Synchrotron-Radiation Study of Phase Transitions in Phosphorus at High Pressures and Temperatures

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Abstract

Results are reported of an investigation using synchrotron radiation into the effects of temperatures up to 1173 K on pressure-induced phase transitions in phosphorus. A cubic-type multi-anvil press was employed and a diffraction pattern in an energy-dispersive mode was taken for a period of time, typically 200 s, without suffering from a deterioration of the sample material. The pressure of the first transition, orthorhombic-rhombohedral (As-type), decreases with increasing temperature at a rate of 2.3 MPa K⁻¹ and the As-type structure is stable at a pressure as low as 2.6 GPa at a temperature of 1073 K. The volume discontinuity at the transition, ∆V, is 10% at room temperature and remains almost unchanged with increasing temperature. The axial ratio c/a, when the rhombohedral structure is referred to the hexagonal system, changes mostly with pressure but only slightly with temperature, approaching √6 = 2.45 on going to the second transition, rhombohedral–simple cubic. The pressure of this transition, in contrast to the first one, is independent of temperature but ∆V at this transition, 3.7%, continuously decreases with increasing temperature.

1. Introduction

Synchrotron-radiation sources have several unique features that are not available with conventional X-ray sources. Of these the most beneficial for the structural study of materials under combined high-pressure–high-temperature conditions is the high brilliance of radiation, with which one can acquire diffraction intensity data from very small quantities of sample materials within a short period of time. It is thus possible to investigate structural changes occurring in materials that have limited chemical stability at elevated temperatures.

Crystalline phosphorus, one of the Group Vb elements, has an orthorhombic layered structure (space group Cmca, a = 3.31, b = 10.50, c = 4.38 Å) that is stable at ambient pressure and temperature. With increasing pressure it undergoes two step transitions, first to a rhombohedral (As-type) structure (R3m) and next to a simple cubic structure (Pm3m) (Jamieson, 1963). The decrease in lattice parameters and the change in volume at these transitions have been precisely determined (Kikegawa & Iwasaki, 1983). It is of interest to see how this transition sequence is affected by an increase in temperature. For high-pressure diffraction experiments powdered samples are often used. Phosphorus in the powdered form remains chemically stable as long as it is kept at ambient temperature, but at elevated temperatures it is apt to react with environmental materials and its grain size gradually increases. Unless the time of data acquisition is short, one cannot obtain reliable information on the structural change at high temperatures.

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in compressed phosphorus. This difficulty can be overcome if one performs diffraction experiments using synchrotron radiation, as will be shown below.

2. Experimental procedures

Orthorhombic (black) phosphorus samples for the high-pressure high-temperature study were prepared by crushing single crystals grown by a method described elsewhere (Shirotani, 1982; Endo, Akahama, Terada & Narita, 1982). Powders thus prepared were loaded in a cylindrical capsule (sample chamber) made of sintered boron nitride. It was shown that, if the capsule was pre-heated at 1273 K for 2 h to remove binding material (B$_2$O$_3$), no reaction took place between the sample and capsule materials even at a temperature as high as 1173 K. The capsule was embedded in the center of a cube-shaped pressure-transmitting medium made of a mixture of boron and epoxy resin, as shown in Fig. 1. A briquette of sodium chloride powder, serving as a pressure marker, was placed immediately above the sample. The sample temperature was raised by transmitting electric current through a pair of graphite disk heaters and was measured by a chromel–alumel thermocouple fixed between the capsule and the pressure marker. The effect of pressure on the e.m.f. of the thermocouple might give a temperature reading higher than the real one (Getting & Kennedy, 1970). However, since there were no data on this effect applicable to the pressure range and the apparatus adopted here, no correction was made for it. The sample temperature was thus overestimated by at least 10 K.

The high-pressure apparatus employed was a cubic-type multi-anvil press, MAX 80, installed at the Photon Factory, National Laboratory for High Energy Physics. The design, construction and performance of the press have been described elsewhere (Shimomura et al., 1985). The cube containing the sample and heater was pressed with six tungsten carbide anvils, with square faces of either 6 or 4 mm in an edge length, depending on the pressure to be generated. The diffraction experiments were carried out at the beam line 4C where white radiation was available (the accelerating voltage of the electrons in the storage ring was 2.5 GeV). A set of entrance slits was placed in front of the press to obtain an incident beam 0.3 mm in diameter. The diffraction patterns were recorded with a pure Ge solid-state detector in an energy-dispersive mode. A fine post-sample beam collimator was used to prevent unwanted scattering, mainly from the pressure-transmitting medium, from entering the detector window and thus to give lower background and sharper diffraction peaks in the pattern. The pressure at the sample position was determined by measuring the lattice parameter of the pressure marker (i.e. NaCl) and referring to Decker’s (1971) equation of state ($P-V-T$ relation). The error in the pressure determination was ±0.07 GPa at 3 GPa and ±0.2 GPa at 10 GPa. The press height relative to the incident-beam level could be varied so that the sample and the pressure marker were irradiated by the incident beam separately. This press mechanism enabled us to observe the diffraction pattern without suffering from the overlapping of peaks from the two kinds of materials. It took 200 s to obtain one pattern with the highest peak intensity of 1000–8000 counts (depending on pressure). With this exposure time successive recording of 20 or 30 patterns was made without any deterioration of the sample materials.

3. Orthorhombic–rhombohedral transition at high temperatures

The lowest frame of Fig. 2 shows a synchrotron-radiation diffraction pattern of phosphorus held at 2.3 GPa and 973 K. Eleven diffraction peaks are seen in the photon energy range covered, ten (shown shaded) of which can be indexed in terms of the orthorhombic structure. The other, at an energy of 9 keV, is an escape peak from the strongest 040 reflection. The intensity of this reflection is abnormally high, probably owing to the presence of preferred orientation of grains in the sample, and it was not possible to determine the temperature variation of the atomic positional parameters in the compressed phosphorus. However, it was possible to detect an anisotropy in the thermal expansion of the orthorhombic lattice from the shift of the peak position at a pressure of 3 GPa. The
expansion is largest along the c axis and smallest along the a axis. It is to be noted that the axis of the largest thermal expansion under pressure corresponds to the direction of the largest contraction on compression.

In compression and decompression runs made at room temperature an appreciable hysteresis was observed in the transition between the orthorhombic and rhombohedral structures owing to sluggishness in the atomic movement. A longer time equilibration for the sample at a new pressure prior to diffraction data acquisition would reduce the hysteresis, but the restriction imposed on experimental time did not allow us to do this. When the sample temperature was raised, however, atoms acquired sufficient mobility and a quick reversible change in the diffraction pattern was thus observed. Runs at several elevated temperatures have shown that the transition pressure decreases with increasing temperature and the As-type structure forms at a pressure as low as 2.6 GPa at a temperature of 1073 K, as shown in Fig. 3. The slope of the phase boundary is estimated to be \(-2.3 \text{ MPa K}^{-1}\). Since there is a contraction of volume upon transition, this means that the orthorhombic phase has a lower entropy than the rhombohedral one. The volume discontinuity \(\Delta V\) at the transition is 10% of the volume of the low-pressure phase and does not change with increasing temperature.

4. Rhombohedral structure at high pressures and temperatures

The rhombohedral As-type structure can be regarded as a distorted simple cubic structure. If the lattice is referred to the hexagonal system, the axial ratio \(c/a\) of \(\sqrt{6} = 2.45\) just corresponds to the simple cubic lattice without distortion. Any deviation in the axial ratio from this value (or any deviation in the rhombohedral angle from 60°) gives rise to a doublet diffraction peak, 10.4 and 11.0, as shown in the second and third patterns of Fig. 2, whose separation represents the magnitude of the deviation (or distortion). It decreases with increasing pressure and finally the doublet peak merges into a single peak, 110, of the simple cubic structure, as seen on going from the second to the top patterns of Fig. 2.* In addition to the change in the distortion of the lattice, there must be a change in the magnitude of the relative displacement of the two f.c.c.-type sublattices, that gives rise to a change in the relative intensity of diffraction peaks (Kikegawa & Iwasaki, 1983). However, the presence of preferred orientation did not allow us to measure it.

*The peaks on the left- and right-hand sides of the strongest 01.2 (or 100) reflection are from the capsule material (BN) and their relative intensity varies as it enters, as a result of the decrease in the total volume, into the region seen by the detector.
The axial ratio \(c/a\) was measured over a wide range of pressure and temperature and the results are expressed as isoaxial-ratio lines in the \(P-T\) plane in Fig. 4, where small solid circles represent the points of measurement. It can be seen that, except in the highest-pressure region, \(c/a\) depends mostly on pressure but insignificantly on temperature. At 2-6 GPa \(c/a\) is as large as 2.67 and it decreases to 2.50 at 10 GPa. The density of the isoaxial-ratio lines is somewhat larger in the lowest- and highest-pressure regions, showing that \(c/a\), when plotted as a function of pressure, changes rapidly on approaching either the low-pressure or the high-pressure phase. This may be regarded as a 'premonitory' effect.

5. Rhombohedral–simple cubic transition at high temperatures

In a previous study (Kikegawa & Iwasaki, 1983), the transition pressure from the rhombohedral to the simple cubic phase had been determined to be 10 GPa at room temperature. With increasing temperature neither a decrease nor an increase in the transition pressure was observed, as shown in Fig. 5, indicating that the two phases have almost the same entropy. No appreciable hysteresis was observed for this transition. Of particular interest is the temperature dependence of the magnitude of \(\Delta V\) at the transition. Geometrical considerations suggest that the distortion of the rhombohedral lattice (and the relative displacement of the sublattices) can continuously decrease to zero and the transition can proceed continuously without any jump.
in the specific volume at the transition, but what is really observed at room temperature is a discontinuous change, \( \Delta V = 3.7\% \) (Kikegawa & Iwasaki, 1983), suggesting that the transition is of first order. Fig. 6 shows a change in the profile of the doublet peak with changing pressure across the transition at two temperatures, 473 and 973 K. At 473 K the doublet peak merges discontinuously into a single peak between 10-7 and 11-1 GPa, whereas gradual merging occurs at 973 K. Computer-aided fitting of the profile (shown by dotted lines) supports this conclusion derived from visual estimation. A change in the slope of the isoaxial-ratio lines in the highest-pressure region in Fig. 4 is a reflection of this temperature dependence. It reminds us of the pressure-induced \( \gamma \rightarrow \alpha \) transition in metallic cerium (Davis & Adams, 1964), \( \Delta V \) becoming gradually small with increasing temperature and finally disappearing at about 650 K. However, as there is a definite difference in internal symmetry between the two relevant structures, the transition in phosphorus at 10 GPa cannot become second order and the critical point does not exist. It will be of interest to measure not only the change in distortion across the transition but also the change in atomic positional parameter, preferably with single crystals, in order to see whether the relative displacement of the sublattices occurs synchronously with it. This kind of investigation may make clear whether or not the boundary between phases with small structural difference terminates by intersecting another boundary at higher temperatures. This is left as a future task.

6. Discussion
All the Group Vb elements are known to exhibit pressure-induced phase transitions. Bismuth is the only element for which the effect of temperature on the transition has hitherto been investigated in detail. The \( P-T \) diagram shown in a review article (Pistorius, 1976) shows that the boundaries between phases I and II, II and III, III and III', III' and V either have negative slope or run vertically, as they do in the \( P-T \) diagrams of phosphorus. Very recently, studies were carried out for antimony (Kikegawa & Iwasaki, 1987) and the boundary between the low-pressure phase (As-type structure) and high-pressure phase (tetragonal structure) is also shown to have negative slope. These general tendencies in the slope of the phase boundaries suggest that entropy (associated probably with the thermal vibrations of atoms) increases or at least does not decrease in the Group Vb elements on going from a low-pressure to a high-pressure phase.

The high brilliance of synchrotron radiation has proved to be a powerful tool for the structural study of materials under combined conditions of high pressure and temperature. The low atomic number and therefore low scattering power of phosphorus required 200 s for diffraction-data acquisition at beam line 4C of the Photon Factory. A much shorter period of time will be required for materials of high atomic number and it will be possible to extend the temperature range to be investigated. The problem that remains unsolved is how to suppress the growth of crystal grains at elevated temperatures. A study to find an appropriate inhibitor of grain growth is in progress.

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