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Electronic Properties of Black Phosphorus Single Crystals and Intercalation Compounds

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Actual procedures for the preparation of black phosphorus single crystals by a bismuth flux method have been explored and the details are described. The anisotropy and the temperature dependence of the electrical conductivity and the Raman scattering spectra of the crystals obtained by the above-method have been measured. The reflection spectra of crystals which were prepared by a high pressure technique have also been observed and compared with the calculated data. Several preliminary attempts for synthesizing black phosphorus intercalation compounds have been carried out for the first time. Evidence for the intercalation by an X-ray analysis is presented.

Some interesting properties of black phosphorus (BP) single crystals have been extensively explored after the recent success of single-crystal preparation.[1,2] During the first stage of the present study, we started to prepare BP single crystals by the bismuth flux method and measured the electrical and optical properties of these crystals.[1] After that, Shirotani succeeded in the preparation of larger BP crystals by the use of the melt-growth technique under high pressure.[2] Narita's group followed and developed the Shirotani's method,[3] and has revealed the fundamental quantities regarding charge-carrier transport (such as Hall mobilities and effective masses) and structural and transport behaviors under the high pressure of a large BP single crystal.[4,5] It is easier to handle a large crystal; thus, the successful preparation of such large crystals has motivated further studies of BP crystals. Large crystals have showed, not only qualitatively but also quantitatively in some cases, similar behaviors to small crystals prepared by the bismuth flux method. However, some details regarding the properties of these two kinds of the crystals, e.g. temperature-dependence details of the electrical conductivities or the crystal qualities, might not necessarily coincide with each other.

BP is one modification of the phosphorus polymorphs and the BP phase was discovered by Bridgman under high pressure.[6] Some electrical and optical properties of polycrystalline BP were studied by Keys[7] and Warschauer[8] and the crystal structure was reported by Brown and Rundqvist.[9] It crystallizes in orthorhombic form and takes on an infinite puckered-layer structure in which every layer overlaps the next layer and is shifted by a/2 units (Fig. 1).

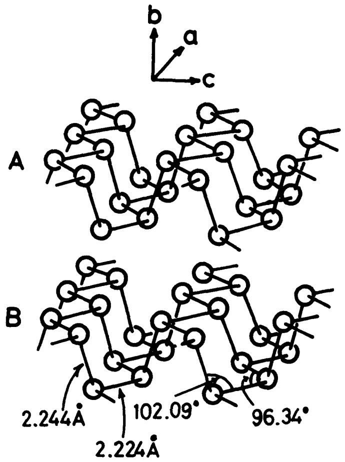

Fig. 1. Layer structure of black phosphorus crystal. B layer is shifted by 1/2 unit along the a axis relative to A layer.

Crystalline BP is known to undergo phase transitions from the orthorhombic form (semiconducting) to the rhombohedral form (semi-metallic) at ≈60 kbar and, finally, to the simple cubic form (metallic) at ≈110 kbar,[10] in which superconductivity (T_c=6 K) was observed.[11,12] Very recently, a more precise measurement of the pressure dependence of electrical properties revealed that a semiconductor-to-semimetal transition occurs at 17 kbar,[13] and T_c for superconduction increases up to 13 K at 300 Kbar for quenched samples.[14]

Moreover, electrical transport properties of BP single crystals, such as the temperature dependence of the conductivities, magnetoresistance,[1] charge-carrier mobilities by Hall effect,[4] effective masses by cyclotron resonance method,[5] and 2-dimensional Anderson localization at low temperature[15] have been reported. The elaborate theoretical calculations for the electron band structure,[16] and the frequencies and the dispersion relations of the phonon modes[17] of BP have been carried out by Morita et al.

In this paper, we report on the actual procedures for single-crystal preparation by the bismuth flux method, the anisotropic properties in the electrical conductivities, and the optical reflection spectra and microscope Raman spectra of BP single crystals. Preliminary results of attempts to synthesize the intercalation compounds of BP are also described.

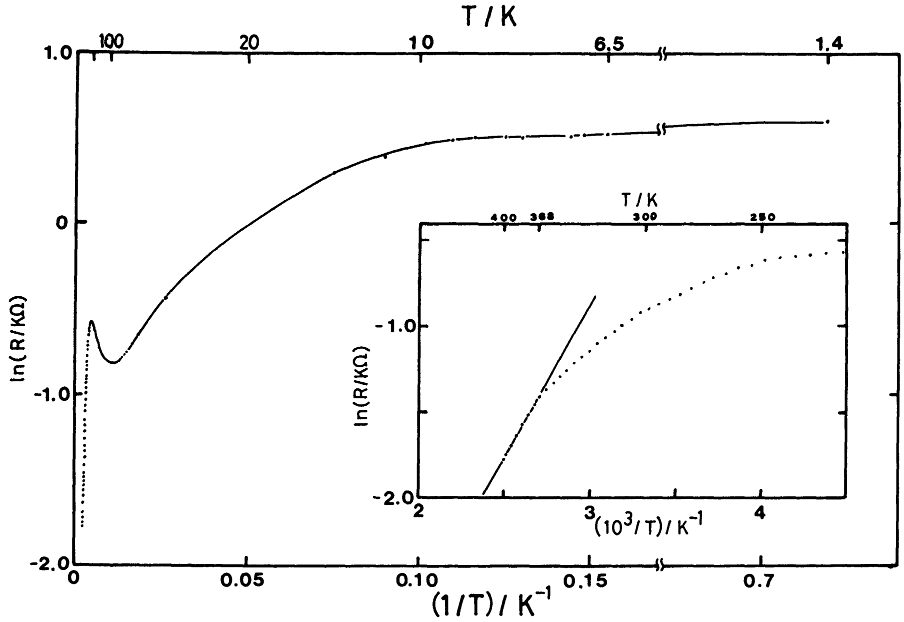

Fig. 2. Temperature dependence of the electrical resistance (a-direction) of a black phosphorus single crystal prepared by the bismuth flux method.

Experimental

In the course of this experiment, we used two kinds of single crystals; one was grown in melted bismuth[1] and the other was melt-grown under high pressure.[2] The former was obtained in rather thin rod or needle form, $10\times0.2\times0.05\ \text{mm}^3$ and the latter was in a block form, the size of which was determined by the size of the high-pressure cell. The typical size of the latter single crystal was $5\times5\times0.5\ \text{mm}^3$.

The details of the preparation procedure from bismuth solution are as follows : Amorphous or polycrystalline BP, 0.25 g, obtained by the conversion of red phosphorus under high pressure, was mixed with high-purity bismuth (37 g) in a Pyrex tube filled with 1/2 atm helium gas (atomic ratio of Bi to P is $\approx$22). It was kept at 400 °C for 44 h and then gradually cooled to room temperature at the rate of 0.2 °C min^{-1}. The crystals, obtained as a residue after dissolving the bismuth matrix with 30% nitric acid, were generally needle shaped with the needle axis coincident with the crystallographic a-axis. Even in melt-grown crystals, such a crystal habit is often recognizable on the cleaved ac-plane. One can determine the a- and c-axes of a crystal by carefully observing the fine stripes near the edges of the surface. Purified white phosphorus was also used as a starting material instead of BP powder.

We measured the anisotropy of the electrical conductivities for the thin rod crystals. Silver paste was used as electrodes. For the measurement along the a-axis only a four-probe method could be applied. The anisotropy of the melt-grown crystals has already been reported by Shirotani,[2] and Akahama et al.[4]

Polarized reflection spectra of a melt-grown crystal were observed in the 400—2000 nm wavelength region using an OLYMPUS MMSP microscope reflectophotometer. Polarized Raman spectra were also observed using the High-Resolution Microscope Raman Scattering Measuring System of Prof. Tominaga's laboratory in Ochanomizu University. The 5145 Å line of an Ar^+ laser (NEC GLG 3200) was used as the exciting light.

As an attempt to chemically modify the BP, intercalations with cesium, lithium, and iodine were tried. In the case of cesium or iodine, a vapor-phase reaction was carried out. The electrolytic method was employed for lithium intercalation. The cathode and anode were a BP crystal and lithium metal, respectively, and a 0.2 mol l^{-1} THF solution of $LiClO_4$ was used for the electrolyte. Electrolysis was carried out under an argon atmosphere in a dry box. Intercalated specimens were directly transferred to a measurement vessel (a cryostat) without being exposed to air.

Thin-rod crystals which were reacted with cesium vapor were analyzed using an X-ray diffraction oscillation camera method. Weak but definitely new spots were recognized and ascribed to a change of the lattice constant for the interlayer direction, b.

Results and Discussion

1. Electrical Conduction. The temperature dependence of the electrical resistance in the a-direction is shown in Fig. 2. The overall behavior of the curve was just like a typical impurity semiconductor[18] and the intrinsic band gap was estimated to be 0.34 eV from the slope of plots of ln R vs. $1/T$ in the high-temperature region (see the inset of Fig. 2).

The anisotropy of electrical conductivities at room temperature is shown in Table 1 for our thin-rod crystals and large melt-grown crystals under high pressure. The large anisotropy between the a- and b-directions (which was observed for our crystals) could not be found for the crystals of Narita's group. They have measured Hall mobilities and effective masses (Table 1). Morita et al. recently showed that the anomalous relationships in the anisotropies of the mobilities and the effective masses along the a- and b-axes, which

Table 1. Anisotropy in the Electrical Properties (Holes)

Crystal axes	a	b	c
Conductivities/S cm^{-1}	0.2×0.1	10^{-3}—10^{-2}	1×0.5[a]
	0.7	0.4	2.5[b]
	10	10^{-3}—10^{-2}	1[c]
Hall mobilities/cm^2 v^{-1} s^{-1} (200K)	1300	540	3300[b]
Relative effective masses, m/m_0 (observed)	0.66	0.28	0.075[d]
Relative effective masses, m/m_0 (calculated)	0.81	0.36	0.09[e]

a) This study. b) Ref. 4. c) Ref. 2. d) Ref. 5. e) Ref. 16.

had not been well understood, could be explained by a theoretical calculation involving an electron-phonon interaction in the regime of a deformation potential model.[19] However, the large difference in the conductivities along the b axis (interlayer direction, see Fig. 1) between our crystals and the crystals of Narita's group has not yet been elucidated. The possible interpretations are defect effects, interlayer misfits, difficulties to obtain proper electrode contacts, and so on. Anyhow, the reliability of the observed values in the interlayer direction may be lower than other directions because of the inapplicability of the four-probe method to measurements in this direction. The needle-like crystals prepared by the bismuth flux method has a two-dimensional Anderson localization character at low temperature, as reported by Iwasaki et al.[15] On the contrary, the temperature dependence of the a-axis conductivity of a Narita crystal does not fit a logarithmic temperature dependence in the corresponding temperature region (below 10 K) which should be observed in the two-dimensional Anderson localization regime.

2. **Reflection Spectra.** Polarized reflection spectra were measured for a cleaved flake of a melt-grown crystal. The observed results are shown in Fig. 3 and are compared with the calculated curves by Asahina and Morita.[20] The absolute values of the reflectances do not coincide with each other, but the overall qualitative features correspond well, except for the low-energy region of the a-polarized reflectance. According to Asahina and Morita,[20] an optical transition around this region may occur through the effect of an interlayer interaction. Thus, the rising reflectance in this region might be caused by a phonon-assisted indirect transition. We measured the temperature dependence of the reflectance down to 40 K and revealed that an enhancement with temperature is more significant in the a-polarized spectra than in the c-polarized spectra (Fig. 4).

3. **Raman Spectra.** A microscope Raman-scattering technique was applied for the thin-rod crystals in order to detect Raman-active lattice phonons of BP. The obtained results are almost coincident with those reported by Sugai et al.[21] The 442 cm^{-1} band was assigned to the B_{2g} mode by Sugai et al,[21] however, recent calculations have shown that there could be two closely located bands, 439 and 441 cm^{-1}. They should be assigned to B_{2g} and B_{3g}, respectively.[17] These two bands could not be separated in our experiment since the microscope optical path reduced the polarization of the scattered light. The origin of the lower band (below 100 cm^{-1}) has not yet been determined.

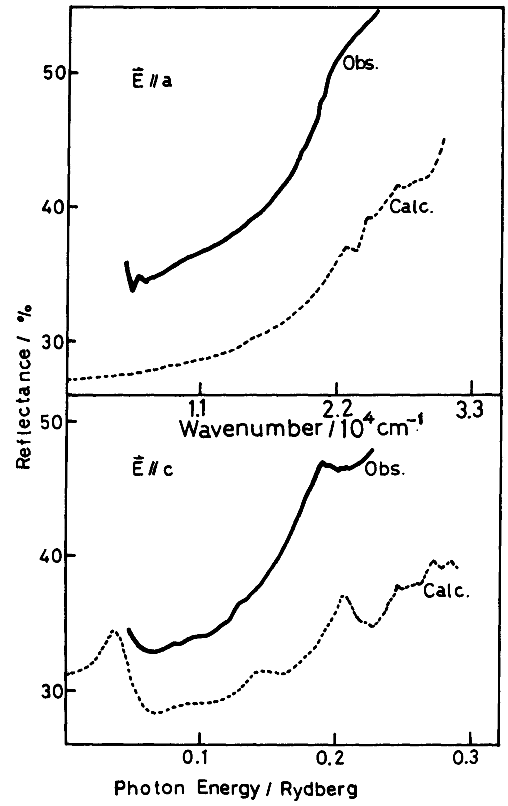

Fig. 3. Polarized reflectances of the ac plane of a black phosphorus single crystal.

4. **Intercalation Compounds.** A single crystal obtained by the bismuth flux method was set in a very thin glass capillary and fully exposed to a cesium vapor at 150 °C for 14 d. In the photographs taken by an X-ray diffraction oscillation camera, the weak spots which correspond neither to BP nor cesium metal were

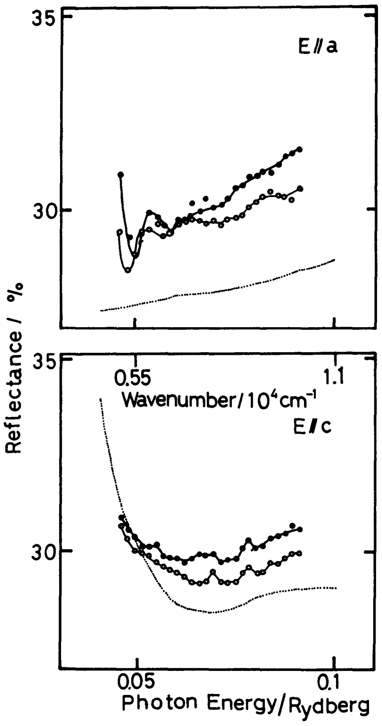

Fig. 4. Temperature dependence of the polarized reflectances.
●: At room temperature, ○: at 40 K, ·····: calculated spectra.

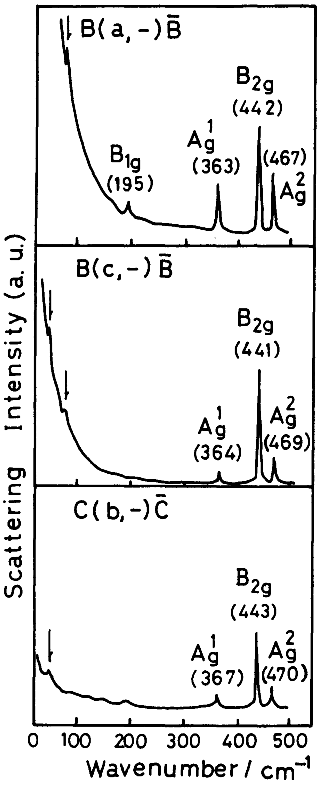

Fig. 5. Raman spectra of a black phosphorus single crystal.

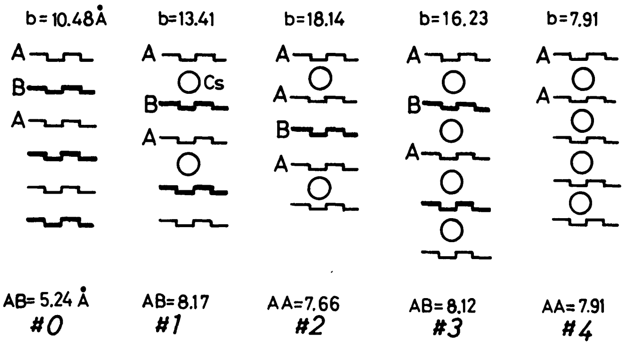

Fig. 6. Possible intercalated structures of various stages for Cs-black phosphorus.

recognized. The cesium vapor was introduced mostly through the cross section of one end of the crystal. Cesium diffusion was so slow that the other end of the crystal was still unchanged after a long exposure to cesium vapor (until the front end changed to an amorphous structure by the complete reaction). Successive X-ray analyses of the crystal (from one end to the other) revealed corresponding layer structures (illustrated in Fig. 6).

The alternately piled up structure (AB type) of a genuine BP crystal (#0) is transformed to a simple overlap structure (AA type) by the highest degree introduction of cesium atoms (or ions) (#4) similar to the first-stage structure (AA type) of graphite intercalation compounds. Other possible structures are also shown in this figure. In the next rank of an intercalation (#3), an AB-type piling is retained, even after a full intercalation of cesium. The interlayer spacing is a little larger than the AA type. In this experiment, four different b-lattice constants were identified in one piece of crystal together with the original b-axis length of a BP crystal.

Further investigations regarding homogeneous intercalation are now being undertaken. The effect of a cesium intercalation on the electrical conductivity of BP was also examined. The best reaction conditions have not yet been established for a cesium intercalation; therefore, we only present typical examples in Fig. 7. The reaction proceeded under the homogeneous heating of a sample tube in which cesium metal and a BP crystal were present. In the case of Fig. 7 (a), the reaction started at the upper-right (point A). With a raising temperature, the resistance decreased remarkably. It should be noted that both the effect of the reaction and the intrinsic change in the BP resistance due to heating are involved in this process.

On the other hand, the process from B to C corresponds to the intrinsic temperature dependence of the resistance of the cesium-intercalated BP crystal. The sample resistance showed almost no change within this temperature range (C–B). This means that this compound has almost a metallic character. However, only two samples showed this type behavior during several attempts. Another example is shown in Fig. 7 (b). In this case, the net change due to a cesium reaction was rather small. The conditions for obtaining a

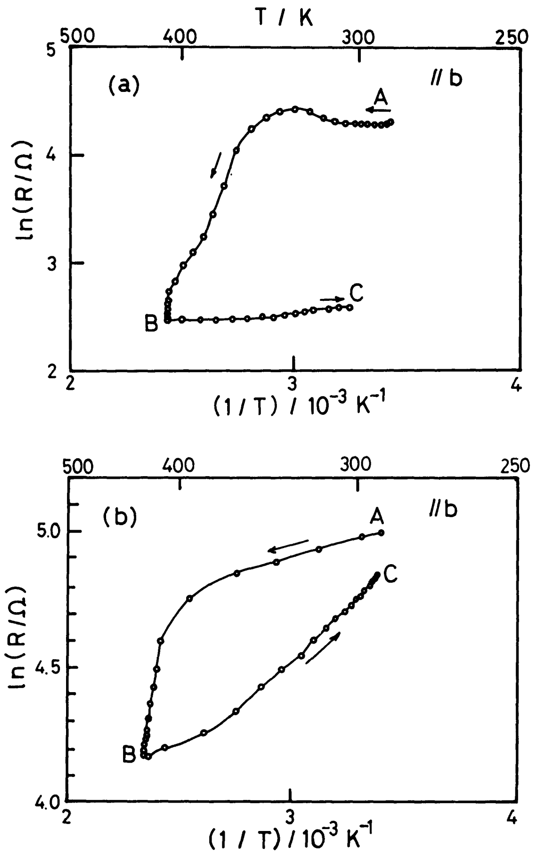

Fig. 7. Temperature dependence of ln(R/Ω) of Cs-black phosphorus.

reproducible result are now being pursued.

To introduce lithium into BP, we empolyed two kinds of electrolytic methods. In the first method, a hexane solution of butyllithium was used as the electrolyte solution; the electrodes were a BP single crystal and a platinum plate. The second type cell consisted of a BP crystal and a lithium metal rod for the electrodes and a $LiClO_4$-THF solution for the electrolyte. In both cases, a swelling of the crystal was observed. The resistances decreased at first to 80—90% and then increased to the values that were higher than the original ones. The latter effect may be due to the partial breakdown of the crystal or the contacts between the crystal and the lead wires. A further investigation is also required to establish the intercalation conditions for the case of lithium. We have also tried to introduce iodine, pyridine, or ammonia into BP. About 20% decreases in the resistance were observed in these cases. Further study is going on, especially for an iodine intercalation.

In summary, we have prepared black phosphorus single crystals from a black or white phosphorus bismuth solution, and have observed electrical and optical properties of these crystals. We have also used crystals prepared under high pressure. We have tried to synthesize novel intercalation compounds between black phosphorus and cesium, lithium, iodine, pyridine, or ammonia. Homogeneous and stable intercalation compounds have not yet been obtained, but evidence for intercalation has been acquired by an X-ray diffraction method. Some increases in the electrical conductivities and the their different temperature dependecies in these intercalation compounds have been observed. Further investigation regarding the characterization of the intercalation compounds of black phosphorus and measurements of their physical properties are now under way.

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