High-pressure phases of cadmium phosphide, Cd_3P_2

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Abstract

The crystal structure stability of Cd_3P_2 has been studied in the pressure range 0–30 GPa using high-pressure X-ray diffraction (XRD) in conjunction with synchrotron radiation. The experimental zero-pressure bulk modulus of tetragonal Cd_3P_2 is 64.7(7) GPa. Experiments were accompanied by first-principle density functional calculation using tight-binding linear muffin-tin orbital method within the local density approximation (LDA) to compare the ground state properties. The calculated bulk modulus is 66.3 GPa, in good agreement with the experimental value. A structural phase transformation has been found with a transition pressure of 4.0 GPa. Tentatively, the crystal structure of the high-pressure phase is orthorhombic with space group *Pmmn* (59). Amorphization of the sample occurs above 25 GPa. The tetragonal to orthorhombic phase transformation has also been observed in electrical resistance measurements using a four-probe method. The first-order character of the transition has been confirmed.

Introduction

At ambient conditions, Cd_3P_2 crystallizes in a primitive tetragonal structure [space group $P4_2/nmc$ (137)] with eight formula units per unit cell (Stackelberg and Paulus, 1935). The Cd atoms are situated in three of four deformed tetrahedral sites, and the P atoms are in octahedral sites. The method of preparation of this material and its semiconducting properties were described first by Haacke and Castellion (1964) and Zdanowicz and Wojakowski (1965). Pistorius et al. (1977) redetermined the crystal structure at ambient conditions, confirming the structure originally reported by Stackelberg and Paulus (1935). The melting curve of Cd_3P_2 in the pressure range 0 – 4 GPa was also studied by the same authors. Several experimental studies have been reported on various properties, such as thermoelectric power and the optical gap (Haacke and Castellion, 1964), transport properties

(Zdanowicz and Wojakowski, 1965), optically pumped laser action (Bishop et al., 1970), photoluminescence (Bishop et et al., 1969a, b), other optical properties and enery band structure (Sobolev and Syrbu, 1974). Cisowski et al. (1980) have measured resistivity and the Hall coefficient as functions of pressure up to 1.2 GPa. However, little is known about the crystal structure stability and possible pressure-induced solid-solid transformations.

Theoretically, first energy band calculations for Cd_3P_2 were performed by a pseudopotential method in the hypothetical crystal structure, in which the conduction band effective masses as well as the interband transition assignments, associated with the optical reflectivity peaks, are deduced (Lin-Chung, 1971). Further studies on the band structure and symmetry operations of Cd_3P_2 in the real crystal symmetry were carried out by a pseudopotential method, in which a qualitative explanation of the band structure and the optical properties can be made (Plenkiewicz and Dowgiallo-Plenkiewicz, 1979a and b). Band structure calculations of Cd_3P_2 for its real symmetry encounter many difficulties and apparently, some approximations are necessary. The main reason for these difficulties is the complicated crystal structure. Cd_3P_2 crystallizes in a primitive tetragonal lattice with 40 atoms per unit cell. Hence, only a few theoretical calculations are reported in the literature.

The present work is an experimental and theoretical study of the high-pressure crystal structure stability of Cd_3P_2. In particular, we emphasize the determination of the equation of state and the bulk modulus of the primitive tetragonal structure.
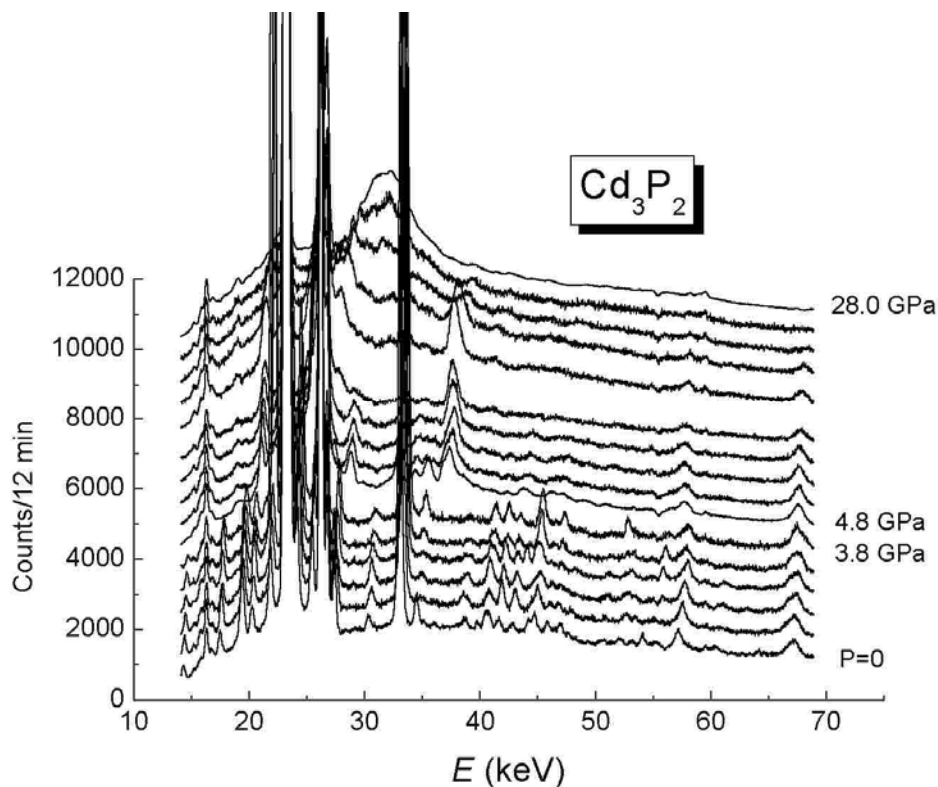
Experimental

Fig. 1. Synchrotron XRD spectra of Cd_3P_2 at various pressures.

Note the phase transformation at about 4 GPa and the amorphization above 25 GPa. The strong peaks at 23.11 and 26.09 keV are due to Cd $K\alpha$ and $K\beta$.

High-pressure powder x-ray diffraction patterns were recorded at room temperature using the white-beam method and synchrotron radiation at Station F3 of HASYLAB-DESY in Hamburg, Germany. The diffractometer, working in the energy-dispersive mode, has been described by Olsen (1992). High pressures were obtained in a Syassen-Holzapfel type diamond-anvil cell. A finely ground powder sample and a ruby chip were placed in a 200 μm diameter hole in an inconel gasket, pre-indented to a thickness of 60 μm. A 16:3:1 methanol: ethanol: water mixture was used as the pressure-transmitting medium. The pressure in the cell was determined by measuring the wavelength shift of the ruby R_1 luminescence line and applying the non-linear pressure scale of Mao et al. (1986). The Bragg angle of each run was calculated from a zero-pressure spectrum of sodium chloride in the diamond-anvil cell.

Figure 1 shows synchrotron x-ray diffraction (XRD) spectra for Cd_3P_2 recorded at various pressures. From each spectrum, values for the lattice parameter and the unit-cell volume were derived and refined. The pressure-volume data were then described by the Birch-Murnaghan equation of state (Birch, 1938 and 1947):

$$P = \frac{3}{2} B_0 (x^{-7/3} - x^{-5/3})[1 - \frac{3}{4}(4 - B_0^{'})(x^{-2/3} - 1)], \tag{1}$$

where $x = V/V_0$, V being the volume at pressure P, and V_0 the volume at zero pressure, B_0 is the bulk modulus and $B_0^{'}$ its pressure derivative, both parameters evaluated at zero pressure. Values of B_0 and $B_0^{'}$ were obtained from a least-squares fit of Equation (1) to the experimental data points.

Further informations have been obtained from electrical resistance measurements carried out in a high-pressure cell with profiled toroid type anvils made of a tungstate carbide alloy (Khvostantsev et al., 1977). The sample of dimensions $0.3 \times 0.3 \times 0.1.5$ mm^3 with four contact wires and a manganine pressure gauge was placed in a teflon capsule filled with the pressure transmitting liquid (a methanol:ethanol mixture). The capsule was centred in the gasket hole of the lithographic stone and compressed between the profiled anvils.

Theoretical procedure

In the present work we have used a tight-binding linear muffin-tin orbital method (Andersen, 1975) within the local density approximation (Barth and Hedin, 1972) to calculate the total energies and ground state properties. The atomic sphere approximation (ASA) has been used (Andersen and Jepsen, 1984). In this method the crystal is divided into space filling spheres centered on each atomic site. Empty spheres were introduced in the high symmetry interstitial sites. Combined correction terms are also included, which account for the non-

spherical shape of the atomic sphere and the truncation of higher partial waves inside the spheres to minize the errors in the LMTO method.

The positions and the radii of the interstitial spheres were calculated using an automated procedure developed by Krier et al. (2005). The scalar relativistic Kohn-Sham-Schrödinger equations were solved taking all relativistic effects into account except for the spin-orbit coupling. In order to calculate the total ground state properties, total energies were calculated for several volumes. The Birch-Murnaghan equation (1) was then fitted to the calculated pressure-volume data to yield the bulk modulus and its pressure derivative.

Results and discussion

The XRD spectra for Cd_3P_2 (Fig. 1) clearly show that a structural phase transformation occurs at about 4 GPa, and that the sample becomes amorphous above 25 GPa. Fig. 2 shows the experimental and theoretical compression curves of tetragonal Cd_3P_2 as functions of pressure. A fit of the Birch-Murnaghan equation (1) to the experimental pressure-volume data gives the zero-pressure bulk modulus $B_0 = 64.7(7)$ GPa. It is difficult to fit the curvature of the equation of state in the small pressure range 0–4 GPa, and for simplicity we have assumed that $B_0´ = 4.00$. Also shown in Fig. 2 is the compression curve calculated by the LMTO-ASA method.
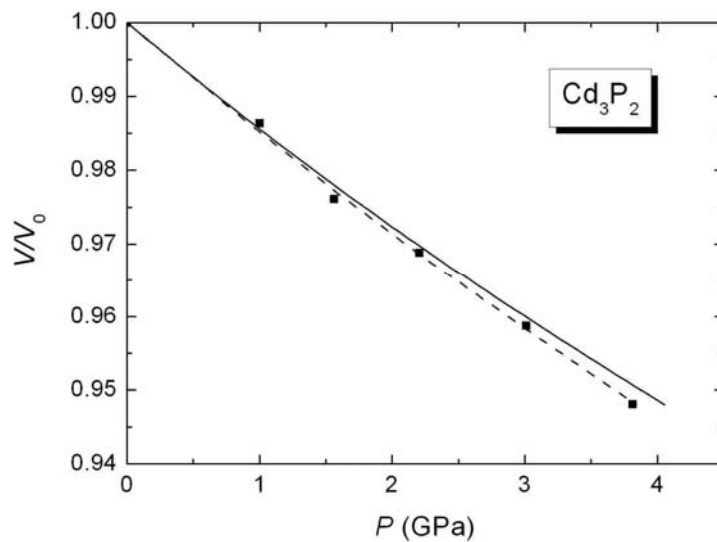

Fig. 2. Room-temperature volume-compression curves of tetragonal Cd_3P_2. The dashed curve through the experimental data points (filled squares) has been calculated from the Birch-Murnaghan equation (1). The theoretical calculation is shown by the full curve.

The predicted zero-pressure lattice parameters are $a_0 = 8.8182$ Å and $c_0 = 12.3570$ Å, i.e. 0.84 % larger than the corresponding experimental values 8.7537 and 12.2669 Å (Pistorius et al., 1977). The calculated bulk modulus $B_0 = 66.3$ GPa is in good agreement with the experimental value given above. For the pressure derivative, the calculations give $B_0´ = 5.11$. The low value of the bulk modulus indicates that Cd_3P_2 is highly compressible. To the best knowledge of the authors, there are no published data with which to compare the present results.
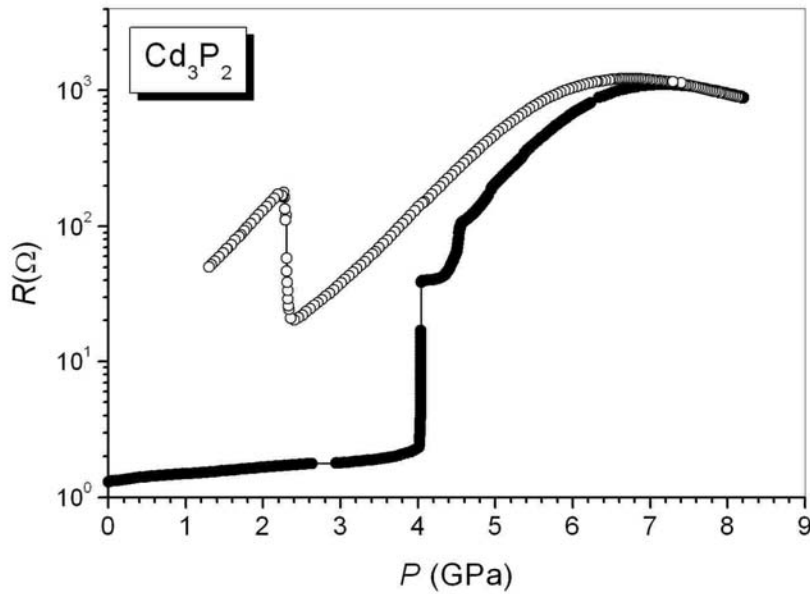
Fig. 3. Pressure dependence of the electrical resistance of a Cd_3P_2 sample at room temperature

Fig. 3. shows the electrical resistance of a Cd_3P_2 sample at room temperature as a function of pressure. The resistance increases linearly with pressure up to a critical pressure, $P_c = 4.0$ GPa, where there is a sharp discontinuity, indicating of a first-order phase transition. Above the transition, the resistance continues to increase and passes through a shallow maximum at about 6.8 GPa. On release of pressure, a hysteresis of about 1.6 GPa moves the transition in decompression to $P_{c,r} = 2.4$ GPa, where again a sharp discontinuity is observed. Remarkably, the slope dR/dP for the low-pressure phase is much larger in decompression than during the initial compression. Such an effect can be explained by the fact that Cd_3P_2 is a self-doped semiconductor, in which a redistribution of structural defects may be driven by the pressure. The high-pressure structure observed by X-ray diffraction above P_c, also implies changes in the band gap and charge mobility. Therefore, the electrical resistance may show quite different characteristics in the two phases.
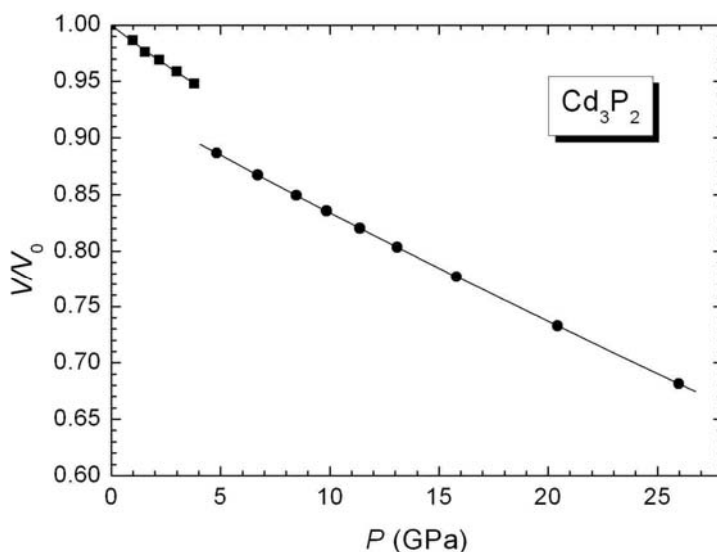

Fig. 4. Experimental compression curves of tetragonal and ortho-rhombic Cd_3P_2.

The relative volume change at the transition is $\Delta V/V = -5.5$ %.

It is likely that the high-pressure phase of Cd_3P_2 is structurally related to the Cd_3As_2 and Zn_3As_2 V phases (Pistorius et al., 1977). The structure of these phases is probably the same as that of Cd_3Sb_2 and Zn_3Sb_2 at ambient conditions, as suggested by Pistorius (1975). The space group is *Pmmn* (59), and the orthorhombic unit cell contains six formula units (PDF#23–1016 and 26–0243). Our diffraction data are consistent with the hypothesis that the unit cell of the Cd_3P_2 high-pressure phase above 4.0 GPa is orthorhombic with space group *Pmmn* (59). The relative volume change at the phase transition is $\Delta V/V = -5.5$ % (Fig. 4).

Conclusions

The high-pressure behaviour of Cd_3P_2 has been studied for the first time in the pressure range up to 30 GPa using high-pressure x-ray diffraction in conjunction with synchrotron radiation. The experimental zero-pressure bulk modulus is found to be 64.7(7) GPa which agrees quite well with the calculated value of 66.3 GPa using the tight-binding linear muffin-tin orbital method within the local density approximation. A structural phase transformation has been observed at 4.0 GPa in compression. There is a hysteresis of 1.6 GPa in decompression. Tentatively, the high-pressure phase above 4.0 GPa has an orthorhombic crystal structure with space group *Pmmn* (59). The relative volume change at the phase transition is $\Delta V/V = -5.5$ %. Amorphization of the sample occurs above 25 GPa.

Acknowledgements

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