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The pressure effect on the superconducting transition temperature of black phosphorus

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Abstract

We have measured the pressure effect on the superconducting transition temperature T_c of black phosphorus up to 160 GPa using a superconducting quantum interference device vibrating coil magnetometer. It was found that T_c had a maximum value of about 9.5 K at about 32 GPa, began decreasing with pressure and reached about 4.3 K at about 100 GPa.

1. Introduction

Black phosphorus (abbreviated to black P, hereafter) is the most stable form among many allotropes of phosphorus at ambient conditions. It is a narrow-gap semiconductor with a layered structure and is known to show a very interesting sequence of structural transitions under high pressure. At 4.5 GPa the structure changes from A17 (orthorhombic) to A7 (rhombohedral), and this is accompanied with a semiconductor-to-semimetal transition. This transformation is very sluggish and these two phases coexist over a wide pressure range, the width of which increases with decreasing temperature. The A7 structure transforms to a simple cubic (sc) one at 10 GPa. The transition is rather sharp and the transport properties change to those of metals. The sc structure is stable under high pressure in spite of very loose packing of the atoms and transforms to a simple hexagonal (sh) one at 137 GPa via an intermediate phase (IM). Recently, Akahama *et al* [1] carried out an x-ray diffraction experiment at much higher pressures and found a structural transition to a bcc structure at 262 GPa.

Black P shows superconductivity at pressures above 5 GPa [2]. The pressure dependence of the superconducting transition temperature T_c has been investigated up to about 25 GPa and is known to depend strongly on the path in the pressure–temperature diagram [3]. The experimental data of Wittig *et al* [2] showed two distinct maxima in the $T_c(P)$ curve at about 12 and 23 GPa, while those of Kawamura *et al* [3] showed a monotonic increase in T_c with pressure and obtained a T_c of 13 K at 25 GPa when pressure was continuously increased at helium temperature. Those authors ascribed such a high T_c to the existence of semiconducting phase in the metal phase, but the details of the strong path dependence of $T_c(P)$ have not been clarified yet. Rajagopalan *et al* [4] calculated the band structure of phosphorus in the sc phase

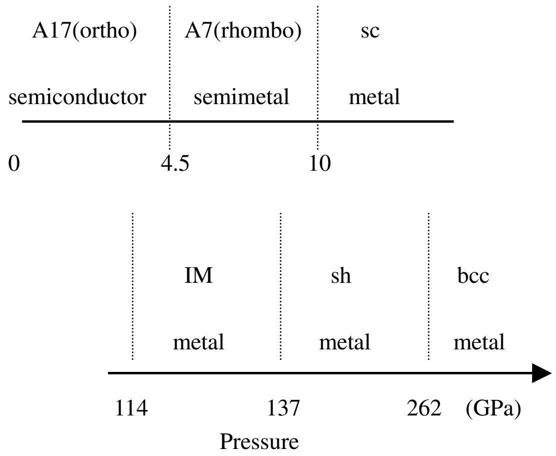

Figure 1. The sequence of transitions in black P under pressure [1].

under high pressure by means of the LMTO method. Using the band structure obtained, they calculated T_c as a function of pressure and found a broad maximum of T_c at around 21 GPa due to the appearance of a new piece of Fermi surface. Considering that experimental data for T_c over a very wide pressure range will give more information about the electronic structure under pressure, we have carried out a dc susceptibility measurement on black P in a DAC up to 160 GPa in order to obtain $T_c(P)$ for pressures covering the stable region of the sc phase and partly the sh phase.

2. Experimental details

We employed a pressure-clamp-type DAC made of hardened 2% Be–Cu alloy and a superconducting quantum interference device (SQUID) vibrating coil magnetometer (VCM) [5] for the susceptibility measurement. The experiments were carried out in three different runs (A, B and C) up to 15, 42 and 160 GPa, respectively. The temperature range was from 1.5 to 40 K and the applied magnetic field was 3 Oe. For run C, a Re gasket was used to achieve high pressure, so the lowest temperature investigated was about 4 K, below which the tail of the diamagnetic signal due to the superconducting transition of the gasket was too large for detecting T_c for the sample. The gasket material was Cu–Be for the other runs. The culet diameter of the diamond anvil was 350, 350 and 150 μm for runs A, B and C, respectively. A small fragment of the single crystal of black P was fixed in the gasket hole without any pressure medium for all runs. The ruby fluorescence technique was employed to determine the pressure up to 100 GPa, above which the pressure was determined from the lattice constant of the Re gasket using the equation of state. Pressure measurements were made at room temperature except in the case of run A, in which the pressure was determined from the shift of T_c for a small chip of Pb located near the sample.

3. Results and discussion

The result for run A is shown in figure 2, in which the superconducting transitions of both black P and Pb are observed. An arrow shows T_c, defined as the middle point of the transition. No corrections, such as subtraction of the background signal, shown in the lowest part of the figure, were made for any of the experimental data. It was found that T_c increased at the rate of 0.58 K GPa^{-1} and the transition width became sharper with increasing pressure. The broad

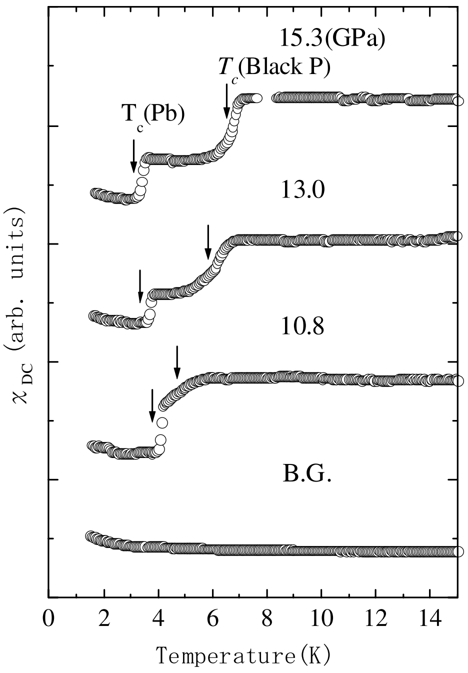

Figure 2. The temperature dependence of the dc susceptibility of black P at various pressures (run A). The sequence is B.G. (background) → 10.8 (GPa) → 13.0 → 15.3.

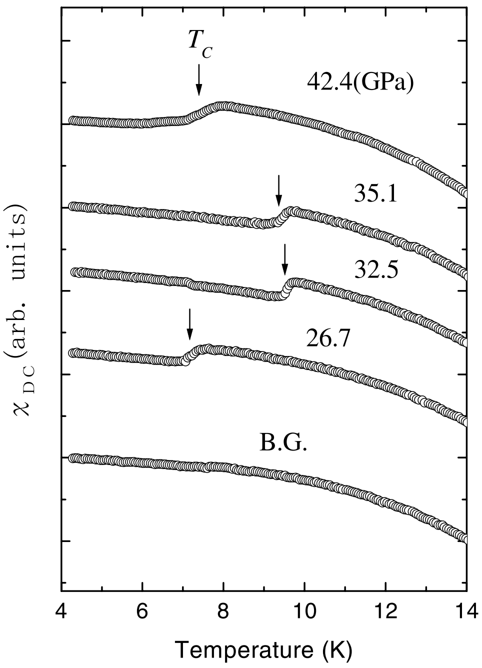

Figure 3. Results for run B. The sequence is B.G. → 26.7 (GPa) → 32.5 → 35.1 → 42.4.

transition of black P observed at 10.8 GPa is not due to the pressure distribution over the sample because the superconducting transition of Pb was sharp and its width did not change so much in this pressure range. The value of 10.8 GPa was very near to that of the phase boundary between semimetal phase and metal phase at room temperature, though the detailed phase boundary at low temperature has not been obtained yet. Considering that the clamped pressure in the DAC used in this work had a tendency to increase with decreasing temperature, the sample may be considered to stay almost in the semimetal phase in the cooling process down to liquid helium temperature. Using a high-pressure apparatus in which pressure was continuously changed at liquid helium temperature, Kawamura *et al* [3] compared the pressure dependences of T_c for black P for three different paths along which the sample was cooled down to liquid helium temperature at constant pressure. They observed a broad superconducting transition in the resistivity measurements when the sample was cooled down after it was transformed to semimetallic rhombohedral phase by applying pressure up to 8.7 GPa at room temperature. When the starting pressure was 0.1 MPa or one high enough to cause complete conversion to the sc metal phase, they observed a sharp transition. Assuming that for the data at 13.0 and 15.3 GPa in this work the sample was already in the metal phase at the clamped pressure at room temperature, a decrease in the transition width with pressure, as shown in figure 2, is consistent with their results.

Figure 3 shows the result for run B. As shown in the figure, T_c takes a maximum value at around 32 GPa. This value of pressure is very large compared to the reported ones [2, 4], which may be explained by considering the difference in the detail of the experimental conditions between the previous and present works, because T_c for black P is very sensitive to the path in the P–T diagram.

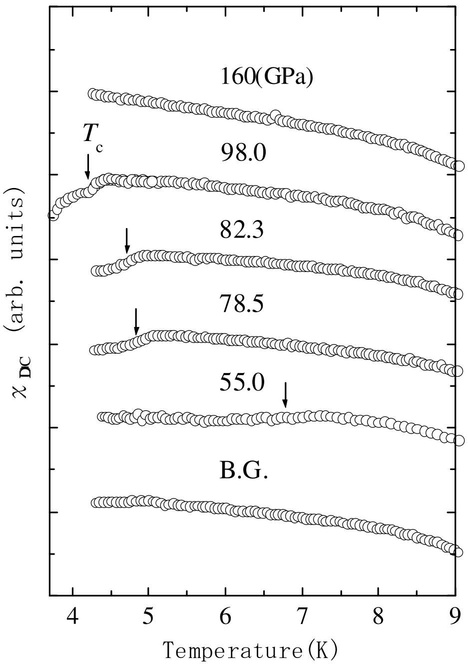

Figure 4. Results for run C. The sequence is B.G. → 55.0 (GPa) → 78.5 → 82.3 → 98.0 → 160.

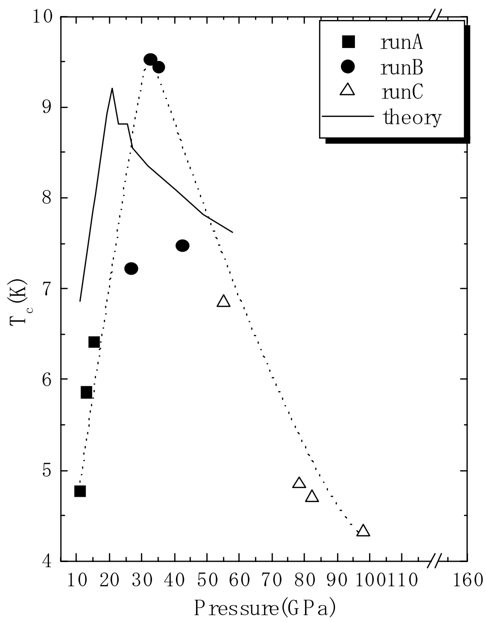

Figure 5. The pressure dependence of T_c.

Figure 4 shows the temperature dependence of the susceptibility of black P at various pressures up to 160 GPa (run C). The susceptibility change at T_c was very small compared to the result shown in figure 2 because the sample was not filled uniformly enough in the sample chamber to form a thin disc with a large diamagnetic factor [6]. As shown in the figure, T_c decreased with pressure and at 160 GPa no significant change could be seen in the susceptibility curve down to 4.2 K.

Figure 5 shows the pressure dependence of T_c obtained from all runs together with the result of the theoretical calculation [4]. As shown in the figure, T_c has a maximum of about 9.5 K at about 32 GPa. Then, T_c decreases with pressure to about 4.3 K at around 100 GPa. At higher pressures up to 160 GPa, T_c was not detected in the temperature range from 4 to 40 K, suggesting that T_c decreased below 4 K. No abrupt increase in T_c was observed for the intermediate phase in the temperature range investigated. The experimental results are roughly consistent with those of the calculation.

Acknowledgment

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