a simple single crystal set-up was employed on Topography Station 3. Because the Bragg angles involved were small (4° 18' with the 022 reflexion and 6° with 004) shielding the photographic plate from the through beam and background radiation was a problem. To facilitate the use of lead bricks for this purpose, the topographs were taken in the pi-polarization mode (sec.1.2.4.1); the small Bragg angles meant that very little
FIG. 9.10
SYNCHROTRON RADIATION REFLEXION TOPOGRAPHS (x12) OF THE LINEAGE FEATURE REGION OF WAFER 5
intensity was lost by doing so (less than a 3% drop). The beam was collimated to image only the lineage feature area of the wafer. The specimen to film distance was 10 cm, and the exposure times of the order of 5 seconds with an average beam current of about 120 mA. Despite every effort, the background on the topographs was still very high, and the best pictures were attained on D4 film, but the resolution of these topographs is not very satisfactory.

In fig.9.11, x12 enlargements of the 022 and 022 topographs are shown, and in fig.9.12 the 004 and 040 topographs. The lineage feature is visible in all of them, along with cellular networks.

9.3.6 The Burgers Vector of the Lineage Feature

Summarizing the results of the previous three sections, it would appear that \( g.b \) is non-trivial (condition for visibility) definitely for the reflexions:

\[
004, \, 0\bar{4}0, \, 400, \, 022, \, 0\bar{2}2, \, 602, \, 6\bar{2}0, \, 511, \, \bar{5}11, \, \bar{5}1\bar{1},
\]

probably for the reflexion \( 3\bar{1}1 \), and possibly for \( 2\bar{2}0 \);

\( g.b=0 \) (condition for invisibility) for the reflexions:

\[
3\bar{1}1 \, \text{and} \, 202.
\]

This suggests that the lineage feature must have its Burgers vector in the direction \([\bar{1}2\bar{1}]\). To test this, topographs could be taken in the following reflexions: \( 1\bar{1}\bar{1}, \, 53\bar{1} \) and \( 13\bar{5} \). With these \( g.b=0 \) should be satisfied and the lineage feature be
FIG. 9.11
SYNCHROTRON RADIATION
TRANSMISSION TOPOGRAPHS (x12)
OF THE LINEAGE FEATURE REGION OF WAFER 5
-250-
FIG. 9.12
SYNCHROTRON RADIATION
TRANSMISSION TOPOGRAPHS (x12)
OF THE LINEAGE FEATURE REGION OF WAFER 5
invisible.

9.3.7 The Nature of the Lineage Feature

It is fair to assume that the lineage feature is composed of dislocations, and knowing the direction of the Burgers vector enables something to be said about the nature of them. The lineage feature, as seen in the topographs, although not a straight line, tends to be roughly in the [013] direction in the region investigated (although it tends to move towards the [001] as it approaches the edge of the wafer). Also, it has been shown (sec.9.2.4) that the feature extended, like a sheet, along the length of the original crystal in the [100] direction. Therefore the line direction, \( \mathbf{l} \) of the dislocations comprising the lineage feature could have components in both these directions, so

\[
\mathbf{l} = A[100] + B[013] = [A B 3B],
\]

where \( A \) and \( B \) are constants.

The Burgers vector direction, \( \mathbf{b} = [121] \), therefore

\[
\mathbf{b} \cdot \mathbf{l} = -A + 2B + 3B = -A + 5B,
\]

thus the dislocations are not pure edge dislocations unless \( A = 5B \) (in which case \( \mathbf{b} \cdot \mathbf{l} = 0 \) and \( \mathbf{b} \) and \( \mathbf{l} \) will be perpendicular). For them to be pure screw dislocations (\( \mathbf{b} \) parallel to \( \mathbf{l} \)) \( A = 0 \), \( B = 1 \). It is therefore likely that the lineage feature is composed of dislocations of mixed type (e.g. see Tanner 1976 chap.4, and references contained within).
9.4 LATTICE MISORIENTATION ACROSS THE LINEAGE FEATURE

9.4.1 Topographic Evidence

As was pointed out in section 9.2.3, a misorientation associated with the lineage feature was evident on certain topographs of Wafer 5. For instance, it can be seen in figs. 9.3 and 9.4 as a sharp contrast reversal across the feature.

The change in contrast was not imaged however, when the specimen was orientated so that the feature lay roughly in the plane of diffraction. This is illustrated by the 511 topograph shown in fig.9.13. The lineage feature is near the bottom right hand corner of the wafer, and is visible on close inspection, but there is no evidence of contrast reversal across it on the image. (The wafer has changed shape due to breakages - see sec.9.3.2; the contrast reversal in the bottom left hand corner is occurring at a crack.) Similarly, it was found that the misorientation was visible in a 311 topograph, but no contrast reversal was visible in a 311 topograph. The misorientation is therefore shown to be a tilt occurring at the lineage feature; the feature running along the intersection of the two angularly displaced regions.

9.4.2 Measurement of the Lattice Tilt

The angular displacement of the two regions either side of the lineage feature was measured by taking a rocking curve from the area containing the feature; the one illustrated in fig.9.14. This was carried out at Daresbury Laboratory using synchrotron radiation from the wiggler (Topography Station 3).
FIG. 9.13 511 TOPOGRAPH (X3 PRINT) OF WAFER 5
The double-crystal arrangement used for plotting the rocking curve is shown in Fig. 9.15. X-rays of wavelength 1 Å were selected using the same silicon monochromator source as before. Two reflections from the same reflection were used, one on the Si (100) reflection from Cu. The rocking curve was taken by scanning an area of one quarter of a second and the intensity of the affected area was recorded at each interval by a scintillation counter whose output was fed into the computer, which fully automated the procedure. The resulting plot is shown in Fig. 9.16.

The scan was repeated, in steps of 2 seconds of arc, with a topograph being taken at each interval, instead of an intensity reading. By moving the plate between exposures it was possible to record four topographs per plate (25 nuclear emulsion). Each exposure was 30 seconds, with an average beam current of 0.1 uA. The scans were repeated several times, each time with a different beam current. The resulting topographs were then taken from the film and the rocking curve was plotted.

**Fig. 9.14** Sketch of topograph in Fig. 9.3 to show the area illuminated to take the rocking curve.
The double-crystal arrangement used for plotting the rocking curve is shown in fig.9.15. X-rays of wavelength 1 Å were selected, using the surface symmetric 400 reflexion from a silicon monochromator (chosen because it matches closely the same reflexion from GaAs — i.e., the similar lattice parameters give similar Bragg angles). The beam was collimated to have a 5 x 5 mm square cross-section. The rocking curve, for the 400 reflexion from the GaAs, was then taken, scanning an angular range of 70 seconds of arc in steps of one quarter of a second. The intensity of the diffracted beam was recorded at each interval by a scintillation counter, whose output was fed into the station computer which fully automated the procedure. The resulting plot is shown in fig.9.16.

The scan was repeated, in steps of 2 seconds of arc; with a topograph being taken at each interval, instead of an intensity reading. By moving the plate between exposures it was possible to record four topographs per plate (25 μm nuclear emulsion). Each exposure was 30 seconds, with an average beam current of 110 mA. A series of these topographs, enlarged five times, are shown below the plot in fig.9.16. They occur at intervals of 4 seconds and correspond in position to the rocking curve above them. Some x13 enlargements of topographs corresponding to selected positions on the rocking curve are shown in fig.9.17. All the topographs image the same area as that from which the rocking curve was taken (see fig.9.14).
FIG. 9.15  DOUBLE-CRYSTAL ARRANGEMENT FOR GaAs 400 REFLEXION  
1 Å WAVELENGTH SYMMETRICAL REFLEXION
FIG. 9.16 ROCKING CURVE OF LINEAGE FEATURE REGION TAKEN OVER AN ANGULAR RANGE OF 70°, WITH CORRESPONDING TOPOGRAPHS (×5) TAKEN AT INTERVALS OF 4°.
FIG. 9.17 X13 ENLARGEMENTS OF TOPOGRAPHS TAKEN AT POSITIONS CLOSE TO THOSE GIVING RISE TO THE FEATURES OF THE ROCKING CURVE OF GaAs SHOWN IN FIG. 9.16
Two sharp peaks occur on the rocking curve; it is supposed they correspond to diffraction from the areas of crystal on either side of the lineage feature. The first peak is from the region that appears dark in the topograph in fig.9.3 (see also fig.9.14), and the last peak is due to the area on the other side of the lineage feature. The angular separation of these two sharp peaks, and hence the tilt across the lineage feature, measures 27 seconds about the [011] axis. This value is in good agreement with that determined by Brown et al (1984).

It is not certain what the origin of the low broad peak, between the sharper two, is. It is genuine; any 'fold-over' effect, taking place due to counter saturation, was ruled out at the time of the experiment. From reference to the topographs, it can only be concluded that this peak is a feature of the 'cross-over', occurring because the axis of rotation of the crystal was not exactly parallel to the ridge of the misorientation.

9.5 EFFECT OF LINEAGE FEATURE ON FETS FABRICATED ON THE WAFER

9.5.1 Measurement of the Pinch-Off Voltages

Measurements were carried out in order to ascertain the effect, if any, that the presence of the lineage feature might have been having on the MESFETs fabricated on Wafer 5. The pinch-off voltages of the FETs on the wafer were measured (prior to any topography) by Sally Kitching at S.T.L., Harlow,
A block diagram of the system employed at S.T.L. is shown in fig. 9.18. This system measures the pinch-off voltage by recording the gate voltage, $V_{GS}$, at which the drain current, $I_D$, falls to 1% of what its saturated value was when $V_{GS}$ = 0. This is more or less equivalent to the first definition of pinch-off voltage given in 8.3.2. The system ensures that the FETs in the same row and column as the FET being measured are turned off during the measurement. The measurement of the pinch-off voltage of each FET takes about 2.6 seconds, so to measure all of the roughly 89 600 FETs on a 2" GaAs wafer takes nearly 65 hours. In view of the time involved, other parameters, such as drain current, were not measured.

9.5.2 Variation in Pinch-off Voltage across the Wafer

The variation in the average array pinch-off voltage across Wafer 5 is shown in fig. 9.19. Each value is the average of the pinch-off voltages of all the FETs in each array. The results plotted in the figure are those of the arrays in the 21st row from the top, in fig. 9.3, going from left to right. The variation has the classic, roughly W-shaped distribution discussed in chapter 8.

9.5.3 Pinch-off Voltages in the Proximity of the Lineage Feature

Fig. 9.20 is a mosaic picture showing eight FET arrays which the lineage feature passes through, or close to, and also an array distant (9 mm away) from the feature. The individual FETs in each of the arrays are easily distinguished
FIGURE 9.13 SCHEMATIC OF STL TEST SYSTEM
FIG. 9.20 MOSAIC OF 571 TOPOGRAPHS (x22) SHOWING THE PASSAGE OF THE LINEAGE FEATURE, THROUGH PART OF WAFER 5, RELATIVE TO SOME OF THE F.E.T. ARRAYS

-264-
Shaded FETs have pinch-off voltages more negative than one standard deviation below the mean for that array.

Mean pinch-off voltage along length of feature shown here is -0.8203 V.

Array 9 mm distant from lineage feature

Fig. 9.21 Mean array pinch-off voltages ± standard deviations for the FET arrays shown in Fig. 9.20
in the picture. In the diagram in fig.9.21 the mean of the pinch-off voltages of all the FETs in each array is given, along with the corresponding standard deviation. The individual FETs shaded were those found to have pinch-off voltages more negative than one standard deviation below the mean value for their respective array. Fig.9.21 demonstrates that there is some correlation between the presence of the lineage feature and drop in pinch-off voltage. This is especially apparent for the 2nd, 5th, 6th and 7th arrays.

The lowering of pinch-off voltage with proximity to the lineage feature is clearly illustrated by fig.9.22. At the top of the figure is a histogram of the pinch-off voltages of the FETs in the lone array in fig.9.20. The next histogram is of the FETs three away (i.e. twice removed) from the lineage feature, or at an equivalent distance from it. (The centres of two adjacent FETs are separated by about 70 \( \mu \text{m} \).) In the remaining histograms the FETs are getting progressively closer to the feature, until at the bottom of the figure the histogram is of FETs actually in contact with the lineage feature. The data for the last four histograms were taken from the first seven arrays shown in fig.9.20. The series of histograms demonstrates that there is a tendency for the pinch-off voltage to shift more negative for FETs in contact with lineage feature or adjacent to those that are. The shift is greatest with the FETs actually in contact with the feature, the drop in pinch-off voltage being of the order of 40mV. For FETs adjacent to these (i.e. one FET removed from the lineage feature) the drop is half as much. The magnitude
FIG. 9.22 HISTOGRAMS OF FET PINCH-OFF VOLTAGES AT VARIOUS DISTANCES FROM THE LINEAGE FEATURE
of the drop is similar to that reported by Miyazawa & Hyuga (1986) and Miyazawa and Wada (1986) (sec.8.4.4).

9.6 THE LINEAGE FEATURE IN GALLIUM ARSENIDE, AND ITS EFFECTS

The bulk of the work cited in this chapter has been concerned with a particular lineage feature occurring in a 2" diameter (100) slice of LEC semi-insulating GaAs, onto which arrays of MESFETs had been fabricated. By x-ray topography the following details about the feature were revealed.

1) The feature occurred along with cellular dislocation networks.

2) Originally it would have extended, like a sheet, along the [100] growth direction of the LEC crystal.

3) In the (100) wafer the lineage feature was accompanied by a lattice tilt of approximately half a minute of arc.

These results confirm the findings of other workers.

4) The likely direction of the Burgers vector of the lineage feature was determined to be [121]

When taken with 2 this suggests that the feature was composed of dislocations of mixed type running in the [100] direction.

5) The lineage feature was found to lower the pinch-off voltage of MESFETs it touched by the order of 40 mV (the mean value was around 800 mV), and to affect others in its vicinity in a similar way but to a lesser extent (see fig.9.22).
The magnitude of this drop is of the same order as that reported by other workers.
GENERAL CONCLUSION

A superficial examination of a sample of 158 'run of mine' diamonds from the Argyle Mine in Western Australia has revealed a higher proportion of stones exhibiting octahedral morphology, and a smaller proportion of macles, than has been reported in samples before; also the predominant colour was found to be grey instead of brown (sec.2.3.3). A classification scheme (of 8 categories), based on the general appearance of the spots of their Laue patterns, was utilized to examine the quality distribution in the Argyle sample, and samples from a selection of South African mines. It was found that, within the limits of the samples investigated, the quality of the Argyle stones was more variable, and on average inferior, to that of the South African diamonds (sec.3.3.4). From a study of the asterism in their Laue photographs, it was determined that lattice distortion in the Argyle diamonds takes the form of mosaic structure (secs. 3.5.6 & 3.5.7). It was possible, nevertheless, to quantify part of the Laue spot classification scheme in terms of 'radius of curvature', assuming bent lattices (sec.3.5.8).

The new technique of shadowed spike topography (sec.5.5) has proved useful for the investigation of average platelet dimensions at different positions on diamonds (sec.5.5.2). By comparison with measurements taken from transmission electron micrographs (sec.6.5), it has been shown that this
non-destructive technique is reasonably reliable for estimating platelet radii below about 200 Å (sec.7.2.2). Results show that in the range 1361.3 to 1371.3 cm\(^{-1}\), the correlation between infrared 'platelet peak' position (sec.7.1.3) and average platelet radius, in the sense of smaller wavenumbers being associated with larger platelets, is not as strong as was once thought (sec.7.2.2.). In order to improve the compatibility between measurements made using spike topography, transmission electron microscopy and infrared spectroscopy, it is proposed that any further research of this kind should be carried out on diamond plates with \(\overline{111}\) type faces (sec.7.2.1).

X-ray topography revealed lineage features associated with cellular dislocation networks in a (100) semi-insulating GaAs wafer (sec.9.2.3). One such feature, studied in detail, was found to have once extended like a sheet along the [100] growth direction of the original LEC crystal (sec.9.2.4). It was determined that the Burgers vector was \(\overline{121}\), suggesting it was composed of dislocations of mixed type running in the [100] direction (sec.9.3.7). In the (100) wafer, the lineage feature was accompanied by a lattice tilt of nearly half a minute of arc (sec.9.4.2). The pinch-off voltages of MESFETs fabricated on the wafer were found to be lowered by about 40 mV if they were in contact with the lineage feature, and nearby MESFETs were also affected, but to a lesser extent (sec.9.5.3).
APPENDIX A

DERIVATION OF THE LATTICE CURVATURE FORMULA

A.1 INTRODUCTION

Assuming that lattice bending is responsible for asterism in Laue photographs, calculations were made, in chapter 3, of the radius of curvature of the Bragg planes giving rise to particular Laue streaks. In this appendix, the relationship used in chap.3 is derived. The derivation is a geometrical one based on the kinematical theory of x-ray diffraction (for an introduction to dynamical theory see e.g. Batterman & Cole 1964 or Hart 1980, and for a comprehensive work see Pinsker 1978, and for the application of the theory to deformed crystals see: Penning & Polder 1961, Bonse 1964, Penning 1966) and assuming simple cylindrical bending of the lattice. The theory is, however, completely general, no prior assumptions being made concerning the orientation of the axis of curvature.

A.2 THE DERIVATION

Fig.A1 shows the geometry of reflexion from a set of Bragg planes in a crystal lattice bent cylindrically about an axis A. The crystal itself is not shown in the diagram (for the sake of clarity), but the volume illuminated by the x-ray
A beam is incident on the crystal, as shown in Fig. 3.11. The length of the crystal parallel to the beam is $d$, and the specimen to this distance, $b$. The diagram of the cross-section incident beam is $\alpha$.

A set of lattice planes is defined for the beam $\alpha$, which is parallel to the center of the cell. The beam $\alpha$ is chosen such that for the incident, the incidence angle may be located for $\alpha$, which all be specificity. In each case, the beam $\alpha$ has the Bragg condition from one set of plane planes of a cylindrically bent crystal lattice.

**FIG. A1**

GEOMETRY OF REFLECTION FROM ONE SET OF BRAGG PLANES OF A CYLINDRICALLY BENT CRYSTAL LATTICE
beam is shaded. (A simplified version of this diagram, which includes the crystal, appears in fig.3.14.) The length of crystal parallel to the beam is \( d \), and the specimen to film distance, \( D \). The diameter of the circular cross-section incident beam is \( h \).

A set of cartesian axes, \( i, j, k \), are defined for the Laue streak being examined. The origin, \( o \), is at the exact centre of the illuminated crystal. The axis \( i \) is concentric with the central axis of the incident beam. The axis \( j \) is chosen such that for a Bragg reflexion taking place at the origin, the incident ray \( S_c \), the reflected ray \( R_c \), and \( j \) will all be coplanar. In other words:

\[
R_c \cdot S_c \times j = 0 \quad \text{and} \quad S_c \cdot j = 0
\]

The orientation of \( j \) is dependent on the Laue streak under investigation, and is redefined for each one. The axis \( k = i \times j \).

Bragg reflexion from the extreme ends of the illuminated volume of crystal (these are separated by the vector \( B \), which passes through the origin) gives rise to the two ends of the Laue streak. Which end of the streak is produced by which end of the crystal is, however, ambiguous and only one of the two possibilities is illustrated here. The vectors \( S \) and \( S' \) represent the rays incident at each end of the crystal, and \( R \) and \( R' \) the corresponding reflected rays. The normals to the curved Bragg planes at the extremities are \( r \) and \( r' \), and the corresponding Bragg angles \( \phi \) and \( \phi' \). The angle that the two
**FIG. A2** MEASUREMENTS FROM THE LAUE PICTURE (DIAGRAM EXAGGERATED)

![Diagram of Laue streak measurement](image)

\[ l = \text{LENGTH OF LAUE STREAK} \]

\[ a \] = DISTANCES OF EACH END OF THE STREAK FROM THE CENTRE OF THE THROUGH BEAM

\[ b \] = DIAMETER OF INCIDENT BEAM

\[ a \text{ and } b \text{ are not interchangeable - by interchanging them two alternative results may be obtained} \]
Fig. A3  Exaggerated Geometry of Laue Streak

The Laue picture produced by the arrangement illustrated in Fig. A1 is represented in Fig. A2. For clarity, it is grossly exaggerated; the Laue streak deviating from radially by far more than is seen in practice (see Chap. 3), and the through beam has a comparatively much greater diameter.

The geometry of this Laue streak relative to the cartesian axis \( j \) is shown in Fig. A3. All lengths have been drawn equal to angle \( ABC \) for the reason described later. For a given Laue streak \( \mathbf{K} \) is a constant defined by \( \alpha \) but \( \mathbf{K} \) is unknown and needs to be determined.

Fig. A4 illustrates the resolution of the Bragg reflected rays, \( \mathbf{K}, \mathbf{G} \), into their component rays \( \mathbf{A}, \mathbf{B} \) along the \( j \) and \( k \) directions. \( r, \mathbf{p}, \mathbf{F}, \mathbf{G} \) are in question and also illustrates the two useful intermediate rays, \( \mathbf{AB} \) is the streak of length \( \mathbf{L} \) defined by the derivation.

\[ \begin{align*}
\mathbf{AB} & \text{ is streak of length } \mathbf{L} \\
\mathbf{OA} &= a, \quad \mathbf{OB} = b \\
\mathbf{OC} &= \mathbf{OD} = h/2 \\
\mathbf{AD} &= g, \quad \mathbf{BC} = g'
\end{align*} \]
normals, R, R' make with the _i_ axis and _j_ axis are $\varphi$, $\varphi'$ and $\gamma$, $\gamma'$ respectively.

The Laue picture produced by the arrangement illustrated in Figure A1 is represented in Figure A2. For clarity, it is grossly exaggerated; the Laue streak deviating from radially by far more than has been found in practice (see chap.3), and the through beam having a comparatively much greater diameter. The geometry of this Laue streak relative to the cartesian axis _j_ is shown in Figure A3. Angle ADF has been drawn equal to angle BCF for the reason described later. For a given Laue streak $\mathcal{K}$ is a constant, defined by $a$, $b$ and $l$, but $\mathcal{L}$ is unknown and needs to be determined.

Figure A4 illustrates the resolution of the Bragg reflected rays, R, R' into their component lengths along the _j_ and _k_ directions, _y_, _y'_, and _x_, _x'_, respectively, and also illustrates the two useful intermediate parameters _z_, _z'_.

The figures described above are all referred to in the derivation which follows.
Referring to Fig. A3,

\[ \Delta OAF : \ OF = OA \cos \alpha = a \cos \alpha \]
\[ AF = OA \sin \alpha = a \sin \alpha \]

\[ \Delta OBE : \ OE = OB \cos \alpha' = b \cos \alpha' \]
\[ BE = OB \sin \alpha' = b \sin \alpha' \]

\[ \Delta DAF : \ \tan \beta = \frac{AF}{DF} = \frac{AF}{OF - OD} = \frac{a \sin \alpha}{a \cos \alpha - h/2} \]

\[ \Delta CBE : \ \tan \beta = \frac{BE}{CE} = \frac{BE}{OE + OC} = \frac{b \sin \alpha'}{b \cos \alpha' + h/2} \]

\[ \therefore \frac{a \sin \alpha}{a \cos \alpha - h/2} = \frac{b \sin \alpha'}{b \cos \alpha' + h/2} \] \hspace{1cm} (A1)

Applying cosine rule to \(\Delta OAB\):

\[ AB^2 = OA^2 + OB^2 - 2OA \cdot OB \cos (\alpha + \alpha') \]

i.e. \[ l^2 = a^2 + b^2 - 2ab \cos (\alpha + \alpha') \]

\[ \therefore \alpha + \alpha' = \cos^{-1} \left( \frac{a^2 + b^2 - l^2}{2ab} \right) = K \ \text{(say)} \] \hspace{1cm} (A2)

Substituting (A2) into (A1)

\[ \frac{a \sin \alpha}{a \cos \alpha - h/2} = \frac{b \sin (K-\alpha)}{b \cos (K-\alpha) + h/2} \]
Differentiating \((K\) is a constant—see chapter 4) 

\[ f'(x) = \frac{a \sin x}{a \cos x - h/2} = \frac{b \left( \sin K \cos x - \sin x \cos K \right)}{b \left( \cos K \cos x + \sin K \sin x \right) + h/2} \]

\[ \therefore \quad ab \sin x \left( \cos K \cos x + \sin K \sin x \right) \] 
\[ + \frac{ab}{2} \sin x \]
\[ = \quad ab \cos x \left( \sin K \cos x - \sin x \cos K \right) \] 
\[ - \frac{bh}{2} \left( \sin K \cos x - \sin x \cos K \right) \]

\[ \therefore \quad ab \sin K \left( \frac{\sin^2 x - \cos^2 x}{2} \right) + \frac{h}{2} \left( a - b \cos K \right) \sin x \]
\[ + 2ab \cos K \sin x \cos x + \frac{bh}{2} \sin K \cos x = 0 \]

\[ \therefore \quad -ab \sin K \cos 2x + \frac{bh}{2} \sin K \cos x \]
\[ + \frac{h}{2} \left( a - b \cos K \right) \sin x + ab \cos K \sin 2x = 0 \]

or say:

\[ f(x) = -2ab \sin K \cos 2x + bh \sin K \cos x \]
\[ + h \left( a - b \cos K \right) \sin x + 2ab \cos K \sin 2x \]
\[ = 0 \]

- 280 -
DIFFERENTIATING (K IS A CONSTANT — SEE EQN. A2):

\[ f'(\alpha) = 4ab\sin K\sin 2\alpha - 6b\sin K\sin \alpha \\
+ h(a-b\cos K)\cos \alpha + 4ab\cos K\cos 2\alpha \]

\[ \therefore \text{BY USING NEWTON'S METHOD (RAPHSON 1690)}: \]

\[ \alpha_1 = \alpha_0 - \frac{f(\alpha_0)}{f'(\alpha_0)} \text{ ETC.} \]

\( \alpha \) MAY BE CALCULATED.

WHERE \( \alpha_0 \) CAN BE \( \frac{1}{2}(\alpha + \alpha') \), AQ.EQUATION (A2)

ASSUMING THAT THE MAGNITUDE OF BENDING TO ONE SIDE OF THE CENTRE OF THE ILLUMINATED CRYSTAL IS EQUAL TO THAT OF THE OTHER, THEN IN FIG. A3 BECAUSE OF THE DEFINITION OF AXIS J:

\[ ABF = BCF = \beta \text{ AS SHOWN.} \]

IT FOLLOWS, SINCE \( S \times B \cdot \cdot \cdot = O = S' \times B' \cdot \cdot \cdot \) (SEE FIGS. A1, A3, A4), THAT:

\[ \tan \delta \sin \phi = \frac{x}{y} = \tan \beta = \frac{x'}{y'} = \tan \delta' \sin \phi' \]

(A3)
FIG. A4 THE \( j \) AND \( k \) COMPONENTS OF THE BRAGG REFLECTED RAYS

\[
y = R_j, \quad x = R_k, \quad y' = R'_j, \quad x' = R'_k
\]

AND FROM FIG. A3 IT IS APPARENT THAT:

\[
z = \frac{a \sin \alpha}{\sin \beta} \quad \text{AND} \quad z' = \frac{b \sin \alpha'}{\sin \beta} \quad (A4)
\]
FROM FIGS. A1 & A4 AND EQTNS. (A4):

\[ |R_1| \cos 2\delta = D + d/2 \]
\[ |R_1|^2 = (D + d/2)^2 + z^2 \]
\[ \cos 2\delta = \frac{(D + d/2)^2}{\sqrt{(D + d/2)^2 + z^2}} \]

\[ |R'_1| \cos 2\delta' = D - d/2 \]
\[ |R'_1|^2 = (D - d/2)^2 + z'^2 \]
\[ \cos 2\delta' = \frac{(D - d/2)^2}{\sqrt{(D - d/2)^2 + z'^2}} \]

RESOLVING THE REFLECTED RAYS INTO THEIR COMPONENTS:

\[ \mathbf{R} = (D + d/2) \mathbf{i} + y \mathbf{j} + x \mathbf{k} \]
\[ \mathbf{R}' = (D - d/2) \mathbf{i} + y' \mathbf{j} - x' \mathbf{k} \]

RESOLVING THE NORMALS:

\[ \epsilon = |\mathbf{R}| \left\{ -\sin\delta \cos \phi \mathbf{i} + \cos \delta \mathbf{j} + \sin \delta \sin \phi \mathbf{k} \right\} \]
\[ \epsilon' = |\mathbf{R}'| \left\{ -\sin \delta' \cos \phi' \mathbf{i} + \cos \delta' \mathbf{j} - \sin \delta' \sin \phi' \mathbf{k} \right\} \]

ASSUME THAT \[ |\epsilon| \approx |\epsilon'| \]
Now, \[
\frac{-S.5}{1S11S1} = \cos \left( \frac{\pi}{2} - \delta \right) = \sin \delta
\]

\[\sin \delta = \left( -1S111 \right) \mid \left( -\sin \delta \cos \phi + \cos \phi \right) + \sin \delta \sin \phi \bar{k} \mid \left( 1S111 \right) \]

\[\sin \delta = \sin \delta \cos \phi \quad (A6)\]

Similarly, \[\sin \delta' = \sin \delta' \cos \phi' \quad (A6)\]

\[\Delta (A5) \text{ can be re-written :} \]

\[\ell = 1S1 \left\{ -\sin \delta \hat{i} + \cos \delta \hat{j} + \sin \delta \tan \phi \bar{k} \right\} \quad (A7)\]

\[\ell' = 1S1 \left\{ -\sin \delta' \hat{i} + \cos \delta' \hat{j} - \sin \delta' \tan \phi' \bar{k} \right\} \quad (A7)\]

Assuming \[1S1 = 1S1' \quad (A7)\]

Combining \((A3)\) and \((A6)\) gives:

\[\tan \phi = \frac{\tan \beta \cos \delta}{\sin \delta} \quad (A8)\]

\[\tan \phi' = \frac{\tan \beta \cos \delta'}{\sin \delta'} \quad (A8)\]

Substituting \((A8)\) into \((A7)\):

\[\ell = 1S1 \left\{ -\sin \delta \hat{i} + \cos \delta \hat{j} + \tan \beta \cos \delta \bar{k} \right\} \quad (A9)\]

\[\ell' = 1S1 \left\{ -\sin \delta' \hat{i} + \cos \delta' \hat{j} - \tan \beta \cos \delta' \bar{k} \right\} \quad (A9)\]
FROM (A5) SQUARING THE MODULI IT IS APPARENT THAT:

\[
\sin^2 \delta + \cos^2 \gamma + \tan^2 \beta \cos^2 \gamma = 1
\]

\[
\therefore \cos \gamma = \frac{\cos \delta}{\sqrt{1 + \tan^2 \beta}} = \cos \delta \cos \beta
\]

AND LIKEWISE:

\[
\cos \delta' = \frac{\cos \delta'}{\sqrt{1 + \tan^2 \beta}} = \cos \delta' \cos \beta
\]

\[
\therefore \text{(A9) can be re-written:}
\]

\[
\begin{align*}
\Gamma &= | \epsilon \{ - \sin \delta \hat{i} + \cos \beta \cos \delta \hat{j} + \sin \beta \cos \delta \hat{k} \} | \\
\Gamma' &= | \epsilon' \{ - \sin \delta' \hat{i} + \cos \beta \cos \delta' \hat{j} - \sin \beta \cos \delta' \hat{k} \} |
\end{align*}
\]
Referring to Fig. A1, vector \( \mathbf{A} \) is the axis about which the lattice curvature takes place. Vector \( \mathbf{B} \) is the vector joining the two extremities of the illuminated volume of the crystal from which the rays \( \mathbf{R} \) and \( \mathbf{R}' \) are reflected, so:

\[
\mathbf{A} = \mathbf{r} + \mathbf{B} - \mathbf{r}'
\]

where \( \mathbf{B} = d\mathbf{i} - h\mathbf{j} \)

Substituting (A10):

\[
\mathbf{A} = -151 \sin \delta \mathbf{i} + 151 \cos \beta \cos \delta \mathbf{j} + 151 \sin \beta \cos \delta \mathbf{k} + d\mathbf{i} - h\mathbf{j}
\]

\[
+ 151 \sin \delta' \mathbf{i} - 151 \cos \beta \cos \delta' \mathbf{j} + 151 \sin \beta \cos \delta' \mathbf{k}
\]

\[
= \begin{cases}
& \{ d - 151 (\sin \delta - \sin \delta') \} \mathbf{i} \\
& - \{ h - 151 \cos \beta (\cos \delta - \cos \delta') \} \mathbf{j} \\
& + 151 \sin \beta (\cos \delta + \cos \delta') \mathbf{k}
\end{cases} 
\]

(A11)
SINCE $a$ IS THE AXIS TO WHICH $\delta$ AND $\delta'$ ARE RADIAL,

$$A \cdot \delta = A \cdot \delta' = 0$$

SO SUBSTITUTING (A10) AND (A11):

$$-\{d - |c| (\sin \delta - \sin \delta')\} \equiv |c| \sin \delta$$

$$-\{h - |c| \cos \beta (\cos \delta - \cos \delta')\} \equiv |c| \cos \beta \cos \delta$$

$$+ |c| \sin \beta (\cos \delta + \cos \delta') \equiv |c| \sin \beta \cos \delta$$

$$= -\{d - |c| (\sin \delta - \sin \delta')\} \equiv |c| \sin \delta'$$

$$-\{h - |c| \cos \beta (\cos \delta - \cos \delta')\} \equiv |c| \cos \beta \cos \delta'$$

$$- |c| \sin \beta (\cos \delta + \cos \delta') \equiv |c| \sin \beta \cos \delta'$$

$$= 0$$

:. $$d \sin \delta - |c| (\sin \delta - \sin \delta') \sin \delta$$

$$+ h \cos \beta \cos \delta - |c| \cos^2 \beta (\cos \delta - \cos \delta') \cos \delta$$

$$- |c| \sin^2 \beta (\cos \delta + \cos \delta') \cos \delta$$

$$= d \sin \delta' - |c| (\sin \delta - \sin \delta') \sin \delta'$$

$$+ h \cos \beta \cos \delta' - |c| \cos^2 \beta (\cos \delta - \cos \delta') \cos \delta'$$

$$+ |c| \sin^2 \beta (\cos \delta + \cos \delta') \cos \delta'$$

$$= 0$$
A.3. THE CASE OF 'PLANAR' PLANES

It has proved difficult to show analytically that the \( \lim_{\theta \to 0} \) given by equation (10) becomes infinite. However, classical defects having \( \theta = 0 \), as the planar condition, give:

\[
\left\{ (\sin \delta - \sin \delta')^2 + \cos^2 \beta (\cos \delta - \cos \delta')^2 + \sin^2 \beta (\cos \delta + \cos \delta')^2 \right\} = d (\sin \delta - \sin \delta') + h \cos \beta (\cos \delta - \cos \delta')
\]

The theory has been based on the reasonable assumption that the crystal lattice is bent cylindrically, however, a future diagram would therefore themselves all be cylindrically curved.

\[ \therefore \text{THE RADIUS OF CURVATURE, } \left| \right| \text{ IS GIVEN BY:} \]

\[
\frac{d (\sin \delta - \sin \delta') + h \cos \beta (\cos \delta - \cos \delta')}{(\sin \delta - \sin \delta')^2 + \cos^2 \beta (\cos \delta - \cos \delta')^2 + \sin^2 \beta (\cos \delta + \cos \delta')^2}
\]

Fig. 6 shows two diagrams of a two-dimensional lattice curved about an axis, A perpendicular to the page. The diagram demonstrates on a different set of planes, it can be seen that apart from the following two special cases:

1) the 'planes' are coincident with a and an 'circular area'

2) three dimensional their counterparts would be cylindrical.

3) the 'planes' radiate from a (known as 'tunneling').

All the planes lie on Archimedean spirals (Archimedes \( \pm 360 \) B.C.), as indicated by the dotted lines in Fig. 6. The same situation can be extrapolated to three dimensions. Over short distances compared with the radius of curvature, the bent Bragg planes can still be regarded as being approximately cylindrical (especially where the curvature is not great), but...
A.3 THE CASE OF 'PLANAR' PLANES

It has proved difficult to show analytically that for the case of unbent Bragg planes, the radius of curvature \(|r|\) given by equation (A12), becomes infinite. However, numerical tests have shown that \(|r|\) becomes very large (tens of metres) as the planar condition is approached.

A.4 THE SHAPE OF THE BENT BRAGG PLANES

The theory has been based on the reasonable assumption that the crystal lattice is bent cylindrically. However, a further implicit assumption was made that the different Bragg planes would therefore themselves all be cylindrically curved. In fact, it turns out that this last assumption is erroneous.

Fig.A5 shows four diagrams of a two-dimensional lattice curved about an axis, A (perpendicular to the page). Each diagram concentrates on a different set of 'planes'. It can be seen that apart from the following two special cases:

1) the 'planes' are concentric with A and on circular arcs (in three dimensions their counterparts would be cylindrical);

2) the 'planes' radiate from A (known as 'fanning');

all the planes lie on Archimedean spirals (Archimedes c.250 B.C.), as indicated by the dotted lines in fig.A5. The same situation can be extrapolated to three dimensions. Over short distances compared with the radius of curvature, the bent Bragg planes can still be regarded as being approximately cylindrical (especially where the curvature is not great), but
FIG. A5
CURVATURE OF A TWO-DIMENSIONAL LATTICE
as the situation in case 2 is approached, so the greater the deviation becomes.

APPENDIX B

DERIVATION OF MOORE & LANG'S FORMULA

Given here is the derivation of Moore & Lang's formula (equation 5.1) for determining average platelet radius from microdensitometer traces of spine topographs. The theory has been largely adopted from the following sources: Moors (1973), Moore & Lang (1973, 1977).

Electron microscopy (chap. 5) shows that platelets may be elongated, within their plane, along one of other of two perpendicular [110] type directions. X-ray diffraction from such an assembly of platelets is analogous to the optical case of Fraunhofer diffraction of monochromatic light from an assembly of circular apertures of the same mean area (e.g. see Pitchburn 1976 chap.6). By this analogy, therefore, each platelet will give rise to a diffraction pattern with the Airy (1834) intensity profile (e.g. see Born & Wolf 1976, chap. 3). This may be represented by the function (due to Lommel 1870):

\[ A^1(x) = 4 j_1(x) x \]  

- 291 -
APPENDIX B

DERIVATION OF MOORE & LANG'S FORMULÆ

Given here is the derivation of Moore & Lang's formulae (equation 5.1) for determining average platelet radius from microdensitometer traces of spike topographs. The theory has been largely adopted from the following sources: Moore (1973), Moore & Lang (1972, 1977).

Electron microscopy (chap.6) shows that platelets may be elongated, within their planes, along one or other of two perpendicular [110] type directions. X-ray diffraction from such an assembly of platelets is analogous to the optical case of Fraunhofer diffraction of monochromatic light from an assembly of circular apertures of the same mean area (e.g. see Ditchburn 1976 chap.6). By this analogy, therefore, each platelet will give rise to a diffraction pattern with the Airy (1834) intensity profile (e.g. see Born & Wolf 1970 chap.8). This may be represented by the function (due to Lommel 1870):

\[
A^2(x) = 4J_1^2(x)/x^2
\]

- (B1)
where $J_1$ is a Bessel function of the first kind and first order (for values see for example Neville 1958) and $x$ is dimensionless and given by:

$$x = \left(\frac{2\pi}{\lambda}\right) R \left(\frac{r}{L}\right) \quad -(B2)$$

The table below compares the meanings of these symbols for the diffraction of light and in spike topography.

<table>
<thead>
<tr>
<th>SYMBOL</th>
<th>DIFFRACTION OF LIGHT</th>
<th>SPIKE TOPOGRAPHY</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda$</td>
<td>Wavelength of light</td>
<td>Wavelength of x-rays</td>
</tr>
<tr>
<td>$R$</td>
<td>Aperture radius</td>
<td>Mean platelet radius</td>
</tr>
<tr>
<td>$L$</td>
<td>Distance from aperture to plane of observation</td>
<td>Distance from specimen to photographic plate</td>
</tr>
<tr>
<td>$r$</td>
<td>Radial distance, measured in plane of observation, from centre of diffraction pattern</td>
<td>Distance measured on topographic image (Corrected measured IQW - see appendix C)</td>
</tr>
</tbody>
</table>

TABLE B

Spike Topography Compared with the Diffraction of Light
The intensity distribution over a spike topograph image is proportional to the convolution of the Airy intensity function, $A^2(x)$ with the projected number density of platelets along the direction of the diffracted beam. Therefore, some topographic feature is required whose platelet density distribution is known. Takagi & Lang (1964) used an abrupt change in platelet concentration at a growth horizon. Moore & Lang (1970) used the edges of the crystal; these may be regarded as naturally introducing an ideal step function in the number density – inside the crystal there are platelets and outside there are none. This step function can be artificially introduced elsewhere within the specimen by casting an x-ray shadow from an absorbing screen. This has been done in sec. 5.4.

Let the step function be $S(t) = 1$ for $t \geq 0$ and $S(t) = 0$ for $t < 0$; $t$ being position, with the edge occurring at $t = 0$. By definition (e.g. see Steward 1983) the required convolution is:

$$y(x) = A^2(x) \ast S(x) = \int_{-\infty}^{\infty} A^2(x') S(x-x') \, dx'$$

Put $t = x-x'$, so $x' = x-t$ and $dx' = -dt$ then,

$$y(x) = \int_{-\infty}^{\infty} A^2(x-t) S(t) \, dt$$
From what has already been said about the step function this becomes:

\[ y(x) = \int_0^\infty A^2(x-t) \, dt \]

and since \( t = x - x' \),

\[ y(x) = \int_{-\infty}^x A^2(x') \, dx' \]

substituting (B1) gives the sigmoidal curve:

\[ y(x) = \int_{-\infty}^x \left[ \frac{2J_1(x')}{x'} \right]^2 \, dx' \]

Moore (1973) tabulated this integral by computer and the shape of \( y(x) \) is shown in fig.B (after Moore 1973). This curve represents the expected change in optical density to be found in crossing the upper or lower boundary of a spike topographic image. (How this is measured was described in sec.5.3.2) Its IQW, that is the width between one quarter and three quarters of the maximum (i.e. between \( y = 8/3\pi \) and \( y = 8/\pi \)), is 1.817 on the dimensionless \( x \) scale. So by substituting \( x = 1.817 \) into equation (B2) the average platelet radius is given by:

\[ R = 1.817 \left( \frac{\lambda}{2\pi} \right) \left( \frac{L}{r} \right) \quad - (B3) \]

The relationship (B3) is valid for the situation where the
$y = \int_{-\infty}^{\infty} \left\{ \frac{2J_1(x)}{x} \right\}^2 dx$

**Fig. B**  CONVOLUTION OF AIRY DIFFRACTION PROFILE WITH STEP FUNCTION  (AFTER MOORE 1973)
spike topographs can be reasonably regarded as a line distribution of Airy diffraction patterns. This will be the case if the specimen is in the form of a thin parallel-sided plate, and a sufficiently narrow section is being imaged that the geometric width of the Laue and spike images is about 100 \( \mu \text{m} \) (see Moore & Lang 1977). Moore & Lang have shown that in circumstances differing from this an extra integration of the Airy diffraction intensity profile is required. Details of this will not be given here, but it is worth while publicizing the correct version of the function now to be convoluted with the step function (their misprinted equation 5), which is:

\[
4 \int_{-\infty}^{\infty} \frac{J_1^2 (x^2 + y^2)^{1/2}}{x^2 + y^2} \, dy
\]

The convolution leads to a function whose shape is very similar to that in fig.B1 but the IQW is now 2.022 (as stated in Moore & Lang), so equation (B3) will become:

\[
R = 2.022 \left( \frac{\lambda}{2\pi} \right) \left( \frac{L}{r} \right) \quad - (B4)
\]
APPENDIX C
CORRECTION FOR MICRODENSITOMETER SLIT WIDTH

In sec. 5.3.2 it was explained that, in order to get the true IQW, \( r \), of the spike topograph optical density profile, from the IQW measured from a microdensitometer trace, it is necessary to subtract the microdensitometer slit width. The following derivation, kindly supplied by Dr. Moreton Moore, shows why this is so.

The trace, \( h \), resulting from a microdensitometer traverse across an image, results from the convolution of the image’s optical density profile, \( f \) with the function, \( g \) representing the microdensitometer slit, or symbolically \( h = f * g \). Fig. C illustrates the functions \( f \) and \( g \).

The convolution is:

\[
h(x) = \int_{-\infty}^{\infty} f(t) g(x-t) \, dt
\]

Put \( u = x-t \), so \( t = x-u \) and \( dt = -du \) then,

\[
h(x) = \int_{-\infty}^{\infty} f(x-u) g(u) \, du
\]
Fig. C  Convolution of spike topograph image profile with microdensitometer slit
From fig. C it can be seen that \( g(u) = G \) when \( 0 < u < \gamma \) and is zero elsewhere (\( \gamma \) is the microdensitometer slit width), so

\[
h(x) = G \int_0^\gamma f(x-u) \, du
\]

Put \( x-u = v \) and,

\[
h(x) = G \int_{x-\gamma}^x f(v) \, dv
\]

Now let \( f(v) = 0 \) for \( v \leq 0 \), \( f(v) = Fv/w \) for \( 0 < v \leq w \) and \( f(v) = F \) for \( v > w \). Then for \( x-\gamma > w, x > w+\gamma \), so

\[
h(x) = G \int_{x-\gamma}^x F \, dv
\]

\[= FG\gamma\]

For \( x \leq 0 \), \( h(x) = 0 \); for \( 0 < x < w+\gamma \), \( h(x) \) takes values between 0 and \( FG\gamma \) therefore the corresponding full width of \( h(x) \) is \( w+\gamma \). Hence the microdensitometer slit width needs to be subtracted from the measured IQW of \( h \) in order to obtain the required IQW of \( f \).
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APPENDIX D
DILUENTING SUBSTRATES AND GALLIUM ARSENIDE

With the help of

Site the layers of the thin-blade structures (the latter being the structure of gallium arsenide), are made up of two interpenetrating face-centred cubic lattices displaced with respect to each other by the vector \( \vec{a} \) (where \( a \) is the lattice parameter). The (111) planes in both these structures are arranged in successive double layers, and the stacking order can be conveniently described by the sequence

\[ \ldots, c, a, c, c, c, a, c, c, a, c, c, c, a, c, c, a, c, c, a, c, c, \ldots \]

The two sets of \( c \) and \( a \) are intergrown, such as to occupy the same site, e.g., \( c \) and \( c \). To the right of the \( a \) site, the third layer can be taken to consist of a layer of gallium atoms, and the capital \( C \) of \( c \) to consist of an arsenic atom. Dislocations and stacking faults involve the introduction of dislocations of pairs of layers represented by the same center, thus retaining the tetragonal bonding. Other faults, which disrupt this bonding, are energetically unfavourable.

- 338 -
APPENDIX D

DISLOCATIONS IN DIAMOND AND GALLIUM ARSENIDE

[Added May 1989]

Both the diamond and zinc blende structures (the latter being the structure of gallium arsenide) are made up of two interpenetrating face-centred cubic lattices displaced with respect to each other by the vector $\frac{a}{2}\langle 111 \rangle$ (where $a$ is the lattice parameter). The $\{111\}$ planes in both these structures are arranged in successive double layers, and the stacking order can be conveniently described by the notation: $\ldots AaBbCcAa\ldots$. The two planes constituting each closely spaced pair of layers are represented by the same letter, e.g. $C$ and $c$. In the case of gallium arsenide, the small letters can be taken to represent planes of gallium atoms, and the capitals, planes of arsenic atoms. Twins and stacking faults involve the insertion, or removal, of pairs of layers represented by the same letter; thus retaining the tetrahedral bonding. Other faults, which disrupt this bonding, are energetically unfavourable.
The \{111\} planes are the most densely populated in both structures, and the shortest distance between two equivalent atoms can be represented by the displacement \( \frac{1}{4}a<110> \); hence it is likely that dislocations will have \( \frac{1}{4}a<110> \) Burgers vectors and \{111\} glide planes. This has indeed been observed experimentally (Evans & Wild 1965, 1966). Since any direction in the lattice may be considered as the sum of successive \( <110> \) directions, the simplest types of dislocations in the diamond and zinc blende structures are those with line direction \( \mathbf{l} \) and Burgers vector \( \mathbf{b} \) both along the same or different \( <110> \) directions. There are three such simple dislocations: the screw type (with \( \mathbf{l} \) parallel to \( \mathbf{b} \)), the so-called 60° dislocation (60° being the angle between \( \mathbf{l} \) and \( \mathbf{b} \)), and the edge dislocation, found in low-angle grain boundaries (which has \( \mathbf{l} \) perpendicular to \( \mathbf{b} \), and a \( \langle 100\rangle \)-type glide plane). There are two distinct sets of 60° dislocations. One has an extra half-plane which terminates between the layers of atoms represented in the notation by different letters. The other has an extra half-plane that ends between atomic layers represented by the same letter.

A partial dislocation occurs at the end of a stacking fault. The partial dislocations associated with the 60° dislocation have Burgers vectors of the type \( \frac{1}{6}a[211] \) and \( \{111\} \)-type glide planes. They are called partial dislocations because two can combine to form a simple dislocation. Various mechanisms involving partial dislocations have been proposed to explain deformation twinning in these structures (e.g. see Van Bueren 1960).
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Single-slit diffraction patterns of sub-nanometre-wavelength synchrotron radiation

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Abstract. The single-slit diffraction patterns of monochromatic x-rays of wavelengths 0.16 nm and 0.1 nm have been recorded on a large linear scale by using a long distance, 16 m, between slit and photographic plate. The spacings of subsidiary maxima ranged from 0.1 mm to 0.6 mm, depending upon the width of the slit. Applications of such diffraction patterns in illumination systems for x-ray phase contrast microscopy and interferometry are envisaged.

The reproduction at x-ray wavelengths of several classical interference and diffraction experiments (e.g. Lloyd’s mirror, Fresnel’s mirrors, slit aperture diffraction) familiar with visible wavelengths was performed so convincingly by Kellstrom (1932) that there has been little call for such experiments to be repeated. However, the advent of powerful synchrotron radiation sources of sub-nanometre wavelengths, and the possibilities thereby generated for new experimental configurations in investigations of Bragg reflection optics in crystals, or of x-ray microscopy, prompts a fresh appraisal of the classical optical interference and diffraction experiments in an x-ray context, with a view to their possible useful application in, for example, production of multiple sources of coherent radiation. An application of the single-slit diffraction pattern as an illumination source for topographic testing of x-ray mirror surfaces has recently been successfully demonstrated by Mancini and Bilderback (1983). They photographed x-ray mirror reflections of the diffraction pattern of a 10 μm wide slit illuminated by synchrotron radiation from CESR (Cornell Electron Storage Ring) after monochromatisation by crystal reflection so as to confine the x-ray energies to 8.04 keV or 16.08 keV (wavelengths 0.154 nm and 0.077 nm, respectively). In the mirror reflections, the perturbations from straightness of the images of principal and subsidiary maxima, and the loss of visibility of subsidiary maxima, provided useful measures of mirror quality.

Kellstrom employed a diffracting slit of 6.6 μm aperture and a distance of 416 mm from slit to photographic plate. His x-ray sources were x-ray tubes run at low kilovoltages to produce dominantly certain characteristic radiations: C Kα (280 eV, 4.4 nm), Cu Lα (0.9 keV, 1.3 nm) and Al Kα (1.5 keV, 0.83 nm). These produced diffraction patterns with minima spacings of 280 μm, 80 μm and 50 μm, respectively. In the experimental arrangement of Mancini and Bilderback the slit-to-film distance was 1.3 m and the spacing between minima was about 20 μm when radiation of 0.154 nm wavelength was used. A special feature of the experiments here reported were the long distances, ~16 m, between diffracting slit and the recording film or plates. This enabled slit diffraction patterns to be recorded on a linear scale more than an order of magnitude greater than that obtained in the above-cited earlier works. Thereby was gained the immediate advantage that degradation of fringe resolution due to grain size in x-ray films was avoided in all experiments. Also, photometric scanning of plates, or direct scanning of the pattern itself, could be done without recourse to inconveniently fine scanning slits. The investigation had two main aims, discussed more fully below. In broad terms, the first objective was to assess the potential usefulness of the slit diffraction pattern for monitoring source characteristics with regard to size and mean position. The second objective was to produce an array of spatially separated beams from which two or more might be selected to constitute novel illumination systems. With these aims in view,
an exploration of the quality of single-slit diffraction patterns as functions of slit opening and of x-ray mean wavelength and spectral range was undertaken.

The experiments were performed at the UK SRS (Synchrotron Radiation Source), Daresbury, operating at 2 GeV. The long beam line No 7 was used. This has x-ray topography cameras at its penultimate station (No 7.5) and end station (No 7.6), situated respectively 65 m and 81 m from the tangent point on the electron storage ring where the bending radius is 5.56 m in a magnetic field of 1.2 T. The cameras at stations 7.5 and 7.6 operate in tandem. Most of the beam path between them is evacuated. The diffracting slit was placed at station 7.5 and the recording films and plates at station 7.6, with or without monochromatisation of the diffraction pattern by crystal reflection. Figure 1 indicates the arrangements. The distance TS is 65 m and SP is 15.9 m. SP' is about 1 m shorter than SP, and MP is 0.2 m. The electron-beam cross section at the tangent point T is highly elongated in the plane of the storage ring. The electron density distribution within the beam is taken to be a two-dimensional gaussian, with full widths at half maximum being about 13 mm in the horizontal (orbit) plane and about 0.25 mm in the vertical plane. In earlier experiments (unpublished) we have studied the source intensity profile by pinhole photography, placing a platinum disc pierced with a 30 μm diameter pinhole at station 7.5 and photographic films at P' on station 7.6. On the spindle-shaped images obtained, the intensity distribution along the long horizontal dimension extends over several millimetres, but the image profile in the vertical plane is dominated by the geometrical image of the pinhole, or its diffraction image. It follows that in order to record a slit diffraction pattern the only possible orientation of the slit S is for its jaw length to lie in the horizontal plane, with observation of the diffraction pattern in the vertical plane. Then with slit opening s and wavelength λ one may expect to resolve subsidiary maxima and minima in the diffraction pattern when \( (\lambda/s) > \left[ \text{(source height at T)/TS} \right] \sim 4 \times 10^{-8} \), i.e. with a slit aperture of less than 25 μm when \( \lambda = 0.1 \text{ nm} \). The diffracting aperture used was continuously variable. It consisted of a pair of ground tungsten rods, each of diameter 1.5 mm, separated by a gap of 50 μm. The rods were mounted on a plate which was attached to a shaft inserted in a horizontally oriented goniometer axis of the camera on station 7.5. The plate also carried a mirror whose surface was parallel to the plane containing the axes of the two tungsten rods. A laser beam aligned parallel to the x-ray beam was reflected from the mirror and was used to set the plane of the rods normal to the x-ray beam initially. Rotation of the goniometer axis away from this initial orientation controlled the effective opening of the slit: complete occlusion of the x-ray beam occurred with rotations of about ±14°. Additional four-jaw slits (i.e. with jaws controlling both horizontal and vertical beam dimensions) were placed both on the ‘upstream’ side of S (i.e. towards T) and on its ‘downstream’ side. They limited the horizontal length of the slit S operable, and prevented radiation from passing above or below the tungsten rods. (They did not, of course, encroach into the beam passing through S.) The highly elongated x-ray source profile in the horizontal plane was put to good use in the following way. By limiting the length of S used to 1 mm, the image received at P' or P became crudely a demagnified pinhole image of the source, as far as its horizontal intensity distribution was concerned: maximum strength in the middle, and fading towards each end. Thus in effect each diffraction pattern recorded contained its own ‘intensity wedge’. Strong exposure in the middle region brought up the higher-order subsidiary maxima, whereas weaker exposure at either end allowed clear observation of the first minima on either side of the principal maximum.

Figure 2 shows the middle regions of three representative diffraction patterns taken with radiation monochromatised by the 111 reflection from a perfect silicon crystal having a surface parallel to (111). Since the reflection was symmetrical (i.e. equal angles of incidence and reflection at the crystal surface), the magnification in the monochromatised image received on P was unity. The second-order reflection of the harmonic \( \lambda/2 \) is extinguished by space group symmetry, and contributions to the pattern from the 333 reflection of \( \lambda/3 \) are quite negligible as a result of the combined effects of reductions of source intensity, of integrated reflection of the monochromator, and of photographic emulsion absorption efficiency at such shorter wavelengths. The Bragg angle scale of the monochromator was calibrated by accurate measurement of the deviation of the Bragg-reflected rays and so the wavelengths used are known to within a few parts per thousand. Diffracting aperture widths of 10 μm or less cannot be measured reliably by optical microscopy either directly or by examination of their radiographs. The values of s given are derived from the measured separation, f, between minima in the diffraction patterns, using the standard Fraunhofer diffraction formula

\[
f = D \lambda / s
\]
Figure 2. Single-slit diffraction patterns of monochromatic x-rays. Width of field in prints = 5.4 mm. (a) Wavelength $\lambda = 0.1 \text{ nm}$, slit aperture $s = 8.8 \mu \text{m}$; (b) $\lambda = 0.162 \text{ nm}$, $s = 8.8 \mu \text{m}$; (c) $\lambda = 0.1 \text{ nm}$, $s = 2.8 \mu \text{m}$.

where $D = \text{distance SP}$. The measured values of $f$ were 0.18 mm, 0.29 mm and 0.58 mm, in figures 2(a), (b) and (c), respectively; and in the first two cases are considered correct to about 1%. The aperture that gave the pattern in figure 2(c), 2.8 $\mu \text{m}$, was the smallest with which patterns of satisfactory contrast and intensity were recorded. Clear fringe patterns spanning a total width of between 3 and 4 mm at P were obtained over a tenfold variation of magnitude of $s$. Three x-ray recording media were used: Agfa-Gevaert Strukturix X-ray film types D7 and D4, and Ilford Nuclear Emulsion type L4, 25 $\mu \text{m}$ thick. The first was fastest, the third gave highest resolution. Because so much of the intensity of the single-slit diffraction pattern is contained within the principal maximum (the relative intensities of maxima: principal, first, second and third subsidiary being respectively 1, 0.047, 0.017, and 0.008), exposures sufficient to give adequately noise-free images of the subsidiary maxima and intervening minima also unavoidably entail high optical density in the principal maximum. To compress this density range so as to produce a fair representation of the whole pattern on photographic prints required some controlled compensation of illumination over the field, both in negative-making and in final printing.

The diffraction patterns obtained with the photographic film located at P' and with addition of a filter of nickel foil, 15 $\mu \text{m}$ thick, in front of the film exhibited a much higher background than those obtained with wavelength selection by monochromator, and no maxima of order higher than four were definitely resolved when using apertures such as those which produced the patterns of figures 2(a) and (b). Indeed, it might be considered surprising that fringes out to this order could be observed without the monochromator. The explanation lies in the relatively narrow wavelength band effective, this being limited on the low-wavelength side by the K absorption edge of nickel, $\lambda = 0.149 \text{ nm}$, and on the high-wavelength side by increasing absorption losses in beam pipe windows and, particularly, in the long air path. With the combined air path at stations 7.5 and 7.6 totalling 3.5 m and the aggregate of beryllium window thicknesses amounting to 1.5 mm, the beam attenuation increased to 100 times that suffered at $\lambda = 0.15 \text{ nm}$ for a wavelength increase to no more than 0.19 nm.

In conclusion, some possible application of the x-ray optical arrangements described above may be considered. One straightforward use is in the assessment of the effective x-ray source dimensions. In the present experiments it was found that whereas well visible fringes were observed with $f \geq 100 \mu \text{m}$, the fringes became nearly invisible when $s$ was increased sufficiently to reduce $f$ to 70 $\mu \text{m}$. Since ST/PS = 4, one may thereby conclude, at the simplest level, that the source profile is effectively equivalent to a rectangle not wider than 280 $\mu \text{m}$. This result is roughly in line with an earlier estimated gaussian source profile having FWHM = 250 $\mu \text{m}$ derived by Hart and Siddons (1982) in a more elaborate experiment involving scanning the source with a silicon monolithic quadruple reflection monochromator which when used in the 660 reflection had a calculated acceptance angle as low as 0.26 seconds of arc (equivalent to a linear distance of 70 $\mu \text{m}$ at T when seen from the working position 55 m from T).

An application which could well reveal intriguing diffraction effects would employ Bragg diffraction in transmission rather than reflection at the monochromator crystal M. X-rays of a given wavelength forming the slit diffraction pattern constitute an array of coherent and mutually slightly divergent beams which would enter the crystal at different
points. Typical angular separations between the subsidiary maxima are similar to typical angular ranges of Bragg reflections of low order by perfect crystals. To each beam entering the crystal in the transmission diffraction geometry there would correspond an 'energy-flow triangle' contained between the incident-beam and diffracted-beam directions subtending from the x-ray entrance point. X-ray interference phenomena characteristic of such a discrete set of overlapping energy-flow triangles, which could be recorded in the spatial pattern of diffracted rays issuing from the monochromator, might constitute an informative probe into the strain fields existing in the monochromator crystal. Note that the linear scale of patterns such as those shown in figure 2 is large enough to allow interposition of an absorbing strip to cut off the principal maximum, or reduce it to an intensity similar to its adjacent subsidiary maxima.

In another application envisaged, selected well-separated subsidiary maxima could be recombined by refraction using a prism of low-absorbing material (e.g. diamond or high molecular weight paraffin). Since prior to recombination the linear separation of corresponding low-order subsidiary maxima on either side of the principal maximum is in the range of millimetres, there would be no difficulty in inserting objects into one beam without encroaching on the other. Such an arrangement might be useful for phase-contrast x-ray microscopy.

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