



Communication

Thermal expansion, heat capacity and Grüneisen parameter of iridium phosphide Ir₂P from quasi-harmonic Debye modelZ.J. Liu^{a,b,*}, T. Song^{b,c}, X.W. Sun^b, Q. Ma^c, T. Wang^b, Y. Guo^a^a Department of Physics, Lanzhou City University, Lanzhou 730070, China^b School of Mathematics and Physics, Lanzhou Jiao tong University, Lanzhou 730070, China^c School of Material Science and Engineering, Lanzhou University of Technology, Lanzhou 730050, China

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ABSTRACT

Thermal expansion coefficient, heat capacity, and Grüneisen parameter of iridium phosphide Ir₂P are reported by means of quasi-harmonic Debye model for the first time in the current study. This model combines with first-principles calculations within generalized gradient approximation using pseudopotentials and a plane-wave basis in the framework of density functional theory, and it takes into account the phononic effects within the quasi-harmonic approximation. The Debye temperature as a function of volume, the Grüneisen parameter, thermal expansion coefficient, constant-volume and constant-pressure heat capacities, and entropy on the temperature T are also successfully obtained. All the thermodynamic properties of Ir₂P in the whole pressure range from 0 to 100 GPa and temperature range from 0 to 3000 K are summarized and discussed in detail.

1. Introduction

Binary transition-metal borides, carbides, and nitrides have received increasing interest due to their fascinating properties, such as high thermal and chemical stability, electrical or thermal conductivity, catalytic activity, and superior hardness [1–5]. These materials such as OsB₂ [6], ReB₂ [7], PtC [8], Ta₂N₃ [9], PtN₂ [10], IrN₂ [11,12], OsN₂ [12], PdN₂ [13], Re₂N [14], and Re₃N [14] with moderate synthesis conditions and very large bulk modulus (close to 400 GPa) are expected to be alternative materials to traditional superhard materials that are of synthesis expensive. However, transition-metal phosphides, especially the noble-metal phosphides have received minimum attention up to date. While the transition-metal borides are characterized by sharing metal-metalloid bonds with a strong covalent component, transition-metal phosphides have strong and highly metalloid-metalloid bonds [15]. When compared with the bonds observed in metal nitrides and carbides, these metalloid-metalloid bonds are even stronger [16]. Recently, transition-metal phosphides have been strengthened to be high performance catalysts with high activity and high stability in not only strong acidic solutions, but also in strong alkaline and neutral media for electrochemical hydrogen evolution [17].

Transition-metal phosphides can be viewed as doping P atoms into crystal lattices of transition metal. Until now, only six different transition metals (Fe, Co, Ni, Cu, Mo and W) are found to form transition-metal phosphides that can be used for electrochemical

hydrogen evolution [17]. While phosphides of non-noble metals have attracted considerable attention as potential hydrotreating catalysts [18], only recently the synthesis and hydrodesulfurization properties of noble-metal phosphides, like as Ph₂P, Ru₂P, RuP, Pd_{4.8}P, and PtP₂ have been described [19–22]. Ir₂P was first reported in 1935 [23] and it was assigned the CaF₂-type structure [24]. Rundqvist *et al.* [25] established the compositional systematics of platinum-metal phosphides and further examined the crystal structure of Ir₂P with single-crystal diffraction method. Raub *et al.* [26] discovered several new superconductors and they reported among them the Ir₂P exhibited a metallic behavior. Until to this year, it was surprised that the cubic Ir₂P has been synthesized at high pressure and temperature by Wang *et al.* [27] Their research shows that Ir₂P has a high bulk modulus and the relatively low shear modulus from theoretical calculations suggests a complicated overall bonding in Ir₂P with metallic, ionic, and covalent characteristics.

In the present work, some important thermodynamic parameters, like as volume thermal expansion coefficient, heat capacity, and Grüneisen parameter of iridium phosphide Ir₂P are investigated by means of quasi-harmonic Debye model for the first time. This model combines with first-principles calculations within generalized gradient approximation using pseudopotentials and a plane-wave basis in the framework of density functional theory, and it takes into account the phononic effects within the quasi-harmonic approximation. The paper is organized as follows: We explain the computational method in

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Section 2. The results of the Debye temperature as a function of volume, the Grüneisen parameter, thermal expansion coefficient, constant-volume and constant-pressure heat capacities, and entropy and on the temperature T are presented and discussed in **Section 3**, and a brief conclusion is drawn in the **Section 4**.

2. Computational methodology

The calculations were performed using Kohn-Sham density functional theory (DFT) within Vanderbilt ultrasoft pseudopotentials [28] and the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [29] as implemented in the Cambridge Serial Total Energy Package (CASTEP) code [30]. The wave functions of valence electrons are expanded in a basis set of plane waves with kinetic energy smaller than a specified cutoff energy E_{cut} . We distinguished Ir $5d^7 6s^2$ and P $3s^2 3p^3$ shells as valence band electrons. The equilibrium crystal structures were achieved via geometry optimization in the Broyden-Fletcher-Goldfarb-Shanno (BFGS) minimization scheme [31] at the required pressures. In the present calculations, the kinetic energy cutoff E_{cut} and the density of the Monkhorst-Pack [32] k -point meshes were chosen high enough in order to ensure convergence of the computed structures and energetics. The values of 500 eV and $10 \times 10 \times 10$ meshes make the self-consistent convergence of the total energy will be 5.0×10^{-6} eV/atom, the maximum force on the atom will be 0.01 eV/Å, the maximum ionic displacement within 5.0×10^{-4} Å and the maximum stress within 0.02 GPa. The total energies at the equilibrium structures were calculated by means of the corrected tetrahedron Blöchl method [33].

Knowledge of the behaviors of solids, like as transition-metal phosphides, when they are under severe constraints such as high-temperature and high-pressure conditions are of a great interest and importance for both the fundamental research and technological applications. To address this interest in the current work, some thermodynamic properties of Ir_2P were studied carefully at the level of quasi-harmonic Debye model approach [34] at high pressure. These calculations were done for thermal expansion coefficient α , heat capacity at constant volume C_V , heat capacity at constant pressure C_P , entropy S , and Grüneisen parameter γ over the temperature range 0–3000 K and varying the pressure from 0 to 100 GPa. In quasi-harmonic Debye model, the non-equilibrium Gibbs function $G^*(V, P, T)$ can be expressed as:

$$G^*(V, P, T) = E(V) + PV + A_{\text{vib}}(\Theta(V), T), \quad (1)$$

where $E(V)$ is the total energy per unit cell for Ir_2P , PV corresponds to the constant hydrostatic pressure condition, $\Theta(V)$ is the Debye temperature, A_{vib} is the vibrational Helmholtz free energy formulated using the Debye model of the phonon density of states as following:

$$A_{\text{vib}}(\Theta; T) = nkT \left[\frac{9}{8} \frac{\Theta}{T} + 3 \ln(1 - e^{-\Theta/T}) - D\left(\frac{\Theta}{T}\right) \right], \quad (2)$$

where $D(\Theta/T)$ represents the Debye integral, n is the number of atoms per formula unit. For an isotropic solid, Θ is expressed by:

$$\Theta = \frac{\hbar}{k} \left[6\pi^2 V^{1/3} n \right]^{1/3} f(\sigma) \sqrt{\frac{B_S}{M}}, \quad (3)$$

where M is the molecular mass per formula unit and $f(\sigma)$ is formulated by

$$f(\sigma) = \left\{ 3 \left[2 \left(\frac{2}{3} \frac{1 + \sigma}{1 - 2\sigma} \right)^{3/2} + \left(\frac{11 + \sigma}{3} \frac{1 + \sigma}{1 - \sigma} \right)^{3/2} \right]^{-1} \right\}^{1/3} \quad (4)$$

and B_S the adiabatic bulk modulus which is approximately presented by the static compressibility:

$$B_S \approx B_V = V \left[\frac{d^2 E(V)}{dV^2} \right]. \quad (5)$$

Therefore, the non-equilibrium Gibbs function $G^*(V, P, T)$ as a function of (V, P, T) can be minimized with respect to volume V as follows:

$$\left[\frac{\partial G^*(V, P, T)}{\partial V} \right]_{P,T} = 0. \quad (6)$$

By solving Eq. (6) we obtain the thermal equation of state. The heat capacity C_V and the thermal expansion coefficient α are given respectively by:

$$C_V = 3nk \left[4D(\Theta/T) - \frac{3\Theta/T}{e^{\Theta/T} - 1} \right], \quad (7)$$

$$\alpha = \frac{\gamma C_V}{B_T V}, \quad (8)$$

where γ is the Grüneisen parameter, which is defined as

$$\gamma = - \frac{d \ln \Theta(V)}{d \ln V}. \quad (9)$$

3. Results and discussion

Very recently, the cubic Ir_2P has been synthesized at high pressure and temperature by Wang *et al.* [27] and it adopts a CaF_2 -type structure up to 40.6 GPa with a space group of $Fm\bar{3}m$, where the atomic positions in the elementary cell are P (0, 0, 0) and Ir (0:25, 0:25, 0:25), respectively. Each iridium atom of Ir_2P is surrounded by four phosphor atoms and $[\text{IrP}_4]$ tetrahedrons are edge – sharing and form a 3D network, and which together with the pressure vs volume ratio data up to 100 GPa at zero temperature are all shown in Fig. 1. Clearly, one can see from this figure that our results obtained with GGA calculations are in good agreement with the LDA calculated and experimental data of Wang *et al.* [27]. Knowledge of the variation in pressure P with volume V for a single phase determines the equilibrium volume V_0 , and gives access to the bulk modulus $B(V) = -V \left[\frac{dP(V)}{dV} \right]$ and the dimensionless pressure derivative of the bulk modulus $B' = \frac{dB}{dP}$. Here, the fitted equation of state parameters, that is the equilibrium volume V_0 of primitive cell, isothermal bulk modulus B_0 and its first pressure derivative B'_0 from the 3rd-order Birch-Murnaghan EOS [35] for Ir_2P are 42.85 \AA^3 , 318.6 GPa and 4.9, respectively. Compared with

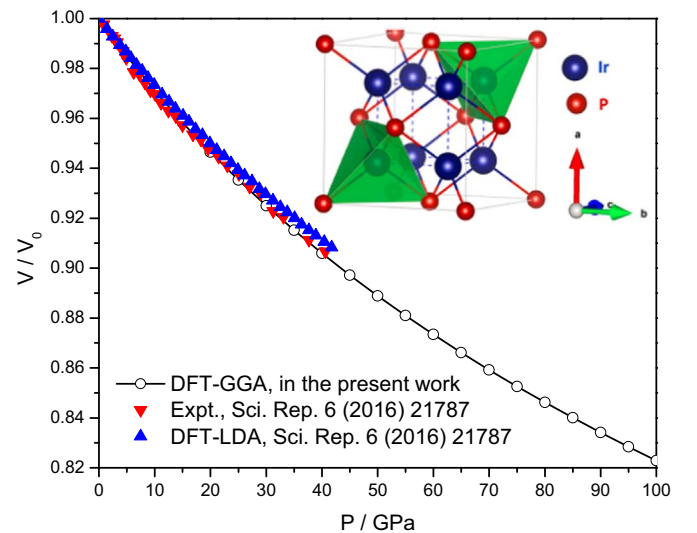


Fig. 1. Comparison of the DFT-GGA-calculated volume ratio for Ir_2P in anti-fluorite phase with experimental and DFT-GGA-calculated data by Wang *et al.* [14]. The inset shows the crystal structure.

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