A new transition metal diphosphide α-MoP_2 synthesized by a high-temperature and high-pressure technique

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Monoclinic α-MoP_2, with the $OsGe_2$-type structure (space group $C2/m$, $Z = 4$) and lattice parameters $a = 8.7248(11)$ Å, $b = 3.2322(4)$ Å, $c = 7.4724(9)$ Å, and $\beta = 119.263°$, was synthesized under a pressure of 4 GPa at a temperature between 1100 °C and 1200 °C. The structure of α-MoP_2 and its relationship to other transition metal diphosphides are discussed. Surprisingly, the ambient pressure phase orthorhombic β-MoP_2 (space group $Cmc2_1$) is denser in structure than α-MoP_2. Room-temperature high-pressure x-ray diffraction studies exclude the possibility of phase transition from β-MoP_2 to α-MoP_2, suggesting that α-MoP_2 is a stable phase at ambient conditions; this is also supported by the total energy and phonon calculations.

Keywords: high-pressure synthesis, monoclinic MoP_2, crystal structure

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1. Introduction

Transition metal diphosphides (TmP_2, Tm = transition metal) represent an important family with rich physical properties that have received renewed research interest owing to the nontrivial topological states associated with exotic properties such as extremely large magnetoresistance (XMR).[1–6] These fundamentally important and technically useful physical properties naturally suggest the exploration of analogue compounds; this led to the discovery of the $OsGe_2$-type structure of TmP_2.[7–9] Since such nonmagnetic TmP_2 generally show XMR, for example in ZrP_2, α- and β-WP_2, β-MoP_2, TaP_2, etc., due to either the non-trivial topological electronic states or compensated carriers,[3–6] $OsGe_2$-type MoP_2 is naturally expected to have similar intriguing physical properties. However, $OsGe_2$-type MoP_2 has not yet been synthesized, leaving open the opportunity to achieve a complete understanding of $OsGe_2$-type TmP_2 by studying the physical properties with varied Tm.

The thermodynamically stable/metastable phases of the binary Mo–P phase diagrams, including Mo_3P, MoP, MoP_2, and MoP_4 and the metastable Mo_8P_5 and Mo_4P_3, have been investigated in the pressure range of 0 GPa–200 GPa[10] by first principles calculations combined with an evolutionary algorithm. Three new thermodynamically stable phases, including Mo_4P (191 GPa–200 GPa), Mo_2P (65 GPa–200 GPa) and Mo_2P_3 (31 GPa–200 GPa), were predicted to exist under pressure.[10] Given that WP_2 has two polymorphic forms, namely, the room-temperature monoclinic (space group $C2/m$) phase α-WP_2 and the high-temperature orthorhombic (space group $Cmc2_1$) phase β-WP_2,[11,12] the use of high-pressure synthesis to explore new Mo–P binary phases would be valuable.

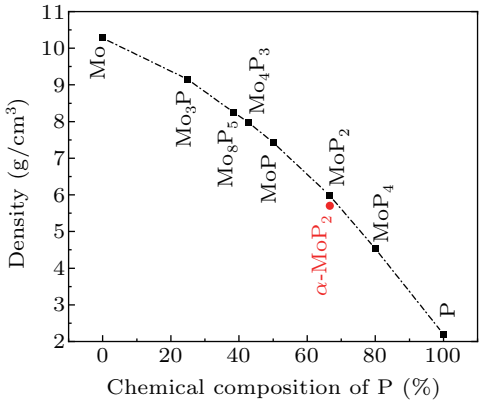


Fig. 1. Densities of α-MoP_2 and other Mo–P compounds. Data for the ambient pressure phases were taken from previous publications.[11,13–15]

In this paper, using high-pressure and high-temperature

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synthesis (HPHT) on a multi-anvil apparatus (SHTech-2000),[16,17] we succeeded in growing high-quality crystals of monoclinic MoP_2, which we name α-MoP_2 to distinguish it from β-MoP_2 with an orthorhombic structure. Surprisingly, the estimated structural densities of the HPHT MoP_2 phases are smaller than those of other phases, unlike most cases[18] seen in the plot in Fig. 1. The structural differences between α-MoP_2 and other TmP_2 are discussed in detail. High-pressure x-ray diffraction (HPXRD) experiments with β-MoP_2 at room temperature and phonon calculations support the stability of the monoclinic phase at ambient conditions.

2. Experimental and computational methods

The staring materials, Mo (Alfa 99.7%) and red phosphorus (Katayama Chemical 200 mesh, 99%) powders, were mixed in the ratio Mo : P = 1 : 2.5 in an Ar filled glove box. The mixture was pre-compressed into a cylinder 3.5 mm in diameter and 4 mm high, and then put into a hexagonal boron nitride chamber. The sample chamber was placed into a Ta heating furnace and then packed into a MgO octahedron. The assembly was pressed in a multi-anvil apparatus at 3 GPa–5 GPa and 1000 °C–1200 °C for 30 min. Detailed information about the HPHT synthesis technique can be found elsewhere.[16]

Examinations of the crystallographic phase and crystal quality of the product were performed with a Bruker D8 single-crystal x-ray diffractometer with Mo K_α (λ = 0.71073 Å) at 298.0 K. Using Olex2,[19] the structure was solved with the SHELXT[20] structure solution program and was refined with the SHELXL[21] refinement package using the least squares minimization. The parameters for data collection and details of the structure refinements are given in Table 1. Atomic coordinates and thermal displacement parameters (U_{eq}) are given in Table 2, anisotropic displacement parameters are given in Table 3 and selected interatomic distances are given in Table 4.

To examine whether β-MoP_2 could be pressed into the α-phase at high pressure and ambient temperature, we performed a HPXRD experiment. Measurements on β-MoP_2 crystals were carried out in a symmetric type diamond anvil cell with a diamond culet size of 300 mm. Silicon oil was used as the pressure transmitting medium[22] and the pressure was measured with the ruby fluorescence technique.[23] High-pressure synchrotron XRD patterns were collected at beamline BL15U1 of the Shanghai Synchrotron Radiation Facility, with a monochromatic beam wavelength of 0.6199 Å, using the MarCCD detector. The Fit2D software package was used to process the XRD data.[24] The XRD patterns of β-MoP_2 were analyzed with Rietveld refinement using the GSAS program package[25] with the user interface EXPGUI.[26]

The total energy calculations and structural optimization were performed using the plane-wave basis, projected augmented wave (PAW) potentials, and generalized gradient approximation with the Perdew–Burke–Ernzerhof exchange–correlation functional as implemented in the Vienna *ab initio* simulation package.[27–31] The frozen-core all-electron PAW potentials were used with $4p^6 5s^1 4d^5$ and $3s^2 3p^3$ treated as valence electrons for Mo and P, respectively. The cutoff energy (900 eV) for the expansion of the wave function into plane waves and Monkhorst–Pack[32] k-meshes (k-point density 0.02 $Å^{-1}$) were chosen to ensure that all the enthalpy calculations are well converged to better than 1 meV/atom. Phonon calculations were performed on the structures to determine their dynamic stability, by using a finite displacement approach as implemented in the PHONOPY code.[33]

Table 1. Crystal information and structure refinement results for α-MoP_2 at 298.0 K.

Empirical formula	α-MoP_2
Formula weight	157.88
Temperature (K)	298.0
Crystal system	monoclinic
Space group	$C2/m$
Unit-cell dimensions	$a = 8.7248(11)$ Å, $\alpha = 90°$, $b = 3.2322(4)$ Å, $\beta = 119.263°$, $c = 7.4724(9)$ Å, $\gamma = 90°$
Volume, Z	183.83(4) $Å^3$, 4
Density (calculated)	5.704 g/cm^3
Absorption coefficient	8.312 mm^{-1}
$F(000)$	288.0
Crystal size	0.214 mm × 0.10 mm × 0.05 mm
Radiation	Mo K_α ($\lambda = 0.71073$ Å)
2θ range for data collection	6.25° to 50.224°
Index ranges	$-10 \le h \le 10$, $-3 \le k \le 3$, $-8 \le l \le 8$
Reflections collected	1661
Independent reflections	196 [$R_{int} = 0.0493$, $R_{sigma} = 0.0270$]
Data/restraints/parameters	196/0/20
Goodness-of-fit F^2	1.279
Final R indices [$I \ge 2\sigma(I)$]	$R_1 = 0.053$, $\omega R_2 = 0.156$
Final R indices (all data)	$R_1 = 0.053$, $\omega R_2 = 0.0156$
Largest diffraction peak/hole/e ($Å^{-3}$)	2.08/−2.11

Table 2. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for α-MoP_2.

	Wyckoff	x	y	z	U_{eq}^a
Mo	4i	0.3403(2)	1	0.7981(3)	12.9(1)
P(1)	4i	0.5980(1)	0.5	0.8987(2)	44(2)
P(2)	4i	0.1345(1)	0.5	0.5242(2)	44(2)

Table 3. Anisotropic displacement parameters ($Å^2 \times 10^3$) for α-MoP_2.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo	12.1(1)	12.5(2)	14.7(2)	0	7.0(9)	0
P(1)	42(5)	43(5)	47(5)	0	21(4)	0
P(2)	41(5)	43(5)	48(5)	0	21(4)	0

Table 4. Selected interatomic distances (Å) for $OsGe_2$-type TmP_2 (Tm = Mo/W).

	Tm = Mo	Tm = W
Tm–Tm	2.942(4)	2.847(1)
Tm–P(1) × 2	2.616(8)	2.666(7)
Tm–P(1) × 2	2.565(7)	2.499(3)
Tm–P(1)	2.567(9)	2.472(5)
Tm–P(2) × 2	2.536(7)	2.474(7)
Tm–P(2)	2.523(1)	2.518(4)
P(2)–P(2)	2.193(2)	2.241(2)

3. Results and discussion

The sample assembly for the preparation of α-MoP_2 was first precompressed under a pressure of 4 GPa and then heated up to 1100 °C within 20 min while maintaining the pressure. After reaction for 2 h at this temperature, the sample was slowly cooled down to 900 °C within 3 h, followed by quenching to room temperature and finally releasing the pressure. The stoichiometric ratio of the sample was examined by element-resolved energy dispersive x-ray spectroscopy, as shown in Fig. 2(b). Average compositions measured at different points on the crystal reveal good stoichiometry with the atomic ratio of Mo : P $(33.51\% : 66.49\%) = 1 : 2$. The analysis of single-crystal XRD data showed that α-MoP_2 crystallized in the $C2/m$ space group with the lattice parameters of $a = 8.7248$ Å, $b = 3.2322$ Å, $c = 7.4724$ Å and $\beta = 119.263°$. The $OsGe_2$-type structure of MoP_2 is different from the orthorhombic phase,[12] which was synthesized for the first time. The diffraction patterns in the reciprocal space along the $(hk0)$, $(h0l)$, and $(0kl)$ directions are shown in Figs. 2(c)–2(e), demonstrating the high quality of the crystal by the perfect reciprocal space reflections without any other miscellaneous points. Information about the crystal and the results of structural refinement are summarized in Table 1.

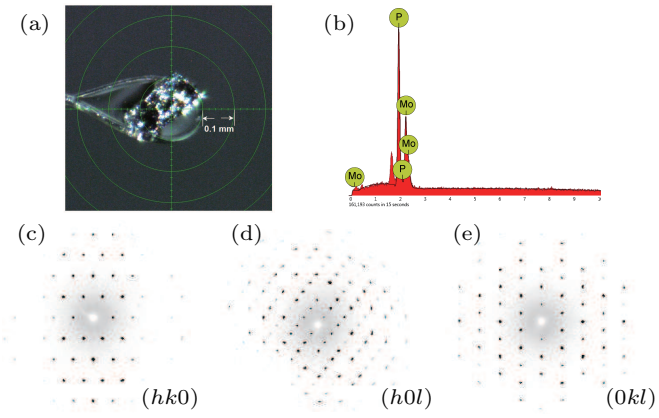


Fig. 2. (a) Optical image of α-MoP_2 single crystal. (b) Energy dispersive x-ray spectroscopy of α-MoP_2 shows that the atomic ratio of Mo : P = 1 : 2. (c)–(e) Single-crystal XRD patterns in reciprocal space along the $(hk0)$, $(h0l)$, and $(0kl)$ directions.

It is necessary to compare the two crystallographic phases of MoP_2 for a better understanding of the structure of α-MoP_2. α- and β-MoP_2 were grown by the HPHT and chemical vapor transport methods, respectively. Orthorhombic MoP_2 crystallizes in the space group $Cmc2_1$, with one Mo and two P ions located on 4a Wyckoff positions and chains of molybdenum polyhedra running along the crystallographic a axis. Monoclinic MoP_2 crystallizes in the space group $C2/m$, with one Mo and two P ions located on 4i Wyckoff positions and chains of molybdenum polyhedra running along the crystallographic b axis. Sketches of the crystal structures of both phases are illustrated in Fig. 3. One of the roles of high pressure is to increase the coordination number (CN) of the atoms. As expected, monoclinic MoP_2 has a higher CN (8 for Mo) than orthorhombic MoP_2 (7 for Mo). Along with the higher CN, the interatomic distances are larger. The shortest Mo–P distance in α-MoP_2 is 2.52 Å, which is larger than the value of 2.48 Å in β-MoP_2. Moreover, the average of eight Mo–P distances in α-MoP_2 is 2.57 Å, which is also larger than the value of 2.49 Å in β-MoP_2.

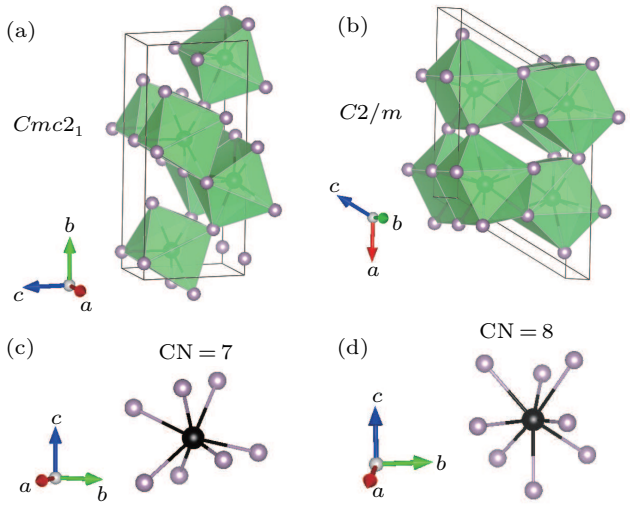


Fig. 3. Schematic crystal structure and the CNs for Mo atoms of (a) β-MoP_2 and (b) α-MoP_2.

In most cases, single-crystal growth for the same phase can be achieved by a variety of techniques. For example, the CrP_4 crystals could be prepared by both HPHT and the Sn flux method under ambient pressure.[15,34] However, for some phases, they can only appear under extreme conditions such as HPHT. Synthesis of α-MoP_2 has not yet been achieved under ambient pressure, maybe because the chemical bonds among the elements cannot be formed, while HPHT conditions provide an environment facilitating the formation of α-MoP_2 rather than pressing a denser phase. From the viewpoint of crystallography, orthorhombic β-MoP_2 has a higher structural symmetry than monoclinic α-MoP_2. Materials with a higher structural symmetry tend to crystallize into close-packed structures with larger densities, which might account for the smaller structural density of α-MoP_2.

Since metal elements of the same group have similar physical properties and larger radii with increasing atomic

number, intermetallic compounds of the same structure generally change steadily in volume with the substitution of metal elements in the same group. Figure 4 shows the lattice parameters for α-TmP_2 as a function of atomic number, including the axes, beta angle and unit cell volume. It is apparent that there is no simple positive evolution between the lattice parameters and the atomic number. According to a simple estimation, WP_2 should have longer axes and a larger volume than MoP_2, which is contrary to the observations in Figs. 4(a) and 4(b). To see the detailed near-neighbor environments in MoP_2 and WP_2, the adjacent bond lengths and bond angles of Mo and W are depicted in Fig. 5. The bond lengths between Tm and P atoms in MoP_2 are all slightly smaller than those in WP_2, except for the bond lengths of the two Tm–P(1). It is worth noting that if Mo is replaced by W, a similar method to a change in external pressure,[35] not only is the metal atom distance reduced but the angle ∠P(2)–Tm–P(2) is increased. This change is hypothesized to be due to the nonlinear extraction behavior shown in Fig. 4, which arises from the effect of the lanthanide contraction that could effectively alter the interatomic space. The distance between Mo metal atoms is 2.942 Å, which is reduced to 2.847 Å in WP_2. Meanwhile, ∠P(2)–Tm–P(2) is increased from 65.05° in MoP_2 to 68.92° in WP_2. Therefore, lanthanide contraction can be applied to control the bond length or strength by simulating the external pressure.

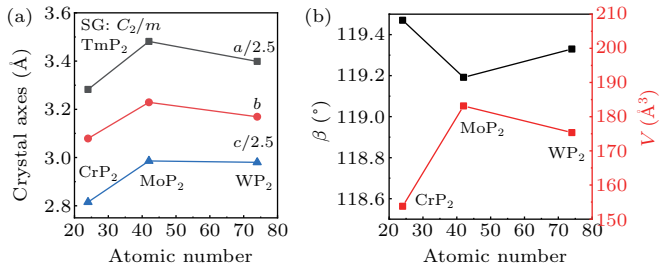


Fig. 4. Lattice parameters a, b, c, β, and volume V in α-TmP_2 (Tm = Cr, Mo, W). SG denotes the space group.

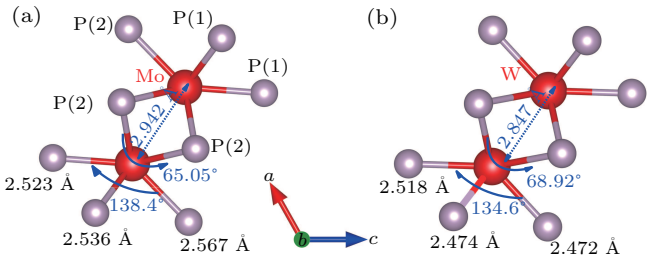


Fig. 5. Nearest-neighbor environments in the α-MoP_2 (a) and α-WP_2 (b) structures.

It should be noted that the HPHT phase α-MoP_2 is quenchable and stable at ambient conditions. Therefore, to establish the temperature–pressure phase diagram for MoP_2, we also tried to synthesize monoclinic MoP_2 by applying a larger pressure on the orthorhombic phase at room temperature. The HP-XRD measurements on β-MoP_2 up to 30 GPa gives the evolution of lattice parameters as a function of pressure seen in Fig. 6(a). It is apparent that all diffraction peaks shift towards higher angles without structural phase change with increasing pressure, consistent with the results of the previous experiment measured from ambient conditions to 6.8 GPa and 839 K[36] The enthalpies of the $Cmc2_1$ and $C2/m$ structures are plotted as a function of pressure in Fig. 6(b), which shows clearly that the $Cmc2_1$ structure is the most stable up to 40 GPa, implying that the application of pressure alone could not achieve the $C2/m$ phase. The results are in excellent agreement with the experiment. Besides, we calculated the phonon dispersion curve for the $C2/m$ phase at 0 GPa using the supercell method, which shows no imaginary phonon frequencies in the whole Brillouin zone, seen in Fig. 6(c), indicating that the $C2/m$ structure is dynamically stable at ambient conditions.

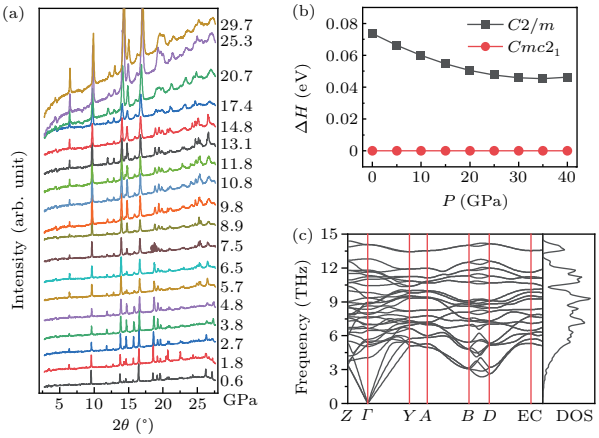


Fig. 6. (a) The selected angle dispersive XRD patterns of β-MoP_2 under various pressures up to 29.7 GPa at room temperature. (b) Enthalpy curves for $C2/m$ and $Cmc2_1$ structures as a function of pressure. (c) Phonon dispersion and phonon densities of states (DOS) curves for the α-MoP_2 at 0 GPa.

4. Conclusion

In summary, using a multi-anvil HPHT synthesis technique we have discovered a new high-pressure phase, α-MoP_2, with a $C2/m$ structure. α-MoP_2 has a larger CN and an anomalous smaller structural density as compared with those of the ambient pressure phase β-MoP_2, which is mainly due to lanthanide contraction. The total energy and phonon calculations indicate that α-MoP_2 is dynamically stable at ambient conditions and could not be obtained by pressing β-MoP_2 at room temperature. Our results provide a new phase of MoP_2 and would be a good guideline for the synthesis of novel transition metal phosphides.

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References

[1] Liu X L, Wang H Y, Su H, Yu Z H and Guo Y F 2020 *Tungsten* **2** 251

[2] Kumar N, Sun Y, Xu N, Manna K, Yao M, Süss V, Leermakers I, Young O, Förster T, Schmidt M, Borrmann H, Yan B, Zeitler U, Shi M, Felser C and Shekhar C 2017 *Nat. Commun.* **8** 1642

[3] Bannies J, Razzoli E, Michiardi M, Kung H H, Elfimov I S, Yao M, Fedorov A, Fink J, Jozwiak C, Bostwick A, Rotenberg E, Damascelli A and Felser C 2021 *Phys. Rev. B* **103** 155144

[4] Du J H, Lou Z F, Zhang S N, Zhou Y X, Xu B J, Chen Q, Tang Y Q, Chen S J, Chen H C, Zhu Q Q, Wang H D, Yang J H, Wu Q S, Yazyev O V and Fang M H 2018 *Phys. Rev. B* **97** 245101

[5] Wang A F, Graf D, Stein A, Liu Y, Yin W G and Petrovic C 2017 *Phys. Rev. B* **96** 195107

[6] Wang A F, Graf D, Liu Y, Du Q H, Zheng J B, Lei H C and Petrovic C 2017 *Phys. Rev. B* **96** 121107

[7] Sims C, Hosen M M, Aramberri H, Huang C Y, Dhakal G, Dimitri K, Kabir F, Regmi S, Zhou X, Chang T R, Lin H, Kaczorowski D, Kioussis N and Neupane M 2020 *Phys. Rev. Mater.* **4** 054201

[8] Wulferding D, Lemmens P, Büscher F, Schmeltzer D, Felser C and Shekhar C 2020 *Phys. Rev. B* **102** 075116

[9] Autès G, Gresch D, Troyer M, Soluyanov A A and Yazyev O V 2016 *Phys. Rev. Lett.* **117** 066402

[10] Cao K, Qu X X, Jiang H, Su Y H, Zhang C and Frapper G 2019 *J. Phys. Chem. C* **123** 30187

[11] Rundqvist S L and Torsten 1963 *Acta Chem. Scand.* **17** 37

[12] Hulliger F 1964 *Nature* **204** 775

[13] Johnsson T 1972 *Acta Chem. Scand.* **26** 365

[14] Leclaire A, Borel M M, Grandin A and Raveau B 1989 *Acta Crystallogr. Sect. C* **45** 540

[15] Jeitschko W and Donohue P C 1972 *Acta Crystallogr. Sect. B* **28** 1893

[16] Liu X L, Yu Z H, Liang Q F, Zhou C Y, Wang H Y, Zhao J G, Wang X, Yu N, Zou Z Q and Guo Y F 2020 *Chem. Mat.* **32** 8781

[17] Li C Y, Liu X L, Yu Z H, Wu W, Zhang L L, Zhou C Y, Zhao J G, Guo Y F and Luo J L 2021 *Phys. Status Solidi B* **258** 2000544

[18] Jeitschko W and Donohue P C 1973 *Acta Crystallogr. Sect. B* **29** 783

[19] Dolomanov O V, Bourhis L J, Gildea R J, Howard J A K and Puschmann H 2009 *J. Appl. Crystallogr.* **42** 339

[20] Sheldrick G M 2015 *Acta Crystallogr. Sect. A.* **71** 3

[21] Sheldrick G M 2015 *Acta Crystallogr. Sect. C.* **71** 3

[22] Liu G, Kong L P, Yang W G and Mao H K 2019 *Mater. Today.* **27** 91

[23] Mao H K, Xu J and Bell P M 1986 *J. Geophys. Res.-Solid Earth.* **91** 4673

[24] Hammersley A P, Svensson S O, Hanfland M, Fitch A N and Hausermann D 1996 *High Pressure Res.* **14** 235

[25] Allen C L and Dreele R B V 2004 *Los Alamos National Laboratory Report LAUR* 86

[26] Toby B 2001 *J. Appl. Crystallogr.* **34** 210

[27] Blochl P E 1994 *Phys. Rev. B* **50** 17953

[28] Dong W, Kresse G, Furthmuller J and Hafner J 1996 *Phys. Rev. B.* **54** 2157

[29] Kresse G and Furthmuller J 1996 *Phys. Rev. B* **54** 11169

[30] Perdew J P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865

[31] Kresse G and Joubert D 1999 *Phys. Rev. B* **59** 1758

[32] Monkhorst H J and Pack J D 1976 *Phys. Rev. B* **13** 5188

[33] The program Phonopy is available at http://phonopy.sourceforge.net/; the force constant matrix is determined by VASP

[34] Kanatzidis M G, Pöttgen R and Jeitschko W 2005 *Angewandte Chemie International Edition.* **44** 6996

[35] Chen K Y, Wang N N, Yin Q W, Gu Y H, Jiang K, Tu Z J, Gong C S, Uwatoko Y, Sun J P, Lei H C, Hu J P and Cheng J G 2021 *Phys. Rev. Lett.* **126** 247001

[36] Soto V, Knorr K, Ehm L, Baehtz C, Winkler B and Avalos-Borja M 2004 *Zeitschrift für Kristallographie-Crystalline Materials* **219** 309