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Pressure-Induced Phase Transition and Superconductivity in Phosphorus

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The pressure-induced superconductivity in black phosphorus was measured along five different paths in a P–T phase diagram. The effect of the pressure on the superconducting transition temperature(T_c) depends strongly on the path in the P–T phase diagram. The results for several paths were compared with those obtained by Wittig et al. If black phosphorus was pressurized at the temperature of liquid helium, the T_c went up to 10.7 K and the onset temperature of transition was beyond 13 K at very high pressures. When red phosphorus was used as the starting material and pressurized at 4.2 K, T_c steeply increased with an increase in the pressure; it increased up to 13 K, while the onset temperature of transition reached 18 K at 30 GPa. This is the highest superconducting transition temperature among the elements. Pressure-induced phase transitions have also been studied by the X-ray techniques using synchrotron radiation at the temperature of liquid nitrogen. The pressure of the transition at 77 K was higher than that at room temperature. Two or three phases coexisted in a wide pressure (6—14 GPa) at 77 K.

The anomalous superconductivities of black phosphorus (black P) have been investigated at low temperatures and high pressures.[1–4] The superconducting transition temperature (T_c) of black P reaches to about 11 K under very high pressures. The T_c vs. pressure curve depends on the path in the P–T phase diagram.[1,2] Wittig et al. have found double maxima in the T_c–P curve.[3] Yokovlev et al. have studied the superconductivity under pressure using a red phosphorus as the starting material.[4]

Black P is transformed from an orthorhombic structure to a rhombohedral structure, and then further to a simple cubic form, with the increase in the pressure at room temperature.[5] The transition from the orthorhombic form to the rhombohedral one is very slow, and these phases coexist over a wide pressure range. The simple cubic form is very stable under pressure and exists at least up to 60 GPa.[6] The mechanism of phase transitions in black P has already been discussed by many authors.[7–12] Iwasaki et al. have determined the P–T phase diagram of black P above room temperature by means of X-ray study with synchrotron radiation.[13] However, the phase diagram has not yet been studied below room temperature. An X-ray beam of synchrotron radiation is quite suitable for high-pressure experiments because of such excellent characteristics as brightness, a small divergence, and a constant energy.[14] By using synchrotron radiation, we have investigated the pressure-induced phase transitions of black P at the temperature of liquid nitrogen.

In this paper we wish to report our results on the pressure-induced superconductivity and phase transitions in black P obtained by the use of new high-pressure apparatuses that can continuously change the pressure at low temperatures.

Experimental

In determining the pressure dependence of T_C by the resistive method, we used the apparatus described in a previous paper.[15] The system consists of a diamond-anvil pressure cell mounted on a booster which is actuated by helium gas. The pressure can continuously be changed at the temperature of liquid helium.

Figure 1 illustrates the sample assembly for the measurement of the resistance. Each diamond anvil was convered by polyvinyl chloride films to a thickness of about 25 µm; these films were used as a pressure medium. Copper electrical leads with a thickness of 10 µm were set between two anvils. The gap width between two electrodes was about 30 µm. This configuration is similar to that is Sakai's method.[16]

A thin rectangular plate of black P was cut from a single crystal in the air and put on the gap between electrodes. The resistance was measured along the *ac* plane of the crystal. The measurement of the resistance under high pressure was carried out along the five different paths depicted in Fig. 2. Path (A1): After the sample was transformed into the simple

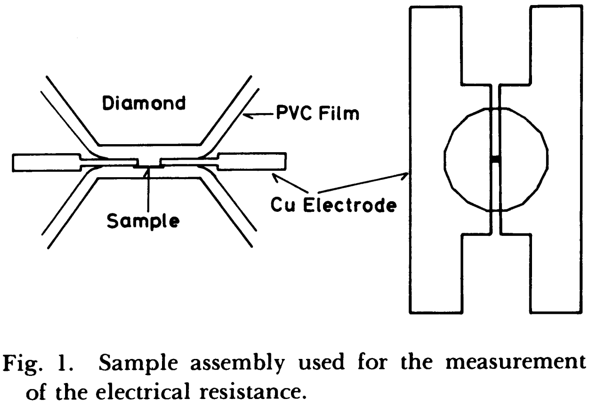

Fig. 1. Sample assembly used for the measurement of the electrical resistance.

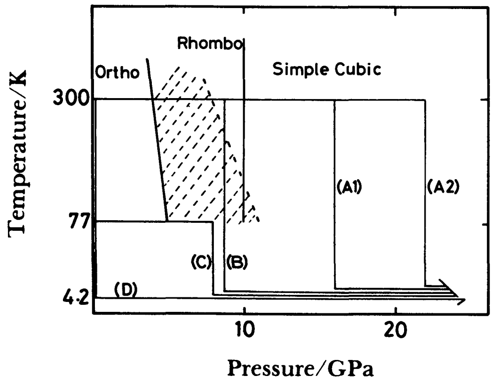

Fig. 2. Schematic phase diagram of black phosphorus: Hatched region shows the pressure range where two or three phases coexist. Five paths along which T_c was measued are also illustrated.

cubic phase by a pressure of 16 GPa at room temperature, the pressure cell was cooled to the temperature of liquid helium, keeping the pressure constant. Then, the pressure was raised further at the temperature of liquid helium. The T_c's were measured at constant pressures. Path (A2): After pressure was applied up to 22 GPa at room temperature, the cell was cooled. Then, the T_c was measured by the same procedure as above. Path (B): Pressure was applied up to 8.7 GPa at room temperature, whereupon the sample was trans formed into the rhombohedral phase. Then, it was cooled to the temperature of liquid helium. Path (C): Pressure was increased to 8 GPa at the temperature of liquid nitrogen. Both orthorhombic and rhombohedral phases coexist under this condition. Then, the cell was cooled to the temperature of liquid helium. Path (D): After the sample had been cooled to the temperature of liquid helium at almost the ambient pressure, pressure was applied. The T_c's were measured at constant pressures. The resistance of the high-purity red phosphorus was also measured along this path. The red P was provided by the Mitsubishi Metal Corporation; its purity was over 99.9999%.

The pressure was determined by means of fixed points for the Bi, ZnS, and GaP transitions at room temperature. To estimate the pressure at low temperatures, we adopted the calibration curve between the generated pressure and the applied force, as determined at room temperature.

A new diamond-anvil pressure cell was developed for X-ray measurement which makes possible a continuous change in the pressure at low temperatures. The details of the high-pressure system have been reported elsewhere.[17] The X-ray measurement at high pressures and 77 K was carried out using a bending-magnet beam line at the Photon Factory (Synchrotron Radiation Laboratory) in Tsukuba. An energy-dispersive X-ray diffraction system was adopted in this experiment. The diffraction patterns of black P and NaCl were recorded at $2\theta=21°$. The diffraction lines of NaCl were used to determine the pressure value according to Decker's scale.

Single crystals of black P were grown at about 1100 °C and at 1 GPa using a wedge-type cubic anvil high-pressure apparatus.[18]

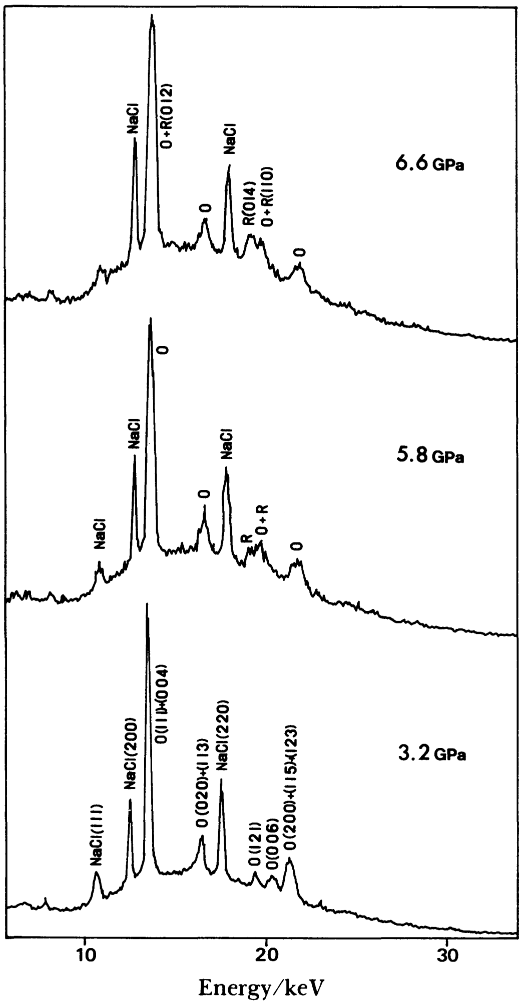

Fig. 3. Energy dispersive X-ray diffraction profiles of black phosphorus in the pressure range 0—7 GPa at 77 K, O: orthorhombic, R: rhombohedral, C: simple cubic.

Results and Discussion

1. Pressure-Induced Phase Transitions at 77 K.

X-Ray diffraction for black P under quasi-hydrostatic conditions has already been studied using a cubic anvil press at room temperature. A cube made of a mixture of boron and epoxy resin is used as the pressure-transmiting medium. The transition from the orthorhombic form to the rhombohedral one begins to occur at about 4.5 GPa. A rate of the transition is very slow. Both phases coexist between 4.5 and 8.1 GPa under quasi-hydrostatic condition.[2] Recently, we have obtained some results on the phase transition in black P under hydrostatic pressure at room temperature by means of an X-ray study with synchrotron radiation.[14] When a 4:1 solution of methanol to ethanol was used as the pressure-transmitting medium, the phase transition occured sharply at around 4.6 GPa, and the pressure range of the coexistence became narrow under hydrostatic conditions. The phase transition from orthorhombic to rhombohedral is very sensitive to the degree of hydrostaticity of the solid and liquid pressure media, even at room temperature.

Figure 3 shows the energy-dispersive X-ray diffraction profiles of black P in the pressure range of 0—7 GPa at 77 K. The pressure was continuously increased at 77 K under quasi-hydrostatic conditions. The (*hkl*) of the diffraction lines for P and NaCl is indicated in Fig. 3. A single-phase pattern of the orthorhombic form was observed at 3.2 GPa. The five peaks in the phase shifted to higher energies with the increase in the pressure. The transition from orthorhombic to rhombohedral started at around 6 GPa. The two diffraction lines of the rhombohedral black P, (014) and (110), were clearly observed at around 6.6 GPa. The diffraction lines of the orthorhombic phase did not disappear at this pressure.

Figure 4 shows energy-dispersive X-ray diffraction patterns in the pressure range of 8—14 GPa at 77 K. The diffraction lines of the orthorhombic and rhombohedral structures were also found to coexist at 8.5 GPa. The transition to the cubic phase appeared at around 10 GPa. The intensity of the (110) line in the simple cubic phase increased with an increase in the pressure. The pattern of the simple cubic became dominant above 13 GPa at 77 K. The coexistence of two or three phases was observed in the pressure range of 6—14 GPa at 77 K under quasi-hydrostatic conditions.

Figure 5 exhibits the X-ray diffraction patterns at 77 K under a decrease in the pressure. As the pressure was reduced to 11.7 GPa at 77 K, the simple cubic phase began to be transformed into the rhombohedral structure, which became dominant at around 10 GPa. The simple cubic rhombohedral transition was nearly reversible with either an increase or a decrease in the pressure at 77 K. The rhombohedral phase was stable on a decrease in the pressure. The diffraction line of the orthorhombic structure could not be observed, even in the very low pressure region, at 77 K.

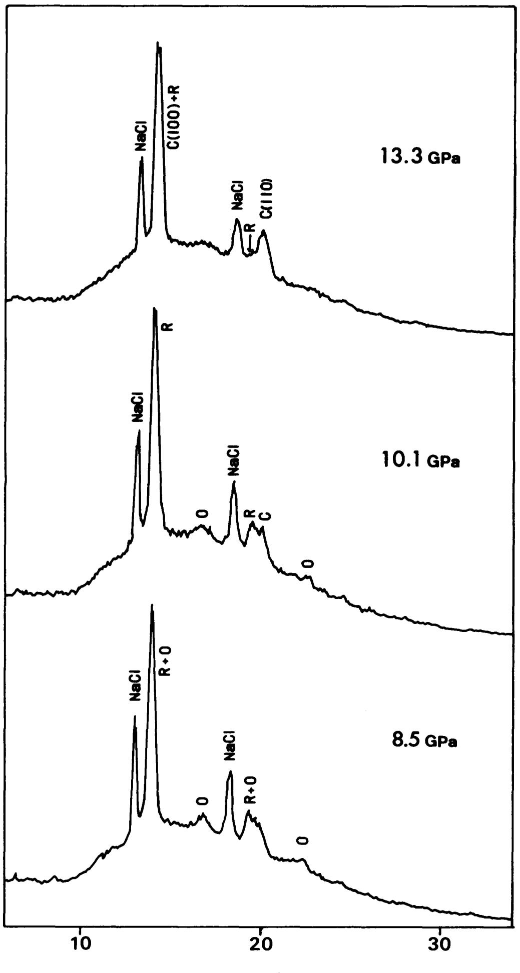

Fig. 4. Energy dispersive X-ray diffraction profiles of black Phosphorus in the pressure range 8—14 GPa at 77 K.

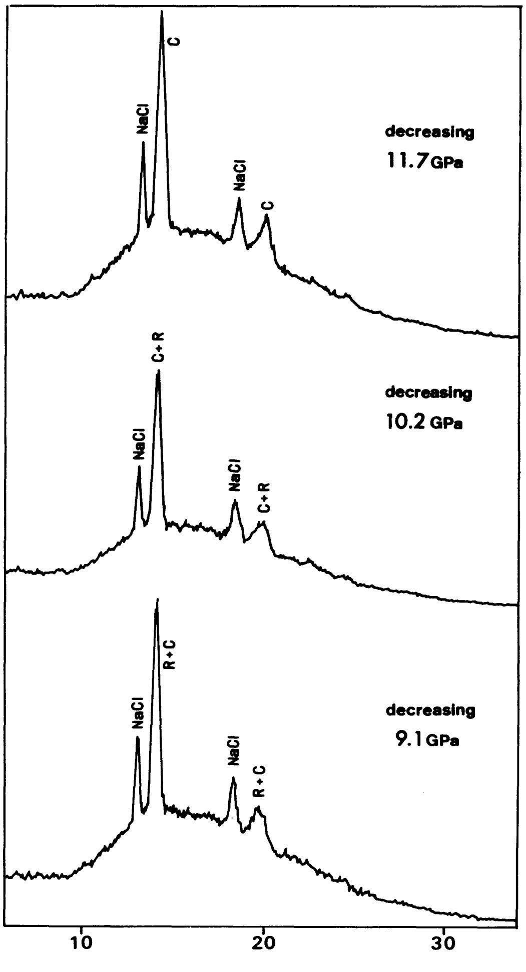

Fig. 5. X-Ray diffraction patterns at 77 K under decreasing pressure.

2. Superconductivity. Figure 6 depicts the pressure-dependence of the T_c along five different paths. Path (A1): Black P shows the metallic behavior at 16 GPa. The ratio of the resistance at room temperature to that just above T_c is about 2.5. The element becomes a superconductor at the T_c of about 6 K at this pressure. The T_c slightly increases with an increase in the pressure. Path (A2): After pressure was raised to 22 GPa at room temperature, the sample was cooled to the temperature of liquid helium at this pressure. The superconductivity of the simple cubic phase was observed at 8.1 K under 22 GPa. The T_c is increased from 5.9 K at 16 GPa in Path (A1) to 8.1 K at 22 GPa in Path (A2) by applying pressure at room temperature. The T_c at 27 GPa was 8.7 K when the pressure was increased from 22 GPa to 27 GPa at 4.2 K. Wittig et al. have reported that the T_c of the simple cubic phase is increased to 10 K at very high pressure.[3] In their experiment, the pressure was always changed at room temperature, and the pressure cell was cooled only for the measurement of T_c. The results for Path (A2) and Wittig's path are shown in Fig. 7. The T_c of the simple cubic phase rapidly increased with the increase in the pressure. On the other hand, the T_c is not sensitive to pressure, as it is pressurized at 4.2 K. The origin of this difference can not be elucidated at present. Path (B): The superconductivity was observed around 5.7 K at 9 GPa. The T_c–P curve along Path (B) is similar to that along Path (A1). Path (C): As is shown in Fig. 4, both orthorhombic and rhombohedral phases coexist at 8 GPa and the temperature of liquid nitrogen. The sample was cooled to the temperature of liquid helium from this condition. The superconductivity was found at around 5.2 K under about 10 GPa. It should be noted that the T_c is higher than that along Path (D) at this pressure. Path (D): The T_c rapidly increased with the increase in the pressure; it went up to 10.7 K, and the onset temperature of the transition was beyond 13 K at very high pressures.

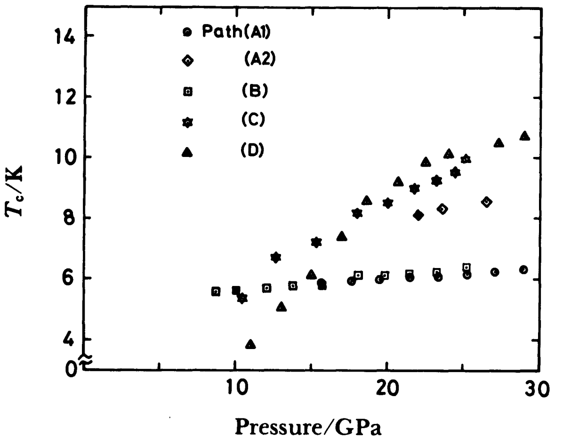

Fig. 6. Pressure dependence of the T_c along five different paths depicted in the Fig. 1.

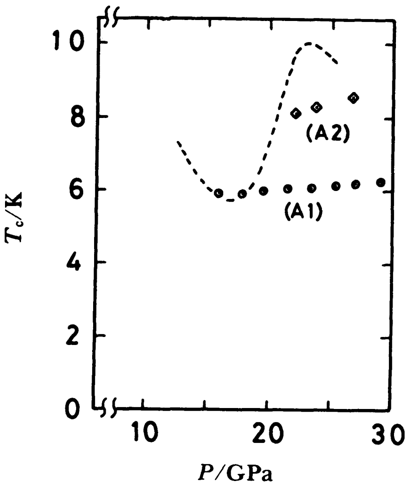

Fig. 7. T_c–P curves of the simple cubic phase: The dashed curve is obtained by Wittig et al.

Figure 8 shows the critical current at 4.2 K and at 29 GPa. The value of dI_c/dT along Path (A1) is about one order of magnitude higher than that along Path (D). The pressure dependence of the residual resistance greatly differs from Path (A1) to Path (D). These results suggest that systems along the paths do not coincide with each other, even under the same pressure.

A red phosphorus (red P) is directly transformed to a black modification at around 8 GPa at room temperature.[20] Yakovlev et al. have studied the superconductivity of black P converted from red P at room temperature and high pressures; they have thus obtained a high superconducting transition temperature.[4] We have also measured the resistance of the high-purity red P along Path (D). The resistance suddenly decreased at about 7 GPa and 4.2 K. The red P had to be converted to the black P under these

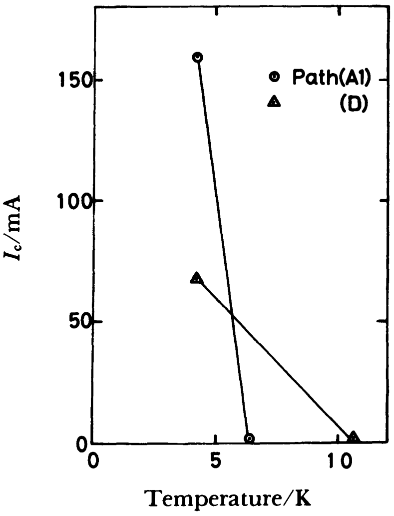

Fig. 8. Critical current of black phosphorus along the path (A1) and (D) at 4.2 K and 29 GPa.

conditions. The superconductivity was observed at around 10 GPa. Figure 9 shows the superconducting transition curves along Path (D). The T_c steeply increased with the increase in the pressure; it went up to 13 K, and the onset temperature of transition reached 18 K at 30 GPa. The T_c somewhat differed for several samples. The transition from superconductivity to the normal state does not readily terminate on the high-temperature side. The width of this transition was 6—7 K. This is very broad compared with the results of black P along Path (D). Figure 10 shows the T_c–P curves along Path (D) when the red P and black P were used as the starting materials. The T_c of the "red P" is much higher than that of black P at very high pressures. Here, the value of the superconducting transition temperature is the highest among the elements. The T_c of the phosphorus along Path (D) is higher than that of the simple cubic phase obtained by Wittig et al.

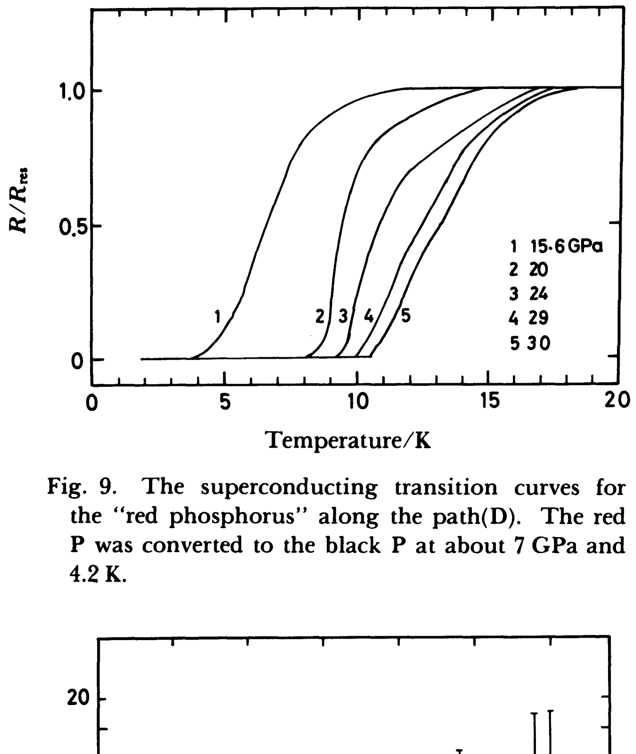

Fig. 9. The superconducting transition curves for the "red phosphorus" along the path(D). The red P was converted to the black P at about 7 GPa and 4.2 K.

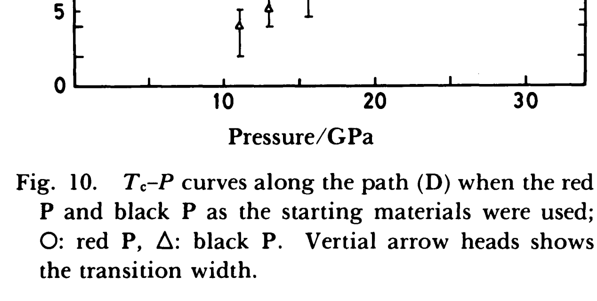

Fig. 10. T_c–P curves along the path (D) when the red P and black P as the starting materials were used; O: red P, Δ: black P. Vertial arrow heads shows the transition width.

The X-ray diffraction of black P with synchrotron radiation has been studied at the temperature of liquid helium and at high pressures. We thus obtained some preliminary results: The orthorhombic form began to be transformed to the rhombohedral form at about 10 GPa; several phases coexist in a wider pressure range.[21)]

These experimental results suggest that the high T_c-superconductivity observed when pressure is applied at 4.2 K is not due to the simple cubic phase only.

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