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Effect of pressure on the high-magnetic-field electronic phase transition in graphite

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The effect of hydrostatic pressure on the magnetic-field-induced electronic phase transition in graphite has been studied. The phase boundary shifts towards higher fields and lower temperatures with increasing pressure. To a first approximation, the pressure effect is accounted for by incorporating in the BCS-like expression for the transition temperature, the pressure dependences of the Fermi energy, and the density of states, which enter through the graphite band parameter γ_2.

The graphite electron system undergoes a phase transition at a low temperature when subjected to an intense magnetic field along the c axis, perpendicular to the layer plane.[1-5] The experimental facts so far established may be summarized as follows. (i) The transition temperature T_c as a function of magnetic field B is universal among samples taken from a batch of single-crystal kish graphite with a minimal concentration of ionized impurities, which we called type A in our earlier reports. The *phase boundary* $T_c(B)$ for the type-A sample is empirically expressed as

$$T_c(B) = T^* \exp(-B^*/B) , \qquad (1)$$

where T^* and B^* are fitting parameters.[1] These parameters have been determined as $T^* = 69$ K and $B^* = 104.7$ T.[4] (ii) When the magnetic field is tilted, the transition field follows a $\cos\theta$ dependence, indicating that only the c-axis component is relevant to the phase transition.[2] This suggests that the phase transition is basically caused by the effect of a quantizing magnetic field on the orbital motion of electrons within the layer plane. (iii) The above empirical relation is to be compared with a BCS-like expression for a Fermi-surface instability,

$$T_c(B) \sim 1.13\varepsilon_F \exp[-1/N(\varepsilon_F)V] . \qquad (2)$$

Note that the density of states at the Fermi level $N(\varepsilon_F)$ in the presence of a high magnetic field is proportional to B because of the Landau degeneracy factor. (iv) As one goes through the transition temperature $T_c(B)$, the conductivity sharply decreases, indicating the development of a gap in the single-particle excitation spectrum.[3,4] (v) In the low-temperature ordered phase, non-Ohmic transport quite reminiscent of collective transport in a charge-density-wave system has been observed.[5] (vi) For samples with a relatively high concentration of ionized impurities, which we called type B, the transition temperature at a given field is suppressed in such a way as to be attributable to the pair-breaking effect of those impurities.[3,4] (vii) Although the *phase boundary* itself is universal among samples with similar ionized impurity concentrations, the *amplitude* of the resistive anomaly at the transition point is very much sample dependent. The resistive anomaly is generally smaller for lower mobility samples with smaller Shubnikov–de Haas oscillation amplitudes. Even for the same sample, mechanical damage can severely reduce the amplitude of the resistive anomaly.

Based on these experimental observations, we believe the nature of the low-temperature phase to be a magnetic-field-induced charge-density wave or a Wigner crystal state. A theoretical model proposed by Yoshioka and Fukuyama[6] is based on the fact that the system becomes inherently one dimensional in character under strong magnetic fields, and becomes susceptible to the so-called $2k_F$ instabilities. In order to gain further insight into the nature of this electronic phase transition, we have carried out a high-pressure experiment on this system. Since the graphite band parameters can be changed by application of high pressure, we can thus study the dependence of the phase-boundary curve on the band-parameter values.

The high-pressure–high-field–low-temperature experiments were carried out in the following way. Quasihydrostatic pressures up to ~ 15 kbar at room temperature were attained by use of a 10-mm-o.d. copper-beryllium piston–cylinder clamp cell. A single-crystal kish graphite sample $\sim 2\times 1\times 0.02$ mm^3 in size was mounted within a 2.5-mm diam Teflon inner cell with six electrical leads attached with silver paint. The Teflon cell was filled with a pressure medium ("Fluorinert" manufactured by the 3M Company). Because of the space limitation, we were not able to place a manometer in the cell together with the sample. The pressure values were therefore deduced from the relation between the clamped pressure and the resulting pressure at low temperatures, which was precalibrated for the cell by use of a lead manometer. An independent estimate of the pressure was obtained by the pressure-induced shift of the Shubnikov–de Haas oscillations of graphite, and the two estimates of the pressure were in good agreement with each other. The present experiments were done at two values of pressure, 5 and 10.5 kbar.

The pressure cell was cooled by direct contact with the cryogenic ^{3}He liquid. High magnetic fields up to 30.2 T were applied by use of a hybrid magnet at the Francis Bitter Magnet Laboratory, MIT. Temperatures under high magnetic fields were determined by monitoring the saturated-vapor pressure of the ^{3}He. Refrigeration in high magnetic fields in the present experiment was severely hampered by eddy-current heating caused by mechanical vibration (generated by the vigorous flow of cooling water in the Bitter magnet) of the thick-metal-walled pressure cell in magnetic fields. The lowest temperature attained in high fields was ~ 0.55 K. Resistance measurements were done by a standard dc method using a probe current of ~ 200 μA. It was experimentally checked that at such a current level the Ohmic heating had negligible effects on the transition point.

Figure 1 shows traces of the magnetoresistance in the low-field region for different pressure values. The effect of pressure on the Shubnikov–de Haas (SdH) oscillations is twofold. First, the oscillatory features are shifted to higher fields with increasing pressure. This reflects the increase of the Fermi-surface volume with pressure. Second, the amplitude of the SdH oscillations is significantly suppressed by pressure. Because the ambient-pressure data is not for the same sample, but for a different sample taken from the same batch, a quantitative comparison of the oscillation amplitude cannot be made. It has been generally observed that an application of pressure significantly reduces the amplitude of the SdH oscillations. The diminished SdH amplitude is partly due to an increase of the effective mass. But, since the SdH amplitude is not recovered when the same sample is brought back to ambient pressure, a more permanent deterioration of the carrier mobility is involved. Such

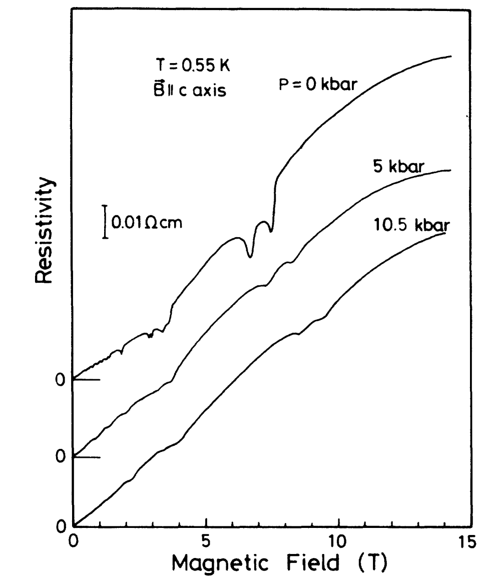

FIG. 1. Traces of magnetoresistivity in the low-field region showing the shift of the SdH oscillations with pressure. The ambient pressure data is for a different sample taken from the same batch of kish graphite as the one used for the high-pressure experiment.

sample deterioration is not uncommon in high-pressure experiments, although its detailed mechanism is not always well understood. Based on point (vii) given above, the mobility decrease in the present case may be attributed to introduction of stacking faults (which are known to occur extremely easily in graphite) by stress exerted on the sample during pressurization and freezing of the pressure medium.

Limited machine time of the hybrid magnet allowed us to carry out measurements on only one sample at two different pressures. Based on our past observation of the consistency of $T_c(B)$ among pure samples as described in (i) above, we are convinced that the result obtained for the selected sample represents the intrinsic property of the whole batch of type-*A* samples. Still, the mobility deterioration that occurs upon pressurization creates particular difficulties for the present experiment, because it could reduce the *amplitude* of the high-field resistivity below the observability limit in the noisy experimental environment of the hybrid magnet. The best candidate for the high-magnetic-field experiments was selected by the following method among several samples using two sets of pressure cells. We compared the SdH amplitudes of two samples after pressurizing them to ~ 5 kbar (~ 7 kbar at room temperature), and kept the better of the two. Then we mounted a new sample in the other pressure cell and made the next comparison. We thus selected the best sample and kept it under that applied pressure for the hybrid magnet run. In this way, we minimized the harmful pressure and temperature cyclings for the best candidate in order not to damage its carrier mobility. After the high-magnetic-field experiment with $P=5$ kbar was completed, the pressure was increased to 10.5 kbar.

Figure 2 shows a few traces of the magnetoresistance in

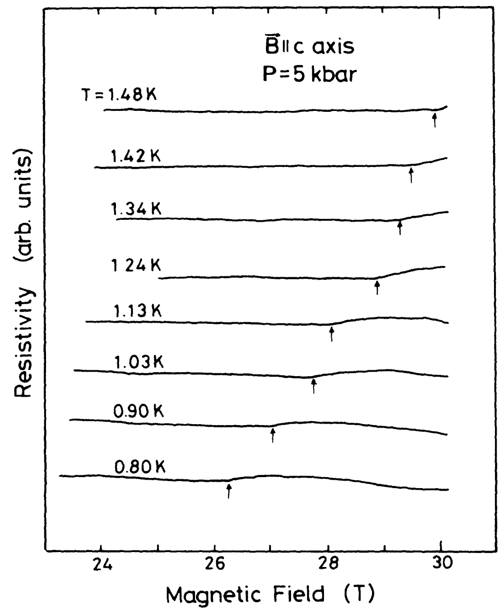

FIG. 2. Traces of magnetoresistivity in the high-field region showing the anomaly (indicated by arrows) associated with the phase transition. The magnitude of the resistivity anomaly is about 1% of the total resistivity.

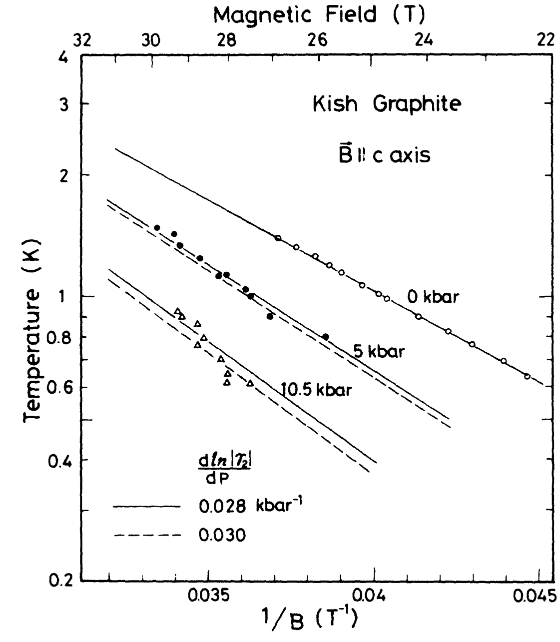

FIG. 3. Onset points of the resistivity anomaly at three different pressures plotted on a $\ln T$ vs $1/B$ scale. The lines represent the pressure dependence of the phase boundary according to Eq. (4). The solid and dashed lines correspond to $(d\ln|\gamma_2|)/dP = 0.028$ and 0.030 kbar^{-1}, respectively.

the high-field region where the onsets of resistivity anomaly are marked by arrows. The data shown in this figure are for different temperatures and at 5 kbar. The magnitude of the resistivity anomaly is much smaller than those typically observed at ambient pressure (see, for example, Fig. 1 of Ref. 4). As the temperature is lowered, the magnitude of anomaly generally diminishes, for a reason that is not well understood. For the sample in Fig. 2, the resistivity anomaly is not well resolved for temperatures below ~ 0.9 K at this pressure.

The onset points of the resistivity anomaly are plotted in Fig. 3 for $P = 5$ and 10.5 kbar together with those for ambient pressure, obtained in earlier studies.[1,3,4] It is clearly seen that the transition temperature at a given magnetic field decreases with pressure. In what follows, we attempt a simple phenomenological analysis for the pressure dependence of $T_c(B)$ based on the BCS-like formulas: Eqs. (1) and (2).

The band structure of graphite near the Fermi level is appropriately described by the Slonczewski-Weiss-McClure parameters:[7,8] $\gamma_0, \gamma_1, \gamma_2, \ldots \gamma_5$, and Δ. The pressure dependence of these parameters has been studied by several workers using such techniques as optical spectroscopy[9,10] and magneto-oscillatory and cyclotron resonance measurements.[11,12] Because each experimentally measured quantity generally depends on more than one band parameter, and because the number of quantities that have been measured under pressure is usually smaller than the number of band parameters, it is necessary to assume a certain number of additional relations in order to deduce the pressure coefficients of the band parameters.[13,14] Among the seven band parameters, the most important for the present problem is γ_2, where $2|\gamma_2|$ is the width of the π band. The reported values for γ_2 lie between -0.0186 and -0.0207 eV. The application of pressure increases γ_2. In the present pressure range, the increase is linear in pressure:

$$\gamma_2(P) = (1+\alpha P)\gamma_2(0) . \tag{3}$$

The values for the logarithmic pressure coefficient $\alpha \equiv (d\ln|\gamma_2|)/dP$ lie between 0.024 and 0.043 kbar^{-1}.[13,14]

Figure 4 schematically shows the lowest electron and hole Landau subbands and their density of states in the magnetic field range of present interest. The dashed and

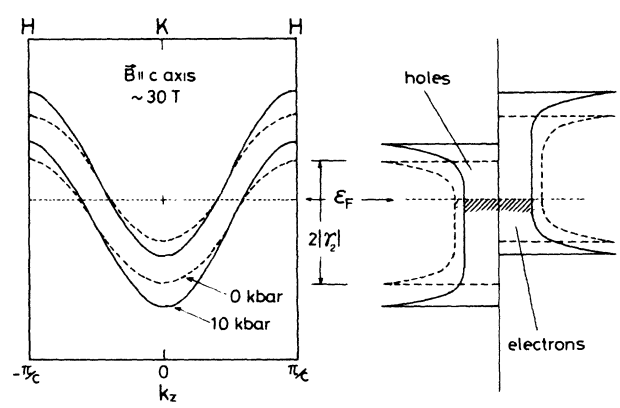

FIG. 4. Schematic diagram of the dispersion along the k_z axis of the lowest electron and hole Landau subbands at $B \sim 30$ T. The dashed curves are for the ambient pressure, and the solid curves correspond to $P \sim 10$ kbar. The figure on the right-hand side shows the corresponding density-of-states profiles.

solid curves correspond to the situations at $P=0$ and 10 kbar, respectively. We now consider the pressure dependence of $T_c(B)$ expected from the functional form of Eq. (2). The preexponential factor is proportional to ε_F and hence to the π-band width $2|\gamma_2|$. The density of states at the Fermi level in the high-field quantum limit is given by a product of the Landau degeneracy factor and the one-dimensional density of state of the lowest-Landau subband. The latter factor is inversely proportional to the π-band width. Therefore, if we tentatively neglect a possible pressure dependence of the pairing interaction V and assume that the sole pressure dependence comes through γ_2, we obtain the following expression for the pressure dependence of $T_c(B)$:

$$T_c(B,P)=T^*(1+\alpha P)\exp[-B^*(1+\alpha P)/B]\,, \quad (4)$$

where T^* and B^* are the same as Eq. (1).

The solid and dashed lines in Fig. 3 represent the phase boundaries as they are shifted by pressure according to Eq. (4). For the solid lines, the pressure coefficient was chosen as $\alpha=0.028$, while for the dashed lines $\alpha=0.030$. It is seen that good agreement can be obtained for a reasonable value of α. Considering the simplicity of the model used here, which only takes into account the pressure-induced change in γ_2, we do not expect it to explain the full details of the pressure effect. In fact, looking at Fig. 3 more closely, especially for the 10.5-kbar data, the slope of the experimental points appears steeper than the calculated curves, and there may also be some deviation from the straight-line behavior. It is possible that pressure dependences of other quantities such as the interelectron-interaction potential responsible for the pairing and the basal-plane effective mass play a role. Nonetheless, it is rather remarkable that the observed pressure effect can be accounted for to a good first approximation by simply considering the pressure-induced change in γ_2. This agreement also gives additional support for the analogy with the BCS-like instability of the Fermi surface we have invoked for the electronic phase transition observed in graphite under high magnetic fields.

In conclusion, we have observed that the application of high pressure causes a substantial shift of the phase boundary for the high-magnetic-field electronic phase transition in graphite. The pressure dependence of $T_c(B)$ is basically understood by considering the effect of the pressure-induced increase of the π-band width within the framework of the BCS-like expression, Eq. (2).

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