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Phase transitions and superconductivity of black phosphorus and phosphorus-arsenic alloys at low temperatures and high pressures

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X-ray diffraction of black phosphorus and phosphorus-arsenic alloys with composition $P_{1-x}As_x$ ($x=0.05,0.1$) has been carried out with synchrotron radiation at low temperatures and high pressures. The first transition from the orthorhombic to the rhombohedral state started at around 7.5 GPa at 21 K. The transition pressure at 21 K is about 3 GPa higher than that at room temperature. The orthorhombic and rhombohedral phases coexisted over the pressure range of 7.5–10.5 GPa at 21 K. The second transition to a simple-cubic phase appeared at around 12 GPa. The rhombohedral and the simple-cubic phases coexisted over the pressure range of 12–15.5 GPa at 21 K. This region was much wider than that observed at room temperature. Similar behavior was found for $P_{0.95}As_{0.05}$ and $P_{0.9}As_{0.1}$ at low temperatures and high pressures. Superconductivity of black phosphorus and the alloys has been investigated at low temperatures and high pressures. Interestingly, superconductivity is observed when pressure is increased at liquid-helium temperature. The superconducting transition temperature (T_c) of these materials rapidly increased to about 10 K at around 25 GPa. The single phase of the simple cubic form was observed at around 16 GPa for black P and 22 GPa for $P_{0.9}As_{0.1}$ at 21 K. A bulk thermal expansion coefficient of the simple-cubic phase was approximately 13×10^{-6} $(\mathrm{deg})^{-1}$. This value is considerably smaller than that of ordinary metals. The small thermal expansion is due to the instability of the simple-cubic structure at low temperatures. The high T_c of the simple-cubic structure may arise from the lattice instability at very low temperatures.

Superconductivity of black phosphorus (black P) is interesting and has been investigated at low temperatures and high pressures.[1–4] The superconducting transition temperature (T_c) versus pressure curve depends on the path in the P-T phase diagram.[1,2] When pressure is increased at liquid-helium temperature the T_c of black P goes up to about 11 K. If red phosphorus (red P) is used as a starting material and pressurized at 4.2 K, the T_c increases up to 13 K, while the onset temperature of the transition reaches 18 K at 30 GPa.[2] This is the highest T_c among the elements. Wittig, Bireckoven, and Weidlich have found a T_c of 10 K and double maxima in the T_c-P curve.[3] Valyanskaya, Stepanov, and Yakovle have studied the superconductivity under high pressure using red P as the starting material.[4] Superconductivity has also been observed in phosphorus-arsenic alloys. The value of T_c goes up to 10 K as pressure is increased at 4.2 K.[5,6]

Black P is transformed from an orthorhombic to a rhombohedral structure at around 5 GPa and then further to a simple cubic structure at around 10 GPa at room temperature.[7–9] By using synchrotron radiation, the phase transitions of black P have already been studied at low temperatures and high pressures.[2,10] The relationship between the structure and the T_c has been discussed. Phosphorus-arsenic alloys with composition $P_{1-x}As_x$ (x: 0.05,0.1,0.2,0.3,0.4,0.5) have been prepared at high pressures and high temperatures. Their alloys are transformed from orthorhombic to rhombohedral form and then further to simple-cubic form with increasing pressure at room temperature.[11] The transition pressure from the orthorhombic structure to the rhombohedral structure is about 5 GPa for the alloys, and is not sensitive to the arsenic content (x). On the other hand, the transition pressure from the rhombohedral form to the simple-cubic form increases remarkably with increasing x. Recently, the pressure-induced phase transitions of black P and $P_{1-x}As_x$ (x: 0.05,0.1) have been studied at low temperatures. In this paper we present the results of x-ray diffraction concerning the black P and the alloys at low temperatures and high pressures, and their superconducting properties are discussed.

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EXPERIMENT

The high-pressure system consisted of a diamond-anvil pressure cell mounted on a booster that was actuated by helium gas. The cell was made from a beryllium-copper alloy except for the diamond-anvil mounting plate. X-ray diffraction at low temperatures and high pressures was measured with the high-pressure cell in a cryostat. The pressure can continuously be changed at low temperatures. Details of the system are described in another paper.[12] X-ray diffraction of black P and phosphorus-arsenic alloys was studied by an energy-dispersive method using white x-rays from synchrotron radiation at low temperatures and high pressures. The diffraction patterns of the samples 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. Figure 1 shows the pressure produced in the cell as a function of applied pressure. The pressure applied by helium gas was measured with a strain gauge. When the applied pressure becomes about 800 mV, the pressure produced in the diamond cell rapidly increased at 21 K. An irreversible behavior was observed for the increasing and decreasing pressure curves.

Black P and phosphorus-arsenic alloys with the composition $P_{1-x}As_x$ ($x=0.05,0.1$) were prepared using a wedge-type cubic-anvil high-pressure apparatus.[13] The upper and lower stages of the apparatus consist of three anvils that slide on a wedge formed into shallow *V*-shaped grooves. The anvil movement is completely synchronized by means of the wedge system. The samples were prepared at 600 °C and 2 GPa for black P,[13] and at 950 °C and 1–3 GPa for the alloys.[11] The composition of the alloys was determined by EPMA.

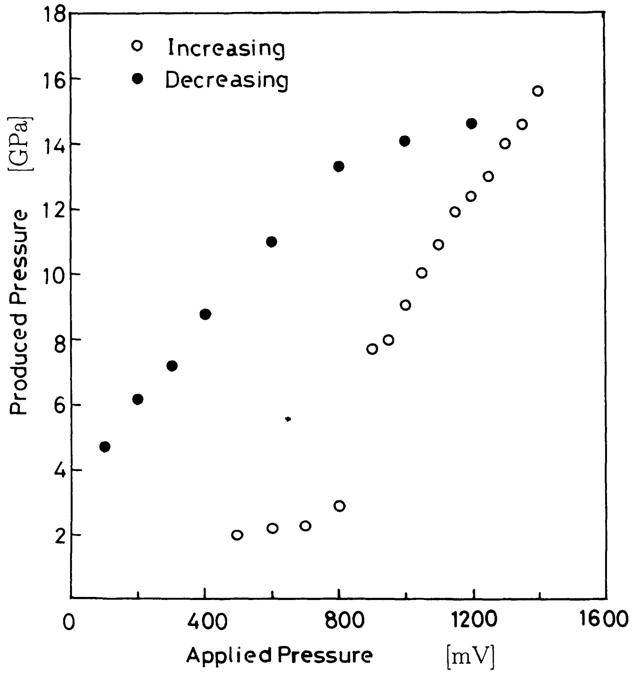

FIG. 1. The pressure produced in the diamond cell vs applied pressure curve.

Using a diamond-anvil pressure cell mounted on a booster, which is actuated by helium gas, the electrical resistivity of the single crystals of black P and the alloys was studied at low temperatures and at high pressures.[1,2] The pressure can continuously be changed at liquid-helium temperature.

RESULTS AND DISCUSSION

The preliminary results concerning the phase transitions of black P at low temperatures and high pressures have already been reported.[10] The x-ray-diffraction study of black P has again been carried out with the synchrotron radiation at low temperatures and high pressures. Figures 2(a) and 2(b) show the energy-dispersive x-ray-diffraction profiles of black P in the pressure range of 0–16 GPa at 21 K. The pressure was continuously increased at 21 K under quasihydrostatic conditions. The (hkl)'s of the diffraction lines for the sample and for NaCl are indicated in the figure. The diffraction lines of the orthorhombic phase shifted to higher energies with increasing pressure. The first transition from orthorhombic to rhombohedral started at around 7.5 GPa under 21 K. The transition pressure at 21 K is about 3 GPa higher than that of room temperature. A single phase of the rhombohedral form was found at around 10.5 GPa. The orthorhombic and rhombohedral phases coexisted over the pressure range of 7.5–10.5 GPa at 21 K. The second transition to the simple-cubic phase appeared at around 12 GPa. This value is about 2 GPa higher than that of room temperature. The rhombohedral and simple-cubic phases coexisted over the pressure range of 12–15.5 GPa at 21 K. The single phase of the simple-cubic form was observed above 15.6 GPa at 21 K.

Figure 3 shows x-ray-diffraction patterns of black P at 21 K under decreasing pressure. As the pressure was reduced from 15.6 GPa, the simple-cubic phase began to be transformed into the rhombohedral one at around 11 GPa under 21 K. The simple-cubic–to–rhombohedral transition was nearly reversible with either an increase or a decrease in the pressure at 21 K. The diffraction lines of the rhombohedral structure was observed at room temperature and atmospheric pressure. The rhombohedral phase was quenched. When pressure was again increased at 21 K, the rhombohedral phase transformed into the simple-cubic one at around 12 GPa.

Phase transitions of phosphorus-arsenic alloys with composition $P_{1-x}As_x$ ($x=0.05,0.1,0.2,0.3,0.4,0.5$) have already been studied at room temperature and high pressures.[11] The alloys are transformed from the orthorhombic structure to the rhombohedral one at around 5 GPa, and then to a simple-cubic one at around 13 GPa with increasing pressure.

Figures 4(a) and 4(b) show energy dispersive x-ray-diffraction profiles of $P_{0.9}As_{0.1}$ at various pressures under 21 K. The diffraction patterns of the orthorhombic phase were found at 5.6 GPa. The first transition from orthorhombic to rhombohedral started at around 8 GPa. This is slightly higher than that of black P. The pattern of the rhombohedral phase became dominant at around 10 GPa. The second transition to the simple cubic form appeared at around 14.9 GPa and 21 K. This pressure is about 3 GPa higher than that of black P. The rhombohedral and the simple-cubic phases coexisted over the pressure range of 15–22 GPa under the quasihydrostatic condition. The single phase pattern of the simple-cubic structure was observed about 22 GPa under 21 K. When the pressure was reduced from 23 GPa to atmospheric pressure, the transition from the simple-cubic form to the rhombohedral one appeared at around 11.5 GPa. The diffraction pattern of the rhombohedral phase was found at room temperature and atmospheric pressure. The pressure of the first and second phase transitions of black P and $P_{0.9}As_{0.1}$ are summarized in Table I. Since the rate of attainment of equilibrium between both phases was very slow, both phases coexisted in a wide pressure range at low temperature. The pressures at which the phase transitions start are given in the table.

The x-ray diffraction of $P_{0.95}As_{0.05}$ was also studied at 21 K and high pressures. The behavior of the alloy was similar to that of black P and $P_{0.9}As_{0.1}$ at low temperatures and high pressures. The transition from orthorhombic to rhombohedral started at around 7 GPa. The transition to the simple-cubic form appeared at around 13.5 GPa under 21 K. The single phase of the simple cubic one was observed above 18 GPa at 21 K.

The rhombohedral structure can be derived from the simple-cubic structure by application of two separate distortions, a rhombohedral shear and a relative displacement along the [111] directions of the fcc lattice into which a simple-cubic lattice can be resolved. The simple-cubic structure can be regarded as a special case of the rhombohedral structure with $c/a=\sqrt{6}$, $\alpha=60°$ and atomic positional parameter $u=\frac{1}{4}$. Geometrical considerations suggest that the rhombohedral lattice can continuously change to the simple-cubic lattice and the transition can proceed continuously without any jump in the specific volume at the transition. However, a discontinuous volume change of about 3% for black P (Refs. 7–9) and the alloys (Ref. 11) is really observed in the ex-

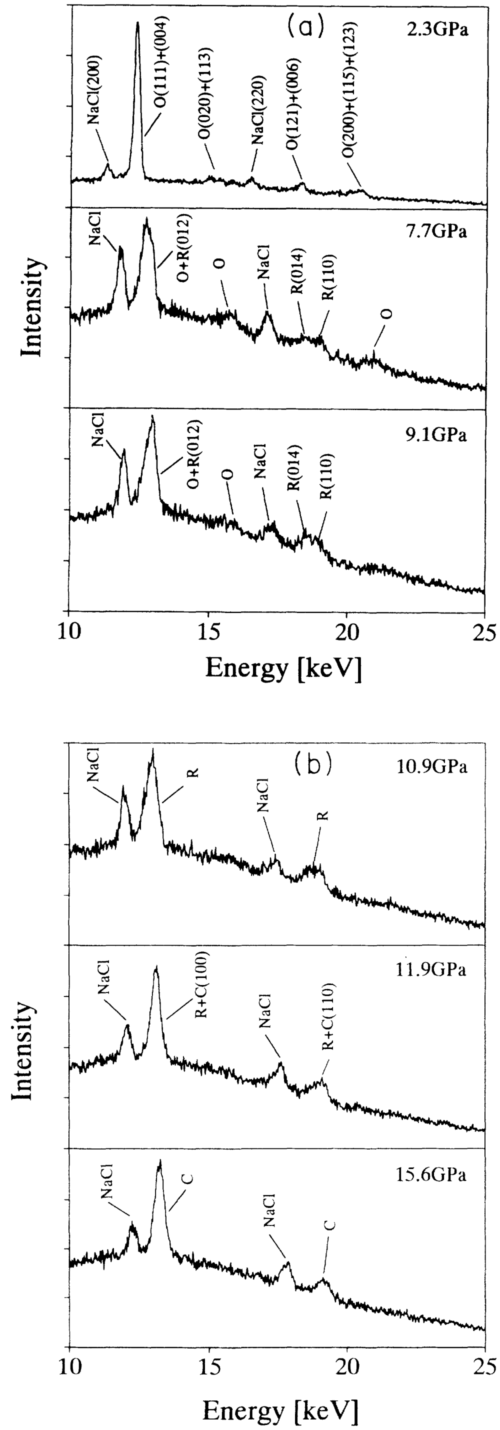

FIG. 2. The energy dispersive x-ray-diffraction profiles of black P over the pressure range of 0–16 GPa at 21 K; *O*: orthorhombic, *R*: rhombohedral, and *C*: simple cubic.

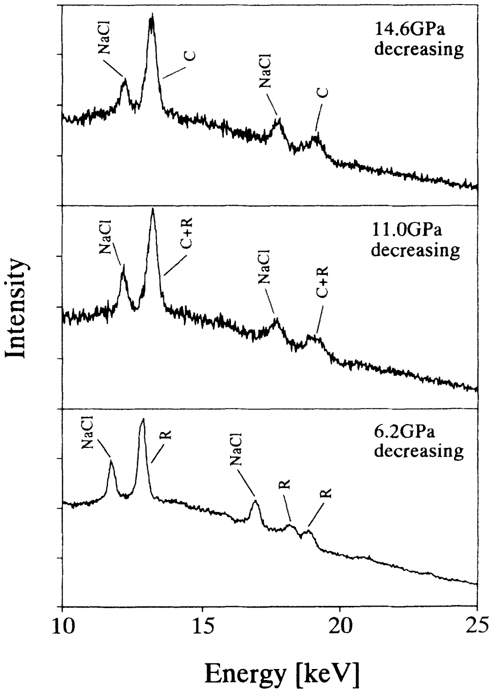

FIG. 3. X-ray-diffraction profiles of black P at 21 K under decreasing pressure.

periments. A 3.7% change of the volume at the rhombohedral–to–simple-cubic transition is calculated by Chang and Cohen.[14] These suggest that the transition is of first order. The cubic-rhombohedral distortion is similar to a one-dimensional Peierls-type distortion along the [111] axis.[15]

Chang and Cohen pointed out that the rhombohedral phase is stable in energy with respect to the simple-cubic structure at zero temperature.[14] We have found the single phase of the simple-cubic form above 15 GPa for black P, above 18 GPa for $P_{0.95}As_{0.05}$, and above 22 GPa for $P_{0.9}As_{0.1}$ at 21 K. However, the rhombohedral and simple-cubic phases coexist over a wider pressure range at 21 K compared with room-temperature data. The stable region of the simple-cubic phase is reduced at low temperatures.

TABLE I. Transition pressures of P and $P_{0.9}As_{0.1}$ at various temperatures. These values show the pressure at which the phase transitions start.

	First transition pressure (GPa)		Second transition pressure (GPa)	
	P	$P_{0.9}As_{0.1}$	P	$P_{0.9}As_{0.1}$
300 K	4.8	5	10	13.5
77 K	6	7	11	14
21 K	7.5	8	12	15

When the rhombohedral structure changes to the simple-cubic one for black P, the coordination number increases from 3 to 6. As a result of the increase in the coordination number, the nearest-neighbor P—P bond distance increases from 2.22 Å for the rhombohedral form at 9.7 GPa to 2.39 Å for the simple cubic one at 10.3 GPa.[8] The bond nature of black P changes from predominantly covalent bonding to metallic bonding. The lattice parameter of the simple-cubic phase in black P and alloys at 21 K was determined from the *d* values of the (100) and (110) reflections. The lattice constants of the simple-cubic form are 2.362 Å for black P, 2.389 Å for $P_{0.95}As_{0.05}$ and 2.392 Å for $P_{0.9}As_{0.1}$ at around 16 GPa under 21 K. The thermal expansion of the simple

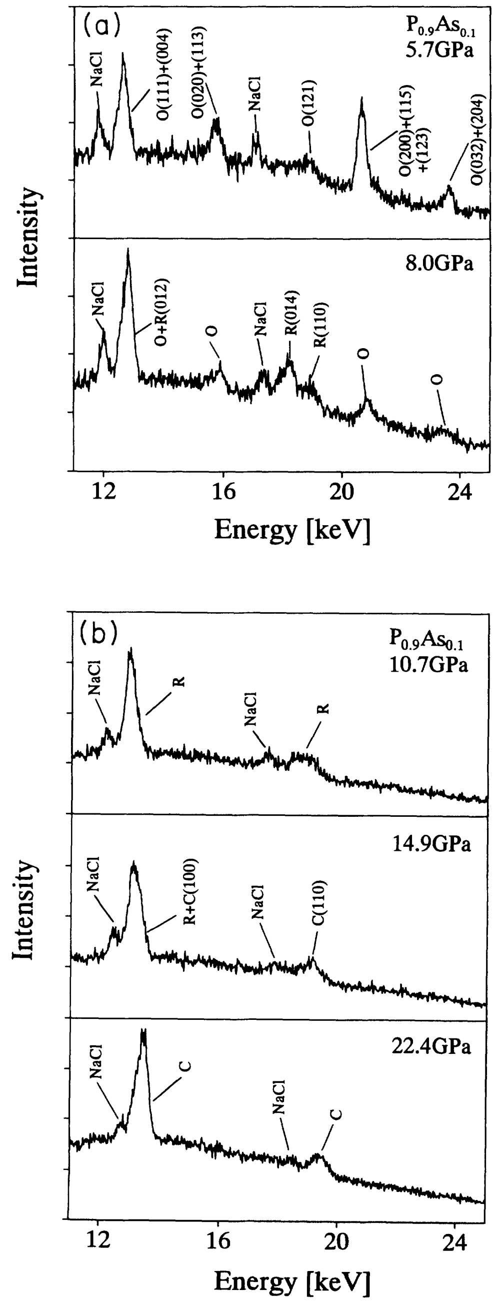

FIG. 4. The energy dispersive x-ray-diffraction patterns of $P_{0.9}As_{0.1}$ over the pressure range of 0–23 GPa at 21 K; *O*: orthorhombic, *R*: rhombohedral, and *C*: simple cubic.

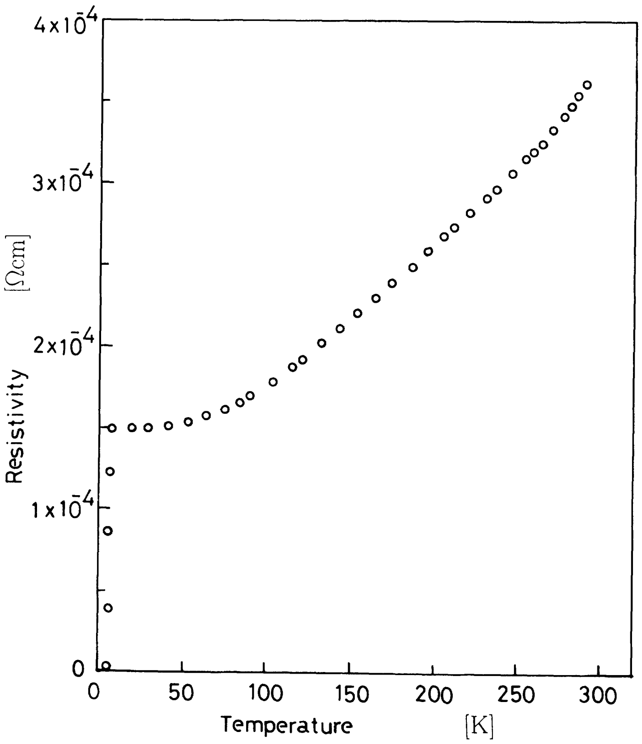

FIG. 5. The temperature dependence of the resistivity of the simple-cubic black P at 15 GPa below room temperature.

cubic phase of black P was studied at 13.6 GPa. The volume/atom of black P at this pressure was 13.38 Å^3 at room temperature. The volume decreased with decreasing temperature and became 13.33 Å^3 at 21 K. A bulk expansion coefficient of the simple-cubic black P was approximately 13×10^{-6} per degree. This value is considerably smaller than that of ordinary metals. Similar results were also found for $P_{0.95}As_{0.05}$ and $P_{0.9}As_{0.1}$. Chang and Cohen suggest that the thermal expansion should be small because of the instability of the simple-cubic structure.[14] The experimental results are consistent with their suggestion.

If pressure is increased at least up to 15 GPa at room temperature, the single phase of the simple cubic form of black P is observed. The temperature dependence of the resistivity of the simple-cubic black P was measured under 15 GPa. Figure 5 shows the resistivity versus temperature curve of the simple-cubic black P at 15 GPa. The resistivity was 3.6×10^{-4} Ω cm at room temperature and decreased monotonically with decreasing temperature. The superconductivity was observed at around 6 K. The resistivity at around T_c (R_c) was 1.5×10^{-4} Ω cm. The resistivity ratio, R_{300}/R_c, is about 2.4.

We have studied the superconductivity of black P and P-As alloys at liquid-helium temperature and high pressures. The interesting superconductivity is found when pressure is increased at liquid-helium temperature. Figure 6 shows the T_c versus pressure curves of black P and $P_{0.9}As_{0.1}$ when pressure is continuously increased at 4.2 K. The T_c of these materials rapidly went up to about 10 K at around 25 GPa. The T_c of the alloy is slightly lower than that of black P. The single phase of the simple-cubic form was observed at around 15.5 GPa for black P and 22 GPa for $P_{0.9}As_{0.1}$ under 21 K. Thus, the T_c of the simple-cubic structure was about 10 K at very high pressures.

As is shown in Table I, the transition pressure from the rhombohedral–to–simple-cubic form increased with decreasing temperature for black P and $P_{0.9}As_{0.1}$. The rhombohedral and simple-cubic phases coexisted over the pressure range of 12–15.5 GPa for black P and 15–22 GPa for $P_{0.9}As_{0.1}$ at 21 K. The coexistence region is much wider than that observed at room temperature. The simple-cubic phase of black P and its alloys may be unstable at very low temperatures.

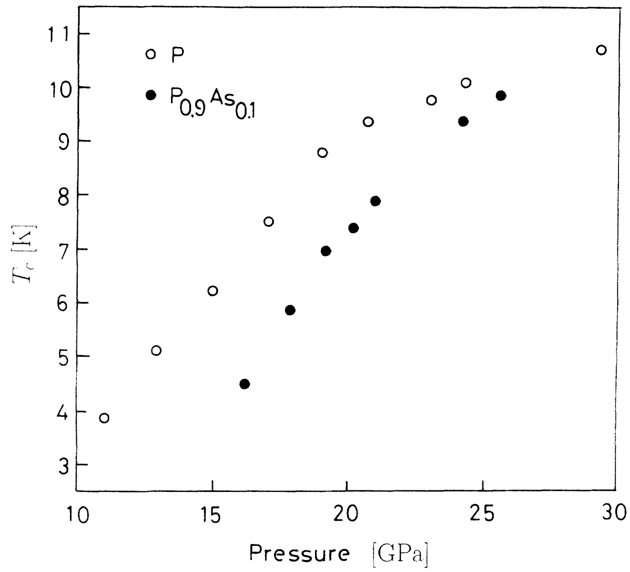

FIG. 6. T_c vs pressure curves of black P and $P_{0.9}As_{0.1}$.

Chang and Cohen have calculated[14] the phonon frequency for the LA mode at the zone corner R point in the simple-cubic Brillouin zone. This phonon mode corresponds to the displacement from the simple cubic to rhombohedral phases. The phonon polarization for the LA mode at the zone corner corresponds to a Peierls-like distortion of the hexagonal planes in the [111] direction. This phonon mode is very soft near the zone corner. The electron-phonon interactions are expected to be strong near the R point.[14,16] As mentioned above, the thermal expansion coefficient of simple-cubic black P is smaller than that of ordinary metals. They suggest that the thermal expansion of the simple-cubic form should be small because its effect increases the discrepancy from this structure. The high T_c of the simple-cubic phase may arise from the lattice instability of this structure at very low temperatures.

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