



## Communication

Thermal expansion, heat capacity and Grüneisen parameter of iridium phosphide Ir<sub>2</sub>P from quasi-harmonic Debye modelZ.J. Liu<sup>a,b,\*</sup>, T. Song<sup>b,c</sup>, X.W. Sun<sup>b</sup>, Q. Ma<sup>c</sup>, T. Wang<sup>b</sup>, Y. Guo<sup>a</sup><sup>a</sup> Department of Physics, Lanzhou City University, Lanzhou 730070, China<sup>b</sup> School of Mathematics and Physics, Lanzhou Jiao tong University, Lanzhou 730070, China<sup>c</sup> School of Material Science and Engineering, Lanzhou University of Technology, Lanzhou 730050, China

## ARTICLE INFO

## Keywords:

A. Ir<sub>2</sub>P  
 D. Thermal expansion  
 D. Heat capacity  
 D. Grüneisen parameter

## ABSTRACT

Thermal expansion coefficient, heat capacity, and Grüneisen parameter of iridium phosphide Ir<sub>2</sub>P 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 Ir<sub>2</sub>P 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 OsB<sub>2</sub> [6], ReB<sub>2</sub> [7], PtC [8], Ta<sub>2</sub>N<sub>3</sub> [9], PtN<sub>2</sub> [10], IrN<sub>2</sub> [11,12], OsN<sub>2</sub> [12], PdN<sub>2</sub> [13], Re<sub>2</sub>N [14], and Re<sub>3</sub>N [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 Ph<sub>2</sub>P, Ru<sub>2</sub>P, RuP, Pd<sub>4.8</sub>P, and PtP<sub>2</sub> have been described [19–22]. Ir<sub>2</sub>P was first reported in 1935 [23] and it was assigned the CaF<sub>2</sub>-type structure [24]. Rundqvist *et al.* [25] established the compositional systematics of platinum-metal phosphides and further examined the crystal structure of Ir<sub>2</sub>P with single-crystal diffraction method. Raub *et al.* [26] discovered several new superconductors and they reported among them the Ir<sub>2</sub>P exhibited a metallic behavior. Until to this year, it was surprised that the cubic Ir<sub>2</sub>P has been synthesized at high pressure and temperature by Wang *et al.* [27]. Their research shows that Ir<sub>2</sub>P has a high bulk modulus and the relatively low shear modulus from theoretical calculations suggests a complicated overall bonding in Ir<sub>2</sub>P 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 Ir<sub>2</sub>P 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

\* Corresponding author at: Department of Physics, Lanzhou City University, Lanzhou 730070, China.  
 E-mail address: [liuzj\\_lzcu@163.com](mailto:liuzj_lzcu@163.com) (Z.J. Liu).

**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  $E_{\text{cut}}$ . 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  $E_{\text{cut}}$  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  $5.0 \times 10^{-6}$  eV/atom, the maximum force on the atom will be 0.01 eV/Å, the maximum ionic displacement within  $5.0 \times 10^{-4}$  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<sub>2</sub>P were studied carefully at the level of quasi-harmonic Debye model approach [34] at high pressure. These calculations were done for thermal expansion coefficient  $\alpha$ , heat capacity at constant volume  $C_V$ , heat capacity at constant pressure  $C_P$ , entropy  $S$ , and Grüneisen parameter  $\gamma$  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<sub>2</sub>P,  $PV$  corresponds to the constant hydrostatic pressure condition,  $\Theta(V)$  is the Debye temperature,  $A_{\text{vib}}$  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,  $\Theta$  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

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

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  $\alpha$  are given respectively by:

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

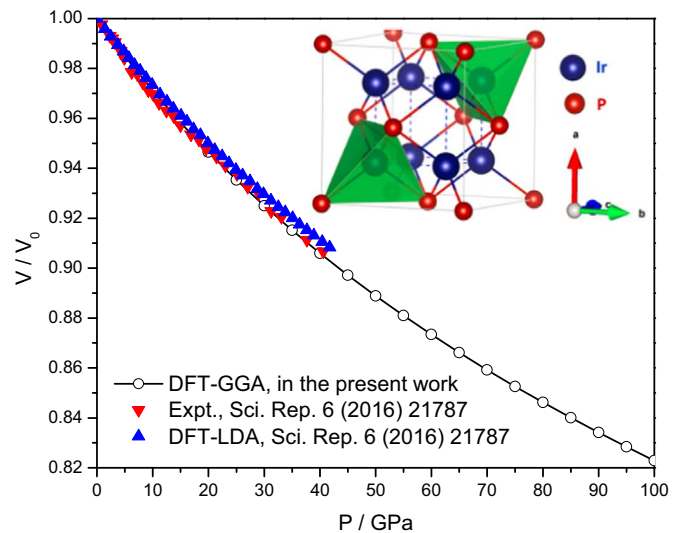
$$\alpha = \frac{\gamma C_V}{B_T V}, \quad (8)$$

where  $\gamma$  is the Grüneisen parameter, which is defined as

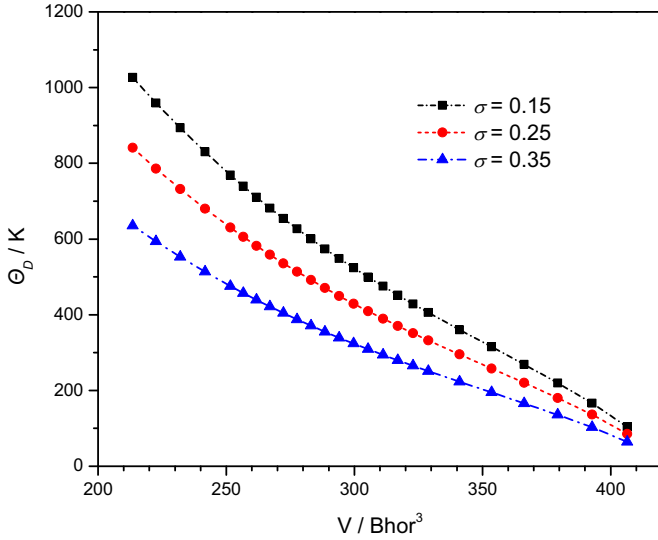
$$\gamma = - \frac{d \ln \Theta(V)}{d \ln V}. \quad (9)$$

## 3. Results and discussion

Very recently, the cubic Ir<sub>2</sub>P has been synthesized at high pressure and temperature by Wang *et al.* [27] and it adopts a CaF<sub>2</sub>-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<sub>2</sub>P is surrounded by four phosphor atoms and [IrP<sub>4</sub>] 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<sub>2</sub>P are 42.85 Å<sup>3</sup>, 318.6 GPa and 4.9, respectively. Compared with



**Fig. 1.** Comparison of the DFT-GGA-calculated volume ratio for Ir<sub>2</sub>P in anti-fluorite phase with experimental and DFT-GGA-calculated data by Wang *et al.* [14]. The inset shows the crystal structure.



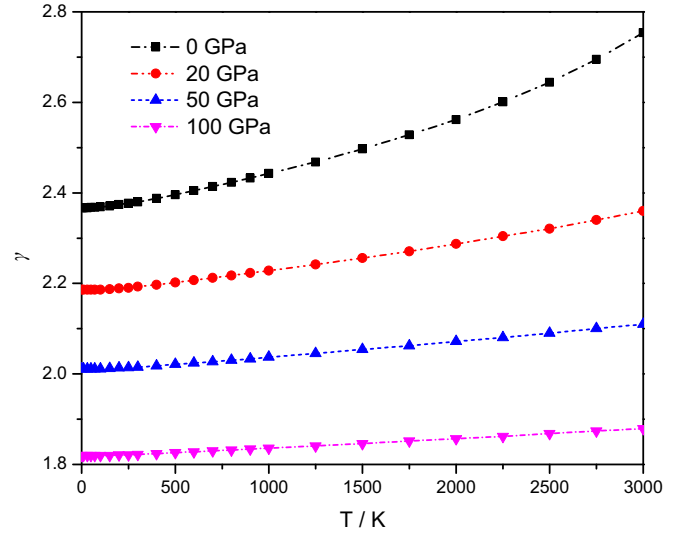
**Fig. 2.** Change of Debye temperature  $\Theta$  for Ir<sub>2</sub>P in CaF<sub>2</sub>-type structure with primitive-cell volume at different Poisson's ratio.

Wang *et al.*'s theoretical and experimental results [27], the good agreement indicates that our calculations are very accurate.

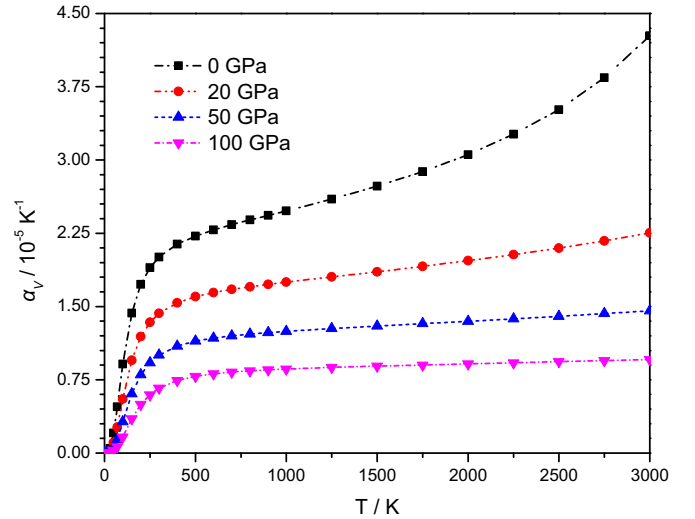
Knowledge of the behaviors of solids under high-pressure and high-temperature environment are of a great interest and importance for both the fundamental research and technological applications. To address this interest in the present work, volume dependences of the Debye temperature  $\Theta$  and temperature dependences of the Grüneisen parameter  $\gamma$ , thermal expansion coefficient  $\alpha$ , constant-volume and constant-pressure heat capacities  $C_V$  and  $C_P$ , and entropy  $S$  of Ir<sub>2</sub>P under high pressure were explored using quasi-harmonic Debye model [34]. Within the Debye model, the Debye temperature  $\Theta$  is one of the fundamental parameters of solids; it is closely correlated with many physical properties, such as thermal expansion, specific heat, melting temperature and so on. The  $\Theta$  is the highest temperature that can be achieved due to a single normal vibration and then it is used to distinguish between high- and low-temperature regions for a solid. The dependence of the Debye temperature on the primitive cell volume for Ir<sub>2</sub>P is depicted in Fig. 2 at three cases of Poisson's ratio ( $\sigma=0.15$ , 0.25, and 0.35, respectively). The Debye temperature generally decreases with the volume increasing and the values are 564.84, 463.75, and 350.83 K for three cases of Poisson's ratio above at zero temperature and pressure. In order to estimate the Grüneisen parameter  $\gamma$ , which describes the anharmonic effects in the vibrating lattice, we need to plot  $\ln\Theta$  versus  $\ln V$ , and the slope of the yielded straight line equals  $\ln$  of the  $\gamma$ . Fig. 3 shows the temperature dependence of Grüneisen parameter for Ir<sub>2</sub>P at different pressures. Here, the temperature up to 3000 K and the pressure up to 100 GPa. It can be seen that the Grüneisen parameter  $\gamma$  increases significantly with pressure decreasing but the temperature effects become less pronounced with the pressure increasing.

From the quasi-harmonic Debye model, the obtained variations of the volume thermal expansion coefficient  $\alpha$  with temperatures at various pressures (0, 20, 50, and 100 GPa) are shown in Fig. 4, and the value calculated at 300 K and zero pressure is about  $2.01 \times 10^{-5} \text{ K}^{-1}$ . It is noted that at zero pressure  $\alpha$  increases exponentially with  $T$  at low temperatures and gradually tends to be slow down at high temperatures. As the pressure increases, the increase of  $\alpha$  with temperature becomes smaller, especially at high temperature. The  $\alpha$  descends drastically with increasing pressure at different temperatures and increases with increasing temperature at different pressures indicating the anharmonic effects are important at low pressures and high temperatures for the cubic Ir<sub>2</sub>P.

Another thermodynamic parameter, heat capacity, is also very



**Fig. 3.** Variation of the Grüneisen parameter  $\gamma$  with the temperature at different pressures for Ir<sub>2</sub>P with CaF<sub>2</sub>-type structure.



**Fig. 4.** Predicted volume thermal expansion coefficient  $\alpha$  of Ir<sub>2</sub>P with CaF<sub>2</sub>-type structure versus temperature at different pressures.

important. The heat capacity of a substance is not only providing essential insight into its vibrational properties, but is also mandatory for many applications. The temperature-dependent behavior of the constant-volume heat capacity,  $C_V$ , and the constant pressure heat capacity,  $C_P$ , at different pressures are shown in Figs. 5 and 6 for Ir<sub>2</sub>P in CaF<sub>2</sub>-type structure. The heat capacities  $C_V$  and  $C_P$  are  $66.72 \text{ J mol}^{-1} \text{ K}^{-1}$  and  $67.68 \text{ J mol}^{-1} \text{ K}^{-1}$  at zero pressure and ambient temperature. It is seen that both curves exhibit a similar trend, but the values of  $C_P$ , as expected, are slightly higher than that for  $C_V$  at higher temperatures. At intermediate temperatures, the temperature dependence of  $C_V$  is governed by the details of vibrations of the atoms. However, under higher temperature, as the anharmonic effect on  $C_V$  is suppressed,  $C_V$  is close to a Dulong-Petit limit ( $C_V(T) \approx 3R$  for mono atomic solids), as shown in Fig. 5. Unlike the constant-volume heat capacity  $C_V$ , the high temperature dependence of entropy  $S$  is nearly insensitive to pressure, as shown in Fig. 7. For the heat capacity, along with Debye temperature, Grüneisen parameter, and thermal expansion coefficient, experimental measurements and other theoretical calculations are needed in order to confirm our results and also to know more about the thermodynamic properties in Ir<sub>2</sub>P under pressure.

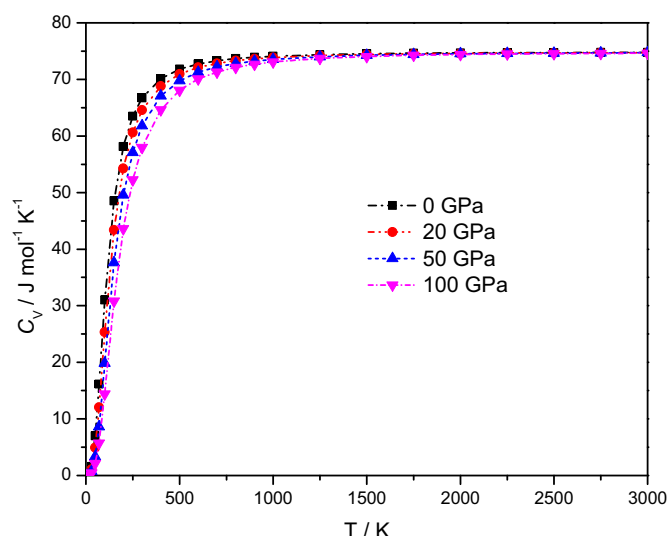


Fig. 5. Predicted constant-volume heat capacity  $C_V$  of  $\text{Ir}_2\text{P}$  with  $\text{CaF}_2$ -type structure versus temperature at different pressures.

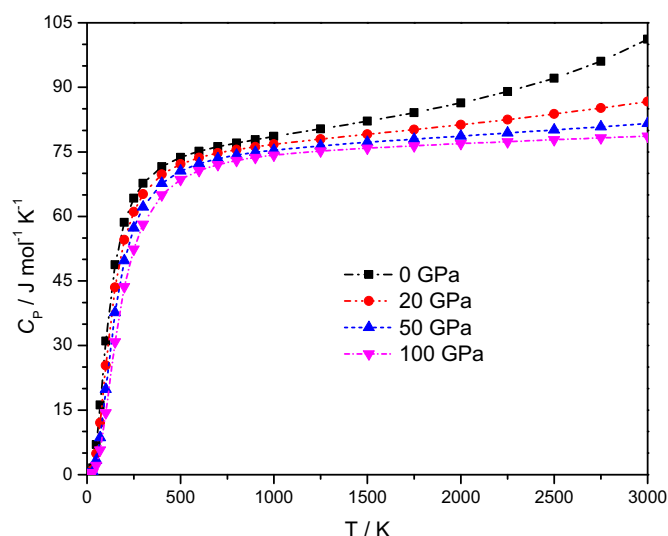


Fig. 6. Predicted constant-pressure heat capacity  $C_P$  of  $\text{Ir}_2\text{P}$  with  $\text{CaF}_2$ -type structure versus temperature at different pressures.

#### 4. Conclusions

In this study, the first-principles calculations of the pressure-volume equation of state and some interesting thermodynamic properties for  $\text{Ir}_2\text{P}$  in  $\text{CaF}_2$ -type structure were reported. The structural parameters (the equilibrium volume, isothermal bulk modulus and its first pressure derivative) are in good agreement with the other theoretical and experimental data. Some basic thermodynamic quantities such as the Debye temperature ( $\Theta_D$ ), Grüneisen parameter ( $\gamma$ ), volume thermal expansion coefficient ( $\alpha$ ), heat capacities ( $C_V$  and  $C_P$ ), and entropy ( $S$ ) of  $\text{Ir}_2\text{P}$  in  $\text{CaF}_2$ -type structure are calculated based on the quasi-harmonic Debye model at various temperatures and pressures, and the results are discussed and interpreted in detail. In the present work, all of the properties of  $\text{Ir}_2\text{P}$  in  $\text{CaF}_2$ -type structure are summarized in the pressure 0–100 GPa ranges and the temperature up to 3000 K.

#### Acknowledgements

The authors would like to thank the supports by the National Natural Science Foundation of China under Grant Nos. 51562021,

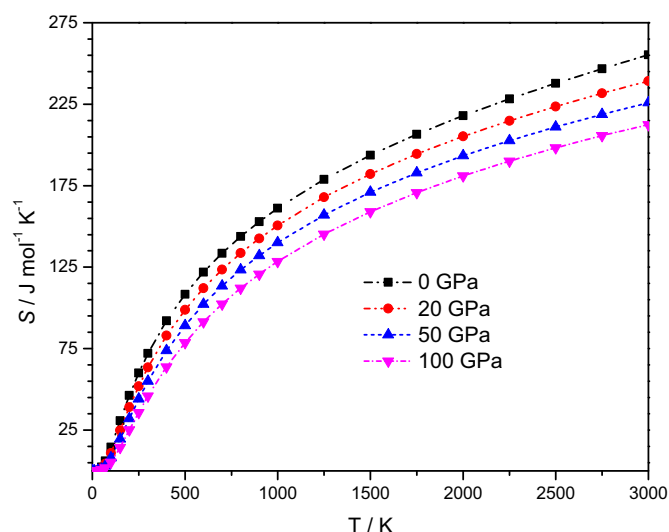


Fig. 7. Predicted entropy  $S$  of  $\text{Ir}_2\text{P}$  with  $\text{CaF}_2$ -type structure versus temperature at different pressures.

11464027, and 11464025, the Natural Science Foundation for Distinguished Young Scholars of Gansu Province under Grant No. 145RJDA323, and the Program for Longyuan Youth Innovation Talents of Gansu Province of China.

#### References

- [1] S.T. Oyama, J. Solid State Chem. 96 (1992) 442.
- [2] M. Zhang, M. Wang, T. Cui, Y. Ma, Y. Niu, G. Zou, J. Phys. Chem. Solids 69 (2008) 2096–2102.
- [3] R.B. Levy, Properties of carbides, nitrides, and Borides: implications, Adv. Mater. Catal. (2013) 101.
- [4] W.-F. Chen, J.T. Muckerman, E. Fujita, Chem. Commun. 49 (2013) 8896.
- [5] Y. Zhong, X. Xia, F. Shi, J. Zhan, J. Tu, H.J. Fan, Adv. Sci. 3 (2016) 1500286.
- [6] R.W. Cumberland, M.B. Weinberger, J.J. Gilman, S.M. Clark, S.H. Tolbert, R.B. Kaner, J. Am. Chem. Soc. 127 (2005) 7264.
- [7] H.-Y. Chung, M.B. Weinberger, J.B. Levine, A. Kavner, J.-M. Yang, S.H. Tolbert, R.B. Kaner, Science 316 (2007) 436.
- [8] S. Ono, T. Kikegawa, Y. Ohishi, Solid State Commun. 133 (2005) 55.
- [9] A. Zerr, G. Miehe, J. Li, D.A. Dzivenko, V.K. Bulatov, H. Höfer, N. Bolfan-Casanova, M. Fialin, G. Brey, T. Watanabe, Adv. Funct. Mater. 19 (2009) 2282.
- [10] E. Gregoryanz, C. Sanloup, M. Somayazulu, J. Badro, G. Fiquet, H.-K. Mao, R.J. Hemley, Nat. Mater. 3 (2004) 294.
- [11] J.C. Crowhurst, A.F. Goncharov, B. Sadigh, C.L. Evans, P.G. Morrall, J.L. Ferreira, A. Nelson, Science 311 (2006) 1275.
- [12] A.F. Young, C. Sanloup, E. Gregoryanz, S. Scandolo, R.J. Hemley, H.-K. Mao, Phys. Rev. Lett. 96 (2006) 155501.
- [13] J.C. Crowhurst, A.F. Goncharov, B. Sadigh, J. Zaug, D. Aberg, Y. Meng, V.B. Prakapenka, J. Mater. Res. 23 (2008) 1.
- [14] A. Friedrich, B. Winkler, L. Bayarjargal, W. Morgenroth, E.A. Juarez-Orellano, V. Milman, K. Refson, M. Kunz, K. Chen, Phys. Rev. Lett. 105 (2010) 085504.
- [15] S.B. Schneider, D. Baumann, A. Salamat, Z. Konôpkova, H.-P. Liermann, M.R. Schwarz, W. Morgenroth, L. Bayarjargal, A. Friedrich, Br Winkler, Chem. Mater. 24 (2012) 3240.
- [16] S. Carenco, D. Portehault, C. Boissière, N. Mézailles, C. Sanchez, Chem. Rev. 113 (2013) 7981.
- [17] Y. Shi, B. Zhang, Chem. Soc. Rev. 45 (2016) 1529.
- [18] S.T. Oyama, T. Gott, H. Zhao, Y.-K. Lee, Catal. Today 143 (2009) 94.
- [19] J.R. Hayes, R.H. Bowker, A.F. Gaudette, M.C. Smith, C.E. Moak, C.Y. Nam, T.K. Pratun, M.E. Bussell, J. Catal. 276 (2010) 249.
- [20] R.H. Bowker, M.C. Smith, M.L. Pease, K.M. Slenkamp, L. Kovarik, M.E. Bussell, ACS Catal. 1 (2011) 917.
- [21] Y. Kanda, C. Temma, K. Nakata, T. Kobayashi, M. Sugioka, Y. Uemichi, Appl. Catal. A-Gen. 386 (2010) 171.
- [22] Q. Guan, C. Sun, R. Li, W. Li, Catal. Commun. 14 (2011) 114.
- [23] W. Blatz, F. Weibke, E. May, Z. Anorg. Allg. Chem. 223 (1935) 129.
- [24] M. Zumbusch, Zeitschrift für anorganische und allgemeine Chemie, 243, 1940, p. 322.
- [25] S. Rundqvist, Nature 185 (1960) 31.
- [26] C.J. Raub, W. Zachariasen, T. Geballe, B. Matthias, J. Phys. Chem. Solids 24 (1963) 1093.
- [27] P. Wang, Y. Wang, L. Wang, X. Zhang, X. Yu, J. Zhu, S. Wang, J. Qin, K. Leinenweber, H. Chen, Sci. Rep. 6 (2016) 21787.
- [28] D. Vanderbilt, Phys. Rev. B 41 (1990) 7892.

- [29] J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865.
- [30] M.C. Payne, M.P. Teter, D.C. Allan, T. Arias, J. Joannopoulos, Rev. Mod. Phys. 64 (1992) 1045.
- [31] B.G. Pfrommer, M. Côté, S.G. Louie, M.L. Cohen, J. Comput. Phys. 131 (1997) 233.
- [32] H.J. Monkhorst, J.D. Pack, Phys. Rev. B 13 (1976) 5188.
- [33] P.E. Blöchl, O. Jepsen, O.K. Andersen, Phys. Rev. B 49 (1994) 16223.
- [34] M. Blanco, E. Francisco, V. Luana, Comput. Phys. Commun. 158 (2004) 57.
- [35] F. Birch, Phys. Rev. 71 (1947) 809.