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P-T phase diagram of phosphorus revisited

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Abstract

Melting and phase transitions of phosphorus allotropes have been studied in the 2–11 GPa pressure range using *in situ* electrical resistivity measurements and synchrotron X-ray diffraction. It was found that the melting curve of rhombohedral phosphorus exhibits positive slope of 58(2) K/GPa and crosses the rhombohedral–simple cubic phase boundary (negative slope of -420(70) K/GPa) at about 8.3 GPa and 1490 K. The melting slope of simple cubic phosphorus can be estimated as +300(90) K/GPa. Calculations of phosphorus phase equilibria have been performed using our experimental and literature data within the framework of the phenomenological thermodynamics. The constructed equilibrium *p-T* phase diagram accurately describes the experimentally observed phase relations in solid and liquid phosphorus up to 12 GPa and 2000 K.

Keywords: phosphorus, high pressure, high temperature, phase transitions, melting, phase diagram

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Introduction

Phosphorus, one of the Group V elements, has been known since the 17th century. Phosphorus crystallizes in a number of allotropic forms: white, red, violet, black, etc. Since the 1980s the main interest has been attracted to the black phosphorus with orthorhombic (*Cmca*) structure [1] (Fig. 1a) which was found to be the most stable allotrope. At room temperature and pressures up to 260 GPa, black phosphorus exhibits a sequence of pressure-induced phase transitions: orthorhombic (*Cmca*) – rhombohedral (*R-3m*) [2,3] – simple cubic (*Pm-3m*) [2,3] – simple hexagonal (*P6/mmm*) [4] – body-centered cubic [5]. However, despite the numerous efforts to study phosphorus at high pressure and room temperature, there have been only few high-pressure studies at high temperatures [6-8].

Based on available experimental data on the orthorhombic-to-rhombohedral phase transition [7] and the melting curve of black phosphorus [8], a tentative phase diagram of phosphorus was proposed in 1987 [8] (Fig. 2). This phase diagram is limited by 5 GPa and 1000°C and describes only two solid phosphorus allotropes i.e. orthorhombic and rhombohedral. Later the first-order liquid-liquid phase transition in phosphorus was discovered [9] which was attributed to the pressure-induced transition of a dense molecular fluid (liquid 1) into a polymeric liquid (liquid 2) [10]. The simplified version of the phase diagram of phosphorus up to 5 GPa has been proposed [10], but it differs from the previous one only by the presence of the liquid 1 - liquid 2 transition line with negative slope, without specifying the position of the liquid 1 - liquid 2 - orthorhombic solid triple point.

In the present work, the melting and phase transitions of three phosphorus allotropes – orthorhombic, rhombohedral and simple cubic (corresponding crystal structures are shown in Fig. 1) – have been studied up to 10 GPa, and the data obtained have been used for thermodynamic calculations of the phase relations in phosphorus. The thermodynamic analysis based on our experimental and literature data allowed us to construct an equilibrium *p-T* phase diagram of phosphorus at pressures up to 12 GPa.

Methods

Powder of amorphous red phosphorus (99.99%) was used as received from Sigma-Aldrich. Under high pressure – high temperature conditions red phosphorus transforms to other allotropes according to with the sequence described in the Introduction.

Melting of phosphorus in the 2–8 GPa pressure range was studied *in situ* by electrical resistivity measurements in a toroid-type high-pressure apparatus with a specially designed high-temperature cell [11]. The cell was pressure-calibrated using room-temperature phase transitions in Bi (2.55 and 7.7 GPa), PbSe (4.2 GPa), and PbTe (5.2 GPa). Temperature calibration under pressure was performed using well-established melting points of silicon, sodium and cesium chlorides, platinum and the Ni-Mn-C ternary eutectic. A sample was placed directly into a graphite heater, and electrical resistivity of the cell was measured at different pressures during stepwise heating up to the melting using the method described previously [12-14]. The onset of melting was detected *in situ* by

an apparent drop in electrical resistance of the cell due to the appearance of the conducting polymeric liquid phosphorus. In a special set of experiments, phosphorus was found not to react with graphite and graphite-like hexagonal boron nitride (hBN) over the entire pressure – temperature range studied.

Melting of phosphorus at pressures of 4-6 GPa has been studied *in-situ* by energy-dispersive synchrotron X-ray diffraction using the MAX80 multianvil system at F2.1 beamline, DORIS III (DESY). Standard assemblies with hBN pressure medium were used. Sample pressure at different temperatures was determined from the thermal equation of state of hBN [15]; temperature was measured by a Pt-10%Rh/Pt thermocouple. Experimental details are described elsewhere [15,16].

Synchrotron X-ray diffraction experiments at higher pressures have been performed using the large-volume multianvil press SPEED-1500 at BL04B1 beamline, SPring-8 [17,18]. Standard 14/8 COMPRES assemblies with Re-foil or graphite heaters and hBN cylindrical capsules were used. All assemblies were equipped with B-epoxy windows transparent to X-rays. Pressure and temperature were either directly measured (pressure standards, thermocouples) or estimated from previously obtained calibrations. The characteristic sequence of energy-dispersive X-ray diffraction patterns taken in the course of a melting experiment under pressure is shown in Fig. 3.

The samples recovered from high-pressure experiments were characterized by powder X-ray diffraction (Equinox 1000 Inel diffractometer; Cu $K\alpha$ and Co $K\alpha$ radiation). X-ray diffraction patterns were analyzed using PD Indexer (© Y. Seto) and Powder Cell [19] software.

Thermodynamic calculations of phase equilibria were performed within the framework of the phenomenological thermodynamics using the Thermo-Calc software [20].

Results and Discussion

Melting of phosphorus in the 2.0-7.7 GPa pressure range has been studied by *in situ* electrical resistivity measurements (the results are shown in Fig. 4 as red half-filled stars). The experimental points at 2.0 and 2.4 GPa apparently reflect the melting of the orthorhombic allotrope, while all others correspond to the melting of rhombohedral phosphorus. The melting curve of the rhombohedral allotrope exhibits a positive slope of 58(2) K/GPa, indicating a lower density of the melt as compared to the solid phase.

Melting of rhombohedral phosphorus was also studied by *in-situ* synchrotron X-ray diffraction using MAX80 (at 3.9 and 4.5 GPa) and SPEED-1500 (at 6.9 GPa) multianvil presses. The results are shown in Fig. 4 (solid and open squares correspond to rhombohedral solid phase and liquid, respectively) and are in excellent agreement with the data obtained by the electrical resistivity measurements.

In experiments at pressures of 3.0 and 3.2 GPa we were able to detect the solid-phase transition of orthorhombic phosphorus to the rhombohedral allotrope by electrical resistivity measurements at a continuous temperature increase (T-scans); the results are represented by blue half-filled diamonds

in Fig. 4. These results are in excellent agreement with the data on this transition obtained earlier by Kikegawa *et al.* [7] in p-scans (see Fig. 2).

A quite different situation is observed for the phase transition of rhombohedral phosphorus to the simple cubic allotrope. According to Kikegawa *et al.* [7], the pressure of this transition does not depend on temperature (at least up to 1100 K) and is 10.3 GPa. However, in our experiments (T-scans at 8.9 and 9.4 GPa, and p-scan at 700 K; see Fig. 4) we observed a significant dependence of the transition pressure on temperature, and the slope of this phase boundary was estimated to be $-420(70)$ K/GPa, which allowed us to locate the rhombohedral–liquid 2–simple cubic triple point at about 8.3 GPa and 1490 K.

The study of the melting of simple cubic phosphorus at SPring-8 was a challenging task: in the majority of experiments the appearance of the liquid phase was accompanied by an immediate blowout (the results we were able to obtain are shown in Fig. 4).

Thermodynamic calculations of phosphorus phase equilibria have been performed based on our experimental and literature data within the framework of the phenomenological thermodynamics. Temperature dependences of the Gibbs energy for white and liquid phosphorus (liquid 1) at ambient pressure were taken from the SGTE database [21].

For orthorhombic, rhombohedral and simple cubic allotropes, the dependencies of Gibbs energy on temperature and pressure were determined in the form

$$G_{wp} + a + bT + \int_0^p V dp$$

based on the temperature dependence of Gibbs energy of white phosphorus [21] by solving the inverse problem using literature data for orthorhombic – rhombohedral [3] and our experimental data for rhombohedral – simple cubic (Fig. 4) phase boundaries. The coefficients a and b are given in Table 1. The molar volumes (V_0), 300-K bulk moduli (B_0), their first pressure derivatives (B_0'), and volume thermal expansion coefficients of solid phosphorus allotropes were taken from [22,23]; the pressure dependencies of the molar volumes were represented using the Murnaghan approximation [24].

Gibbs energy of polymeric liquid phosphorus (liquid 2) as well as molar volumes and bulk moduli of both liquid phosphorus phases were obtained by solving the inverse problem using literature data on the melting of orthorhombic phosphorus [8]. However, during the optimization process only the slopes of two branches of the melting curve (Fig. 2) were used, and not the absolute temperature values, because the melting temperature of orthorhombic phosphorus at ambient pressure (980 K) reported in [8] is overestimated by 100 K compared to the generally accepted value of 883 K [21]. The obtained results show that the low-pressure liquid phase (liquid 1) has 33% higher volume than the high-pressure liquid phase (liquid 2), which is in agreement with the results of *ab initio* quality molecular dynamics simulation of liquid phosphorus under pressure [25]. Furthermore, the bulk modulus of liquid 1 was found to be significantly lower than that of liquid 2 (see Table 1).

The constructed p - T phase diagram of phosphorus is shown in Fig. 4. It should be noted that the calculated melting curve of orthorhombic phase with the appearance of low-pressure liquid phosphorus (liquid 1) and the position of the liquid 1–orthorhombic–liquid 2 triple point (1.61 GPa, 1435 K) differ from the previously reported experimental data [8]. At the same time, the calculated melting temperature at ambient pressure corresponds to the generally accepted value for phosphorus [21], and the calculated melting curve of orthorhombic phase with appearance of high-pressure liquid phosphorus (liquid 2) is in perfect agreement with the results of our *in-situ* experiments in the 2.0-2.6 GPa range.

In general, the proposed diagram accurately describes the observed increase of the melting temperature of orthorhombic phosphorus up to 1.6 GPa and its decrease at higher pressures up to the orthorhombic–rhombohedral–liquid 2 triple point (2.65 GPa, 1153 K), as well as the stability of two liquid phosphorus phases and the existence of the first-order phase transition between them in full agreement with previous publications [9,10,25]. It is also noteworthy that the calculated melting line of simple cubic phosphorus with a positive slope of 316 K/GPa is in good agreement with our experimental data at temperatures above the rhombohedral–liquid 2–simple cubic triple point (8.26 GPa, 1491 K).

Conclusions

Melting and solid-state phase transitions of phosphorus allotropes have been studied *in situ* in the 2-11 GPa pressure range using electrical resistivity measurements and synchrotron X-ray diffraction. While the melting curves of the rhombohedral and simple cubic allotropes have positive slopes of 58(2) and 300(90) K/GPa, respectively, the rhombohedral–simple cubic phase boundary has a negative slope of -420(70) K/GPa, and the rhombohedral–polymeric liquid–simple cubic triple point is located at about 8.3 GPa and 1490 K. Calculations of phosphorus phase equilibria have been performed using our experimental and literature data in the framework of the phenomenological thermodynamics. The constructed equilibrium p - T phase diagram accurately describes the experimentally observed phase relations in solid and liquid phosphorus up to 12 GPa and 2000 K.

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Table 1 Parameters of temperature and pressure dependencies of Gibbs energy of phosphorus phases

Phase	a (J/mole)	b (J/mole·K)	$V_0 \times 10^6$ (m ³ /mole)	B_0 (GPa)	B_0'
Orthorhombic	-2450	1.2	11.43(5) [22]	34.7(5) [22]	4 [22]
Rhombohedral	4950	-1.3	9.62(1) [22]	65.0(6) [22]	4 [22]
Simple cubic	8600	-1.65	9.23(1) [22]	72.5(3) [22]	4 [22]
Liquid 1 [*]	–	–	13.0	11.1	4
Liquid 2 [†]	–	–	9.75	65.0	4

* Temperature dependence of Gibbs energy of molecular phosphorus fluid (liquid 1) was taken from [21]

† $G_{P \text{ liquid } 2} = G_{P \text{ liquid } 1} + 6350 - 1 \times T$ (J/mole)

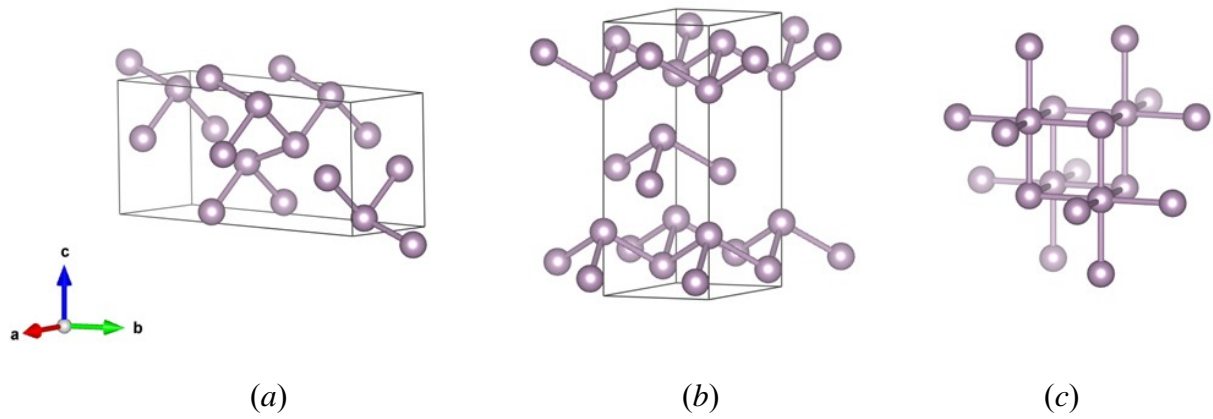


Fig. 1 Crystal structures of phosphorus allotropes: (a) orthorhombic ($Cmca$) [1], (b) rhombohedral ($R-3m$) [2] (hexagonal setting), and (c) simple cubic ($Pm-3m$) [3].

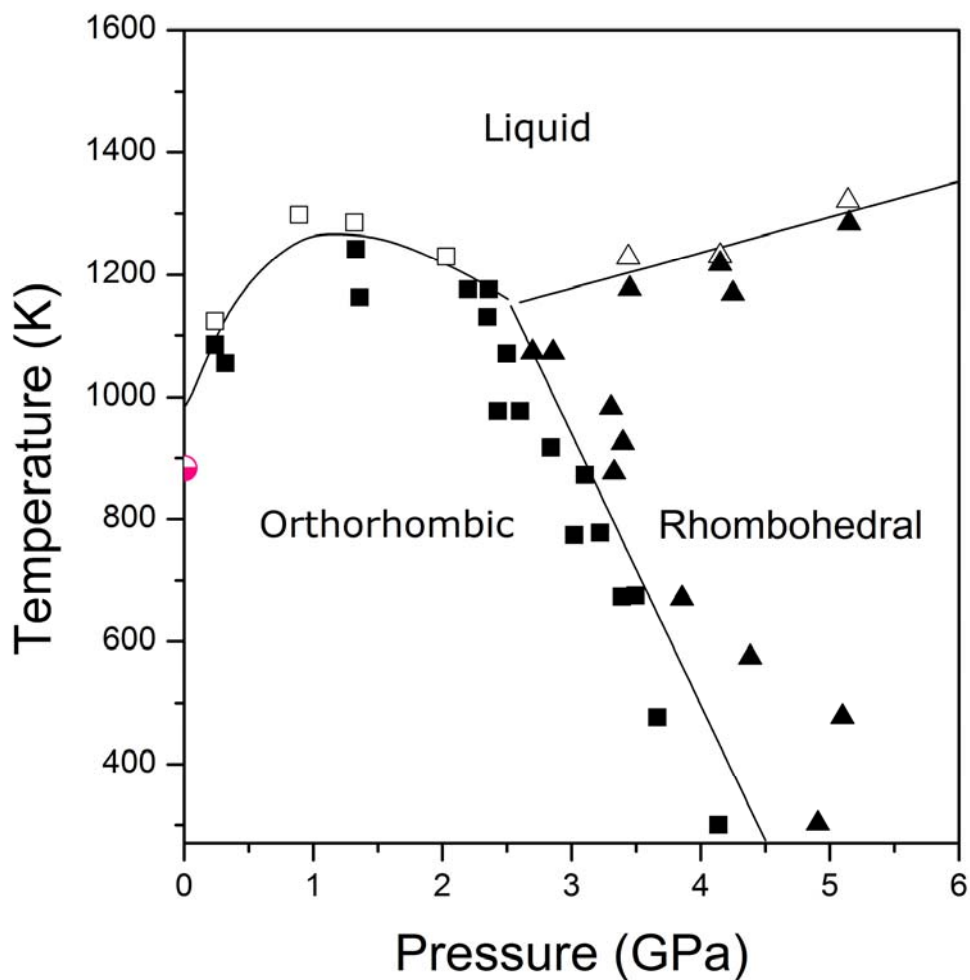


Fig. 2 Tentative phase diagram of phosphorus proposed in 1987 [8] (solid symbols correspond to the solid phases, open symbols – to the liquid). The phase boundary between orthorhombic (solid squares) and rhombohedral (solid triangles) allotropes is drawn according to [7]. The pink half-filled circle indicates the melting temperature at ambient pressure (883 K [21]).

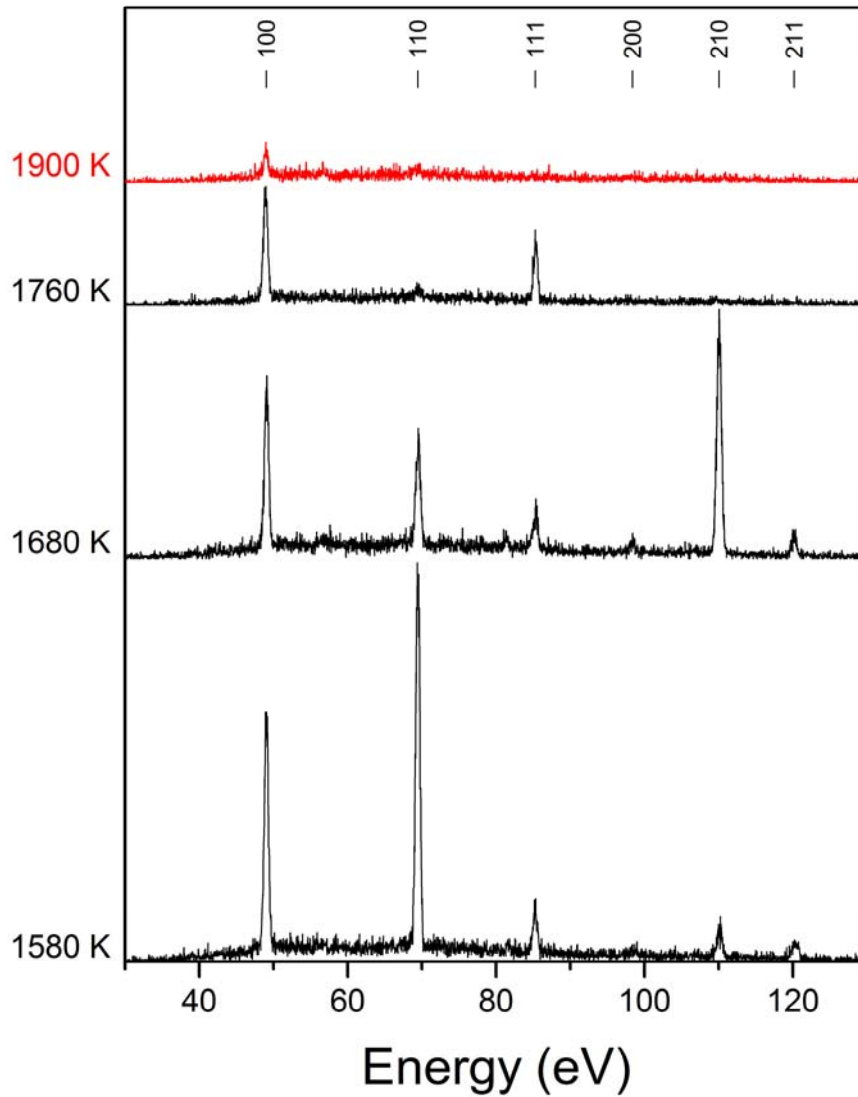


Fig. 3 Synchrotron energy-dispersive X-ray diffraction patterns collected during heating of phosphorus at 9.4 GPa up to the melting using the SPEED-1500 multi-anvil system at BL04B1 beamline, SPring-8. Vertical ticks correspond to positions of diffraction lines of the simple cubic ($Pm-3m$) allotrope which crystal structure does not undergo any change until melting at 1900 K.

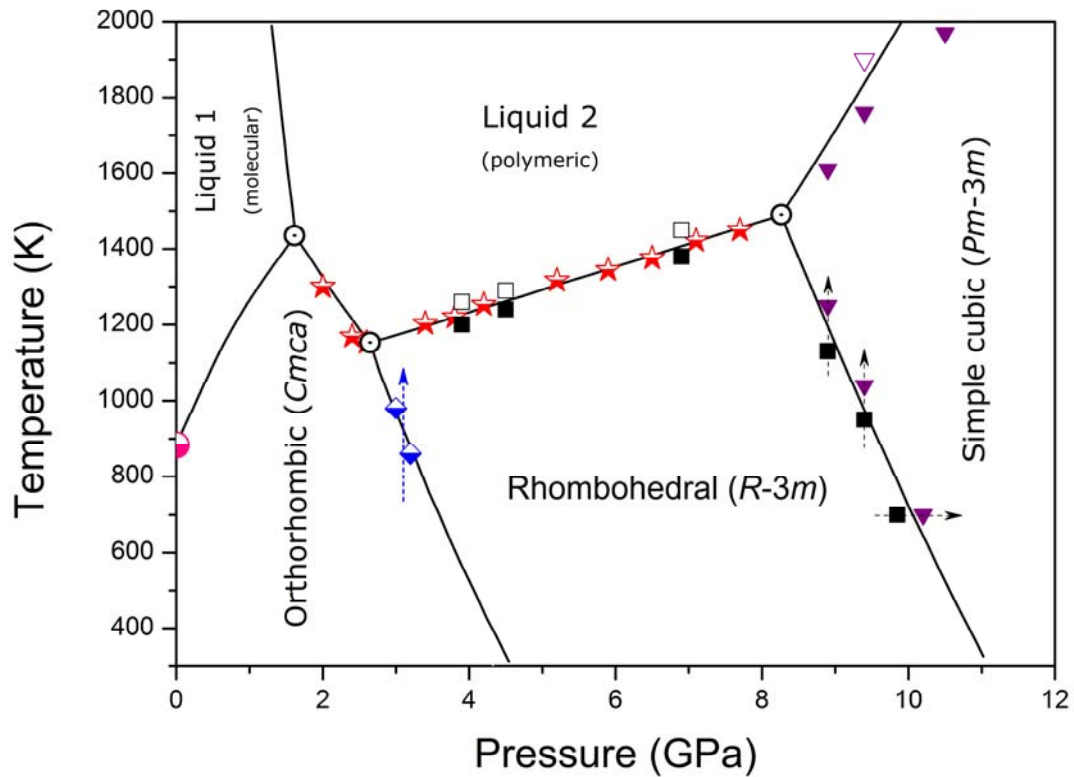


Fig. 4 Equilibrium p - T phase diagram of phosphorus and our experimental data on phase transitions and melting at pressures up to 11 GPa. Red half-filled stars show the melting onset registered *in situ* by electrical resistivity measurements; blue half-filled diamonds correspond to the orthorhombic-to-rhombohedral phase transition. The results of synchrotron X-ray diffraction experiments are shown by squares (corresponding to the rhombohedral phase) and down triangles (corresponding to the simple cubic phase); solid symbols represent solid allotropes, open symbols – liquid (only experimental points close to the phase transition boundaries are shown). The pink half-filled circle indicates the melting temperature at ambient pressure (883 K [21]). All phase boundaries represented by solid lines have been calculated within the framework of the phenomenological thermodynamics using our experimental and literature data.