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Temperature–pressure behavior and equation of state of praseodymium pnictides

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ABSTRACT

This paper reports an analysis on the high-pressure and temperature structural phase transition of praseodymium pnictides (phosphide: PrP and arsenide: PrAs). The Realistic Interaction Potential Approach (RIPA) model has been developed and used to study the structural and elastic properties. Phase transition pressures are associated with a sudden collapse in volume. Phase transition pressures have been reported at high temperature range 0–1000 K. The phase transition pressures and associated volume collapses obtained from present potential model show a generally better agreement with available experimental data than others. The elastic constants and their pressure derivatives are also reported. The temperature and pressure behaviors of bulk modulus for the present compounds are also discussed.

1. Introduction

The rare-earth pnictides have attracted attention both theoretically and experimentally because of the vast variety in their magnetic and electrical properties. The rare earths are some of the structurally simplest materials, and numerous experimental works are available on the pressure behavior of these compounds [1–8]. At ambient conditions these rare earth compounds are characterized by a fixed f^n configuration of atomic-like f-electrons, but the compression resulting from the application of pressure ultimately leads to the destabilization of the f-shell. These rare earth chalcogenides and pnictides are complicated to fabricate into single-phase crystals [9]. They have various practical applications in the field of electro-optic components, grinding alloys, non-linear optics, glass-making, composites lasers, phosphors lasers, and electronics. Among these, praseodymium pnictides (PrX: X=N, P, As, Sb, Bi) PrP and PrAs have been extensively studied, both experimentally as well as theoretically at normal condition [10–18]. But the high-pressure structural properties of praseodymium pnictides have been less reported in the literature. These praseodymium pnictides crystallize in NaCl-type structure (B1) at ambient conditions with space group Fm3m (225). Under pressure, these pnictides have been found to undergo a first-order phase transition from the sixfold-coordinated NaCl structure to the eightfold-coordinated CsCl-type structure (B2) with the space group symmetry Pm3m (221).

Some experimental and theoretical studies on praseodymium pnictides are reported in the literature [10–18]. The structural phase transition, elastic, lattice dynamic and thermodynamic properties of rare-earth compounds PrP and PrAs are investigated using the first-principles calculations within the generalized gradient approximation (GGA) by Kocak et al. [10]. A routine way to cope with the inabilities of DFT functional to describe the localized 4f electrons is to place the 4f electrons in the core. Also PAW potentials in which the f states are treated as valence states are available, but these potentials are not expected to work reliable when the f electrons are localized. The electronic structure of the praseodymium monopnictides and monochalcogenides is studied using the self-interaction corrected (SIC) local spin

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density (LSD) approximation by Vaitheeswaran et al. [11]. This method allows for a description of the Pr ions with some f electrons localized in atomic like orbitals. Shirotoni et al. [12] found B1–B2 transitions in PrP and PrAs at 26 and 27 GPa using synchrotron radiation; powder X-ray diffraction patterns of Pr compounds were measured using a diamond-anvil cell and an imaging plate up to 42 GPa at room temperature. The incident beam was monochromatized by a Si (111) double crystal. The pressure in the diamond-anvil cell was determined from a pressure shift in the sharp R-line fluorescence spectrum of ruby grain. A 4:1 methanol–ethanol solution was used as pressure medium. Adachi et al. [13] have experimentally investigated a crystallographic transition from B1 to a tetragonal structure (distorted-B2) at around 26 GPa with a volume collapse of 12.1%. Svane et al. [14] reported the electronic structure of rare earth chalcogenides and pnictides with the ab-initio self-interaction corrected local-spin-density approximation (SIC-LSD). Some structural transitions were observed by use of synchrotron radiation, powder X-ray diffraction in Pr-pnictides [15–17]. On the theoretical note the mechanical and thermal properties of praseodymium monochalcogenides and monopnictides are calculated using elastic constants, which have been derived from two body inter-ionic potential theory [18]. Even if considerable development has been made in experimental point of view the theoretical description of the structural properties of praseodymium pnictides at room temperature is still not well established.

As evident from literature the theoretical works on these praseodymium pnictides (PrP and PrAs) are less reported, so we have devoted efforts to explore these compounds theoretically. We have studied structural high pressure and temperature investigation of these compounds theoretically using the realistic model including temperature effect. The present article provides an efficient study of structural, mechanical and thermal properties of PrP and PrAs using the Realistic Interaction Potential Approach (RIPA) model [19]. The theoretical calculations are carried out at zero temperature, consequently the Gibbs free energy becomes equivalent to enthalpy (H). This is not the realistic approach because experiments are performed at room temperature and not at zero temperature ($T=0$ K). This fact causes disagreement in comparability of theoretical results with experimental data. To attain better comparability of theoretical results we have taken account of the room temperature in pressure induced theoretical calculations. The main aspire of this analysis is to study the structural, mechanical and thermal properties at room and high temperatures. The rest of this paper is planned as follows: the method of calculation is given in Section 2; the results and discussion are presented and discussed in Section 3 and the conclusion of this investigation is given in Section 4.

2. Method of calculation

2.1. Calculations of structural properties

Pressure causes a change in the volume of the crystal, and therefore it alters the charge distribution of the electron shells. As a result of this, a deformation of the overlapping electron shells of the adjacent ions takes place which leads to an increased charge transfer (or three body interaction (TBI) [20]). This interaction becomes more important to consider due to the decrease in inter-ionic spacing of the lattice crystal when pressure gets increased and when anions experience sufficient overlap. Besides, increase in overlap energy, the transferred charge due to overlap in electron shells modifies the coulomb energy by $(1+(2n/z)f(r))$, where n and z are the number of electrons in outermost shell and ionic charge of compound, respectively. The $f(r)$ is the TBI parameter and is dependent on the nearest neighbor distance (r) as [20–28]

$$f(r)=f_0\exp(-r/\rho) \tag{1}$$

The effect of TBI is introduced in the expressions of Gibbs free energy ($G=U+PV-TS$), in order to obtain the stability condition for a crystal structure. Here, U is the internal energy, which at $T=0$ K is equivalent to the lattice energy, P is the pressure, V is the volume and S is the entropy.

The Gibbs free energies for rock-salt (NaCl, B1) and cesium-chloride (CsCl, B2) structures at room temperature T=300 K are given by

$$G_{B1}(r)=U_{B1}(r)+PV_{B1}(r)-TS_1 \tag{2}$$

$$G_{B2}(r')=U_{B2}(r')+PV_{B2}(r')-TS_2 \tag{3}$$

with V_{B1} ($=2.00r^3$) and V_{B2} ($=1.54r'^3$) as unit cell volumes, and S_1 and S_2 as the entropies for B1 and B2 phases, respectively. In fact the condition for a transition is that the difference in free energy between two phases should approach to zero.

$$\Delta G=\Delta H-T\Delta S \tag{4}$$

After calculating Gibbs free energies at room temperature, we have extended this study to high temperatures.

The first terms in (2) and (3) are lattice energies for B1 and B2 structures and they are expressed as

$$\begin{aligned}U_{B1}(r)=&\frac{-\alpha_m z^2e^2}{r}-\frac{(12\alpha_m ze^2f(r))}{r}-\left[\frac{C}{r^6}+\frac{D}{r^8}\right]\\&+6b\beta_{ij}\exp[(r_i+r_j-r)/\rho+6b\beta_{ii}\exp[(2r_i-1.414r)/\rho]\\&+6b\beta_{jj}\exp[(2r_j-1.414r)/\rho]\end{aligned} \tag{5}$$

$$\begin{aligned}U_{B2}(r')=&\frac{-\alpha'_m z^2e^2}{r'}-\frac{(16\alpha'_m ze^2f(r'))}{r'}-\left[\frac{C'}{r'^6}+\frac{D'}{r'^8}\right]\\&+8b\beta_{ij}\exp[(r_i+r_j-r')/\rho]+3b\beta_{ii}\exp[(2r_i-1.154r')/\rho]\\&+3b\beta_{jj}\exp[(2r_j-1.154r')/\rho]\end{aligned} \tag{6}$$

where α_m and α'_m are the Madelung constants for NaCl and CsCl structures, respectively. C (C') and D (D') are the overall van der Waals (vdW) coefficients of B1 (B2) phases, β_{ij} ($i,j=1,2$) are the Pauling coefficients. ze is the ionic charge and b (ρ) are the hardness (range) parameters, r (r') are the nearest neighbor separations for NaCl (CsCl) structure $f(r)$ is the three body force parameter. S_1 and S_2 are the entropies for NaCl (CsCl) structure.

The first terms in Eqs. (5) and (6) are long range Coulomb energy, second terms are three body interactions corresponding to the nearest neighbor separation r (r') for B1 (B2) phases, third terms are vdW (van der Waals) interaction,