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NEGATIVE MAGNETORESISTANCE AND ANDERSON LOCALIZATION IN BLACK PHOSPHORUS SINGLE CRYSTALS

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The electrical resistance of black phosphorus single crystals at low temperatures was analyzed as functions of temperature and magnetic field. Logarithmic dependence of the conductivity on both variables was found. This fact, together with the negative magnetoresistance observed at 4.2 K, suggests the existence of the two dimensional Anderson localization of valence-band holes in black phosphorus single crystals at low temperatures.

Since 1981, black phosphorus(P) has been extensively studied as a narrow gap (0.34 eV) p-type semiconductor of layered structure. Several experiments have been done on optical[1-5)] and electrical[1,6)] properties, and the energy band calculation has also been reported.[7)] However, as there have been few studies on black P at low temperatures, it is of importance to study the low-temperature properties of black P, especially in relation to the recent experiments on anomalous superconductivity of metallic black P by Kawamura et al.[8)] In this letter we report the transport properties of semiconducting black P crystals at low temperatures under atmospheric pressure.

Black P single crystals were prepared from a bismuth solution.[1)] Black P crystallizes in orthorhombic form under atmospheric pressure and takes an infinite puckered layer structure in the ac plane.[9)] The temperature and magnetic field dependence of the electrical resistance along the a-axis was measured below 10 K with the four-probe method.

Figure 1 shows the plot of the conductance, G, along the a-axis versus T on a logarithmic scale. The temperature dependence of G in this figure is satisfactorily described by

$$G = G_0 + A\ln T,$$

where A is $9.4 \times 10^{-5}\ \Omega^{-1}$. Maruyama et al. observed the negative magnetoresistance in black P single crystals at 4.2 K.$^{1)}$ We measured the magnetoconductance, $\Delta G(H) = G(H) - G(0)$, under the field, H, up to 2.4 T at 4.2 K as shown in fig. 2. The magnetic field was parallel to the b-axis. The magnetic field dependence of $\Delta G(H)$ is well described by

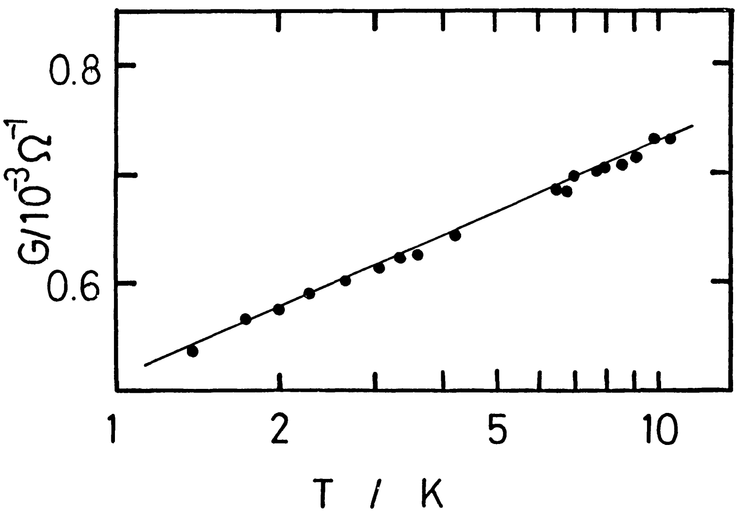

Fig. 1. The temperature dependence of the conductance, G, along the a-axis.

$$\Delta G(H) = G_H + B\ln H,$$

where B is $2.5 \times 10^{-5}\ \Omega^{-1}$. Note that $B > 0$ means the negative magnetoresistance. Such logarithmic dependence of G on T and H strongly suggests the two dimensional Anderson localization as will be discussed below. This interpretation is further supported by the observation of the anisotropy in magnetoresistance with respect to the direction of magnetic field.$^{1)}$

Resistivity normally increases under external magnetic field, since Lorentz force disturbs the acceleration of electrons along the electric field. Therefore, the negative magnetoresistance observed in heavily doped semiconductors had not been explained for three decades. In recent years, however, it has been theoretically interpreted by the localization of charge carriers in random potentials.$^{10)}$ In two dimensional electron systems with random potentials all the wave functions are localized, and application of magnetic field suppresses the localization of the wave functions, resulting in the decrease of resistivity. The theory predicts that ln T and ln H terms are involved in the sheet conductivity, $\sigma_\Box$, in two dimensional systems:

$$\delta\sigma_\Box(H) = (e^2/2\pi^2\hbar)\ \ln H$$

$$\delta\sigma_\Box(T) = (e^2/2\pi^2\hbar)\ \ln T \qquad (e^2/2\pi^2\hbar = 1.2 \times 10^{-5}\ \Omega^{-1}),$$

where the coefficients of ln H and ln T terms do not depend on systems.

On the other hand, in three dimensional systems $\delta\sigma$ is proportional to $\sqrt{T}$ or $\sqrt{H}$. We analyzed the data also in terms of such square-root formulae, but found very poor fitting. This means that the electron system in our black P crystal should be regarded as two dimensional rather than three dimensional. The coefficients of ln H and ln T of the sheet conductivity are calculated to be $1.1 \times 10^{-4}\ \Omega^{-1}$ and $4.1 \times 10^{-4}\ \Omega^{-1}$, respectively. (The sample was 110 μm in length, and 25 μm in width.) These values are 9 - 34 times as large as the value expected from the theory. Main reason for the discrepancy is the uncertainty in the current distribution perpendicular to the ac plane in the black P sample which has large anisotropy in σ (a:b:c = $0.2:10^{-3}:1$).11)

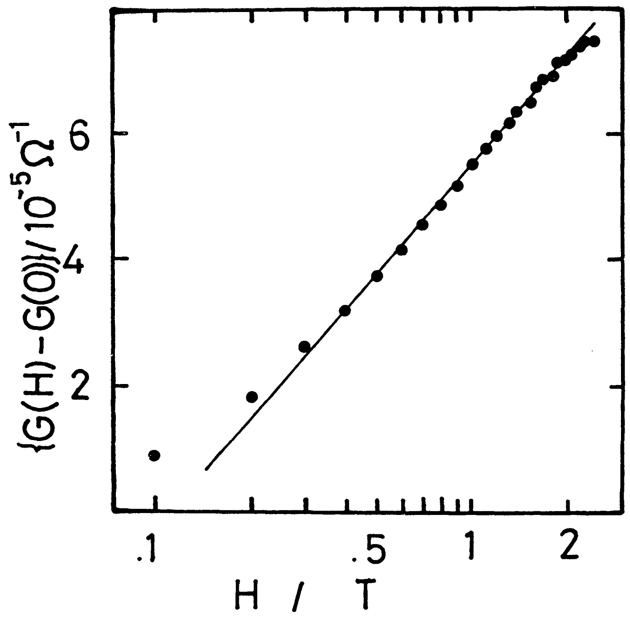

Fig. 2. The magnetic field dependence of the magnetoconductance, ΔG(H)=G(H)-G(0) at 4.2 K. The magnetic field was parallel to the b-axis.

Maruyama11) and Shirotani12) reported large anisotropy of the conductivity tensor. On the other hand, Akahama et al. reported rather isotropic conductivity in the samples prepared under high pressure.6) From the layered crystal structure of black P we naively expect the two dimensional nature of electronic properties, and our present data confirms it. We think that the quality of a crystal is very crucial to the electrical properties, such as conductivity and the dimensionality of the localization.

In conclusion, the present results show two dimensional Anderson localization of valence-band holes in black P at low temperatures. There still remains the problem on the discrepancy between the theoretical and experimental coefficients of ln T and ln H. More detailed study is now in progress and will be published elsewhere.

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References

1) Y. Maruyama, S. Suzuki, K. Kobayashi, and S. Tanuma, Physica, 105B, 99 (1981).
2) S. Sugai, T. Ueta, and K. Murase, J. Phys. Soc. Jpn., 50, 3356 (1981).
3) M. Ikezawa, Y. Kondo, and I. Shirotani, J. Phys. Soc. Jpn., 52, 1505 (1983).
4) Y. Harada, K. Murano, I. Shirotani, T. Takahashi, and Y. Maruyama, Solid State Commun., 44, 877 (1982).
5) M. Taniguchi, S. Suga, M. Seki, A. Mikuni, S. Asaoka, H. Kanzaki, Y. Akahama, S. Endo, and S. Narita, Technical Report of ISSP, Ser. A, No.1449 (1984).
6) Y. Akahama, S. Endo, and S. Narita, J. Phys. Soc. Jpn., 52, 2148 (1983).
7) H. Asahina, K. Shindo, and A. Morita, J. Phys. Soc. Jpn., 51, 1193 (1982).
8) H. Kawamura, I. Shirotani, and K. Tachikawa, Solid State Commun., 49, 879 (1984).
9) J. C. Jamieson, Science, 139, 1291 (1963).
10) E. Abrahams, P. W. Anderson, D. C. Licciardello, and T. V. Ramakrishnan, Phys. Rev. Lett., 42, 673 (1979).
11) Y. Maruyama, Kagaku To Kogyo, 37, 214 (1984).
12) I. Shirotani, Mol. Cryst. Liq. Cryst., 86, 1943 (1982).

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