



STRUCTURAL SCIENCE
CRYSTAL ENGINEERING
MATERIALS

Volume 75 (2019)

Supporting information for article:

Perovskite R-3c phase AgCuF₃: multiple Dirac cones, 100% spin polarization, and its thermodynamic properties

Mingquan Kuang, Tingzhou Li, Zhengxiang Cheng, Houari Khachai, R. Khenata, Tie Yang, Tingting Lin and Xiaotian Wang

S1. Quasi-harmonic Debye model

In quasi-harmonic Debye model, the solid non-equilibrium Gibbs free energy is represented as follow:

$$G^*(V; P, T) = E(V) + PV + A_{vib}(\theta_D(V); T)$$

here, $E(V)$ is the total energy per unit cell, PV term represents the constant hydrostatic pressure condition, A_{vib} represents the vibrational Helmholtz free energy, and the $\theta_D(V)$ is Debye temperature.

The concrete form of A_{vib} is given as:

$$A_{vib}(\theta_D(V); T) = nkT \left[\frac{9\theta_D}{8T} + 3 \ln \left(1 - e^{-\frac{\theta_D}{T}} \right) - D\left(\frac{\theta_D}{T}\right) \right]$$

where n is the number of atoms per formula unit, and the Debye integral $D(y)$ is expressed as:

$$D(y) = \frac{3}{y^3} \int_0^y \frac{x^3}{e^x - 1} dx$$

also, the form of Debye temperature for isotropic solid is:

$$\theta_D = \frac{\hbar}{k} [6\pi^2 V^{1/2} n]^{1/3} f(\sigma) \sqrt{\frac{K_s}{M}}$$

where M represents molecular mass per formula unit, K_s denotes the static bulk modulus, which is defined as:

$$K_s \approx K_{Static} = V \left[\frac{d^2 E(V)}{dV^2} \right]$$

and the $f(\sigma)$ is given as:

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

here, σ denotes Poisson ratio.

The equilibrium volume $V(T, P)$ curve (equation of states(EOS)) can be acquired from:

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

Define the isothermal bulk modulus B_T as:

$$B_T(T, P) = -V \left(\frac{\partial P}{\partial V} \right)_T$$

which is calculated at $V(T, P)$.

Heat capacity C_V can be computed from:

$$C_{V, vib} = 3nk_B \left[4D \left(\frac{\theta_D}{T} \right) - \frac{3\theta_D/T}{e^{\theta_D/T} - 1} \right]$$

Grüneisen parameter γ_{th} can be given from:

$$\gamma_{th} = - \frac{d \ln \theta_D(V)}{d \ln V}$$

based on γ_{th} , the coefficient of thermal volume-expansion α_V is represented as:

$$\alpha_V = \frac{\gamma_{th} C_{V, vib}}{B_T V}$$

S2. Formation and cohesive energies

The formation energies of $\bar{R\overline{3}c}$ AgCuF_3 (FM state) can be defined as follows (Emery & Wolverton, 2017; Vinichenko *et al.*, 2017; Zhou *et al.*, 2016):

$$E(f) = E(\text{AgCuF}_3) - \mu(\text{AgF}) - \mu(\text{CuF}_2) \text{ or } E(f) = E(\text{AgCuF}_3) - \mu(\text{AgF}_2) - \mu(\text{CuF});$$

Where $E(\text{AgCuF}_3)$ is the total energy of the FM AgCuF_3 , $\mu(\text{AgF})$, $\mu(\text{AgF}_2)$, $\mu(\text{CuF})$, and $\mu(\text{CuF}_2)$ are the chemical potentials of AgF , AgF_2 , CuF , and CuF_2 at FM state.

The calculated results of $E(f)$ have been listed in Table S1, in this work, four cases of $E(f)$ have been taken into consideration. And from this table, one can see that all cases of $E(f)$ have negative values, reflecting that AgCuF_3 is structural stable.

Table S1 calculated formation energies of FM state for $\bar{R\overline{3}c}$ AgCuF_3

Type e	constituent	symmetry	constituent	symmetry	$E(f)$ (eV)
1	AgF (Marchetti <i>et al.</i> , 1971)	FM-3M	CuF_2 (Zheng <i>et al.</i> , 2012)	P21/C	-0.068
2	AgF_2 (Romiszewski <i>et al.</i> , 2007)	P21/C	CuF (Jagau <i>et al.</i> , 2015)	Gas	-3.272
3	AgF_2 (Grzelak <i>et al.</i> , 2017)	PBCN	CuF (Jagau <i>et al.</i> , 2015)	Gas	-3.498
4	AgF_2 (Fischer <i>et al.</i> , 1971)	PBCA	CuF (Jagau <i>et al.</i> , 2015)	Gas	-3.259

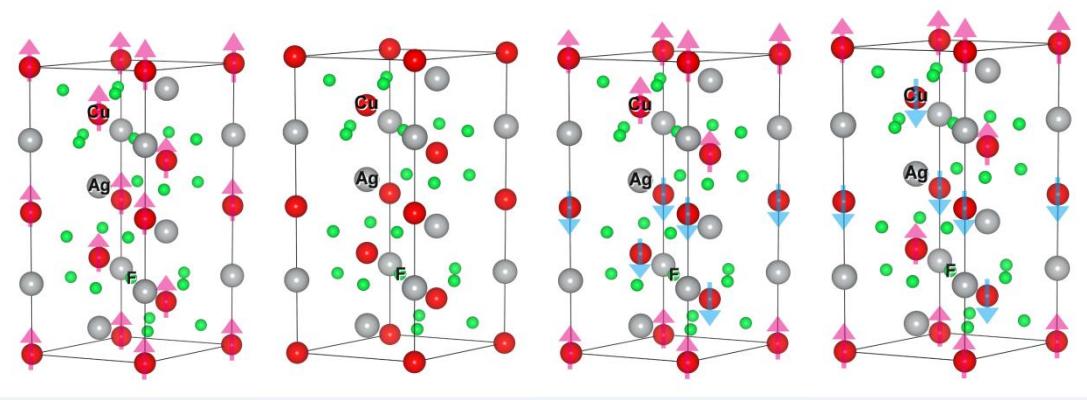
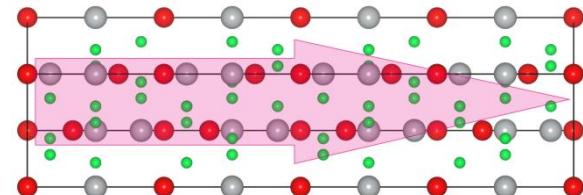
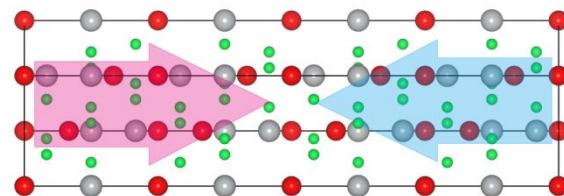
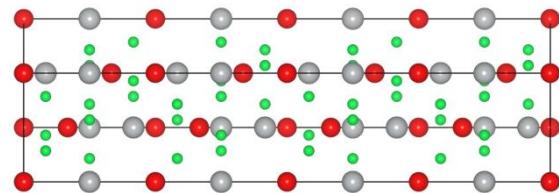
(a) $\Delta E_{FM} = 0$ meV (b) $\Delta E_{NM} = +85$ meV (c) $\Delta E_{AFM1} = +6$ meV (d) $\Delta E_{AFM2} = +93$ meV(e) $\Delta E_{FM} = 0$ meV(f) $\Delta E_{AFM} = +27$ meV(g) $\Delta E_{NM} = +160$ meV

Figure S1. (a)-(d) Magnetic structures of conventional cell for evaluating ground state. (e)-(g)

Magnetic structures of $1 \times 1 \times 2$ superlattice for evaluating ground state.

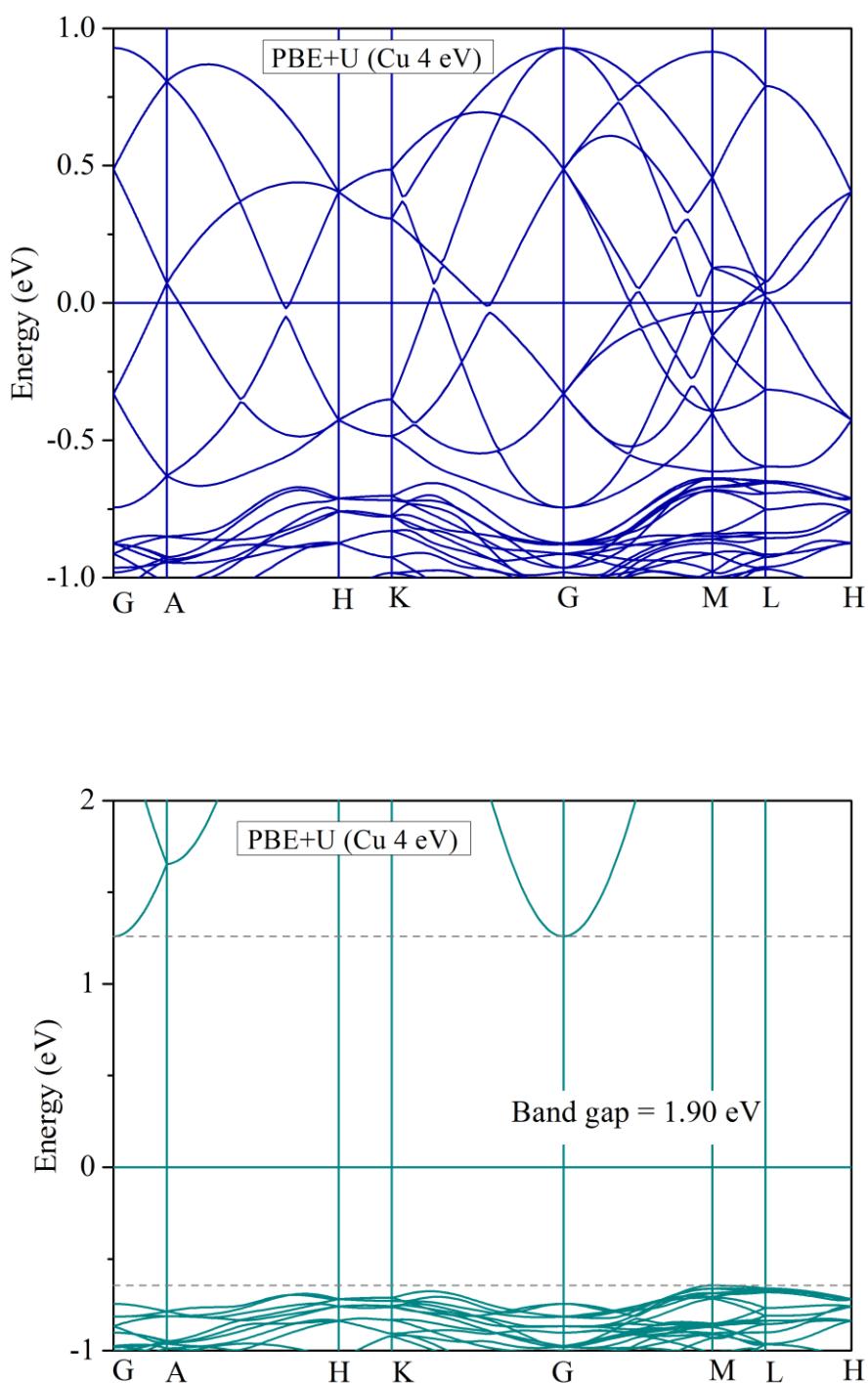


Figure S2. Band structures with PBE+U ($U = 4$ eV for Cu-3d orbit).

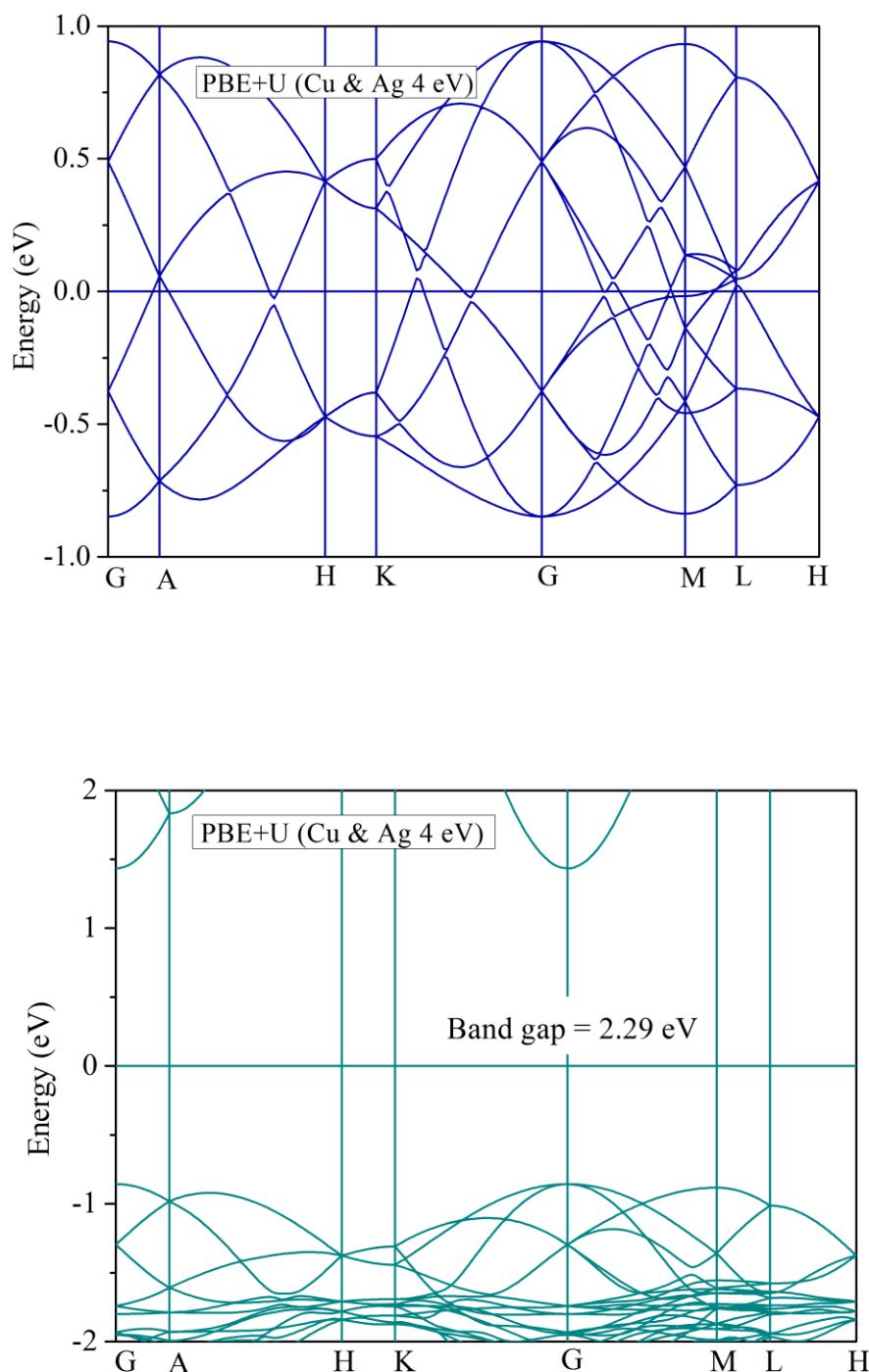


Figure S3. Band structures with PBE+U ($U = 4$ eV for Cu-3d and Ag-4d orbitals).

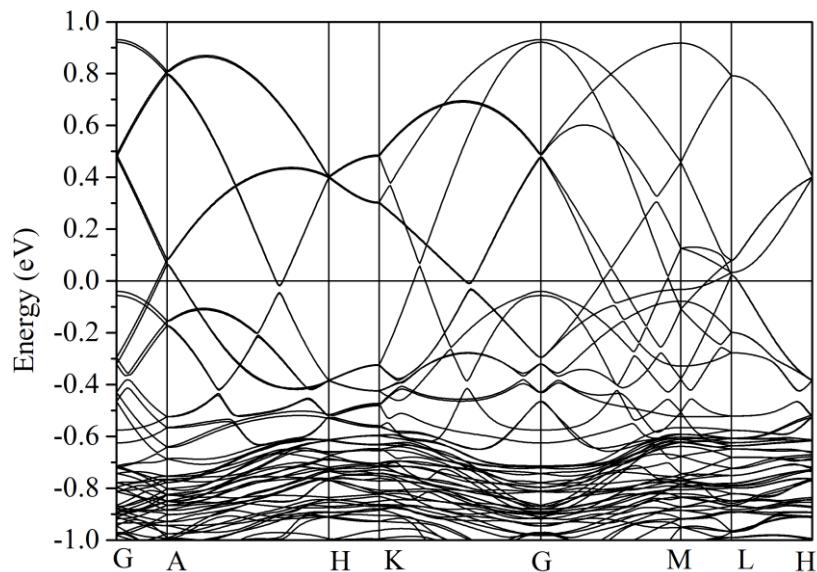


Figure S4. Band structures of AgCuF_3 with the effect of SOC.

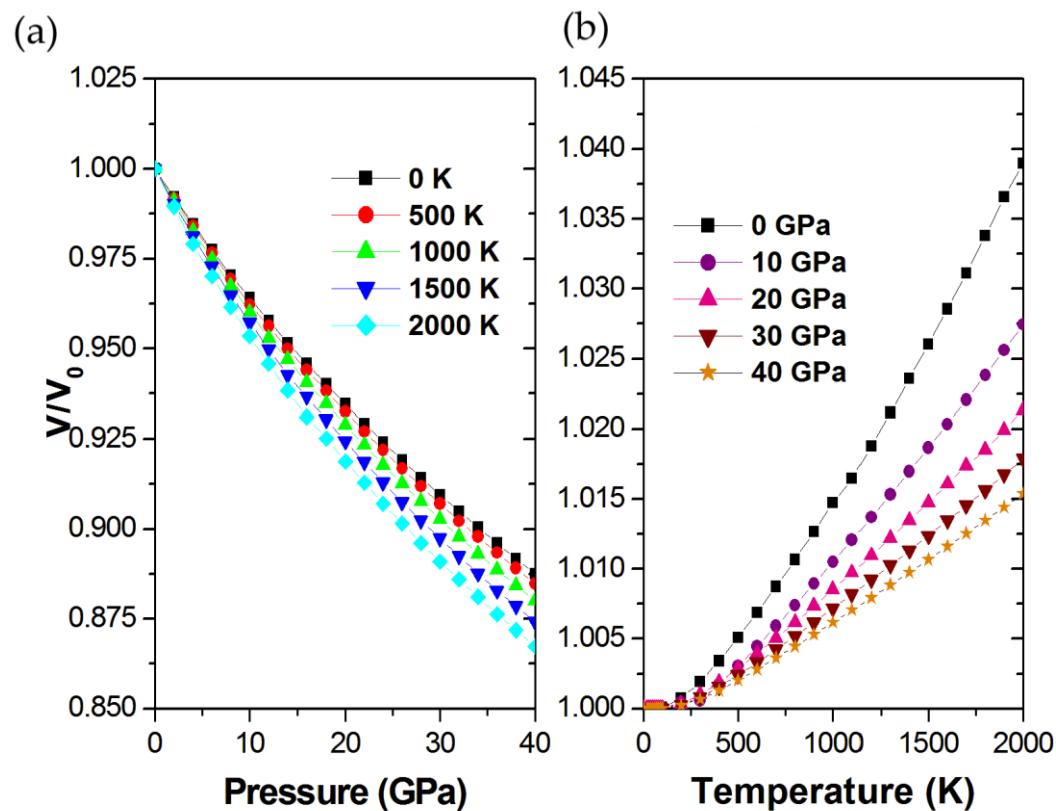


Figure S5. (a)The dependency of V/V_0 rate respect to pressure at different given temperatures. (b)

The dependency of V/V_0 rate respect to temperature under different pressures.

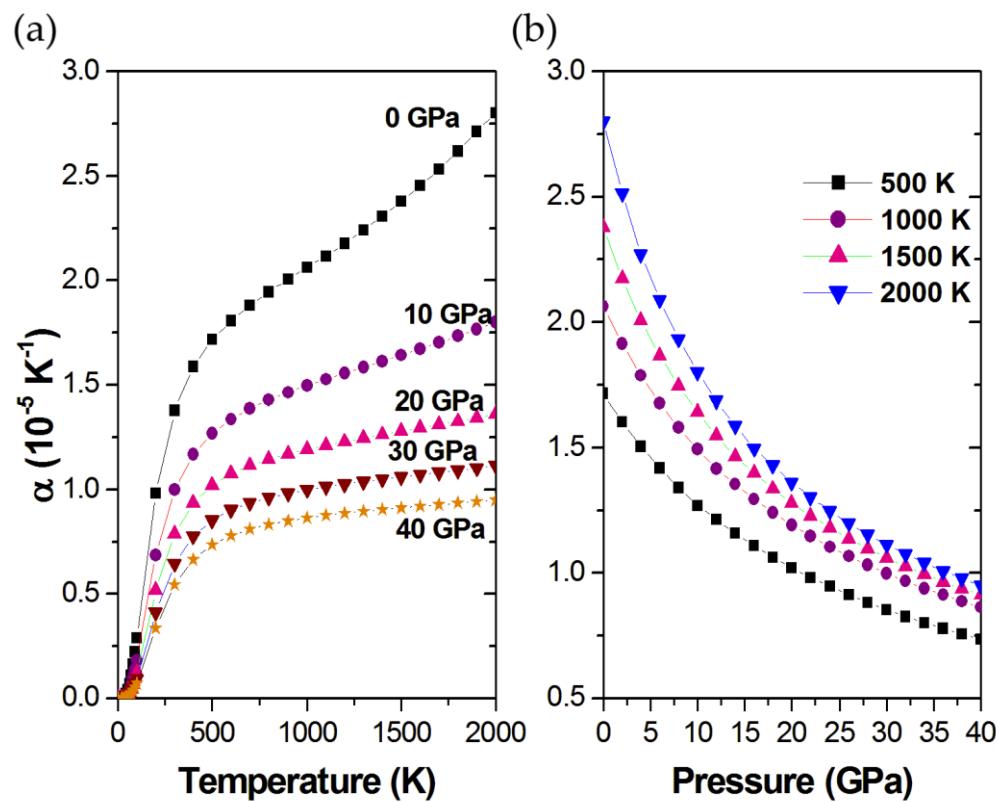


Figure S6. (a) The dependency of α_V respect to temperature at different given pressures. (b) the dependency of α_V respect to pressure at different given temperatures.

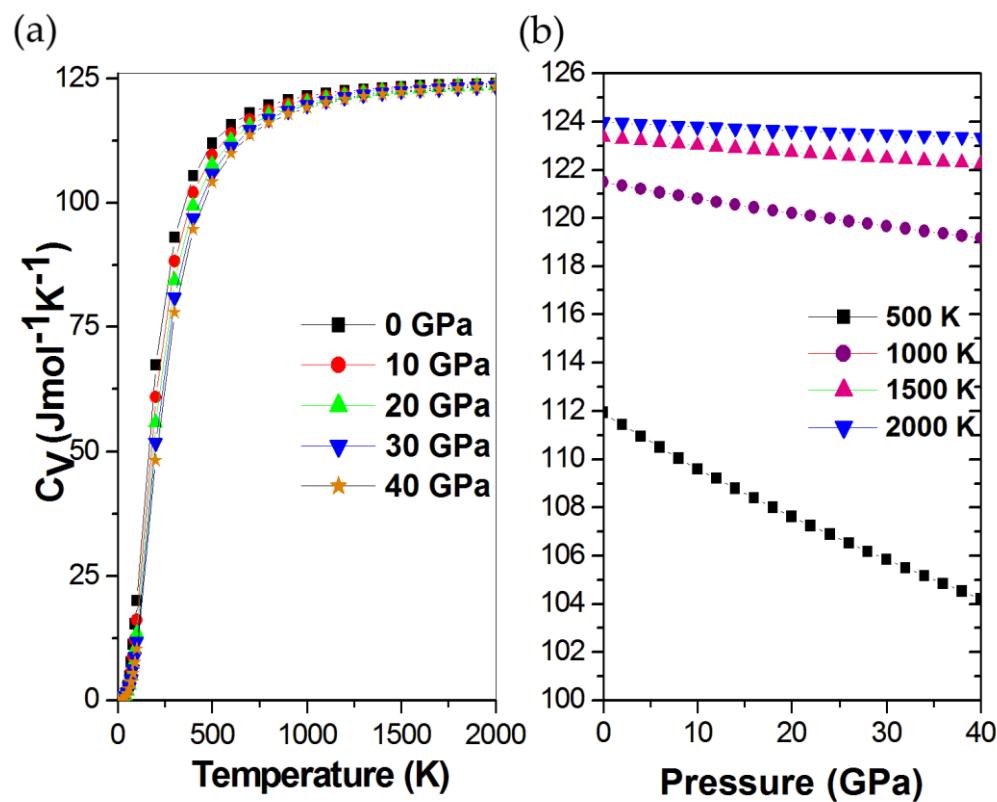


Figure S7. (a) The dependency of heat capacity C_V respect to temperature at different given pressures. (b) the dependency of heat capacity C_V respect to pressure at different given temperatures.

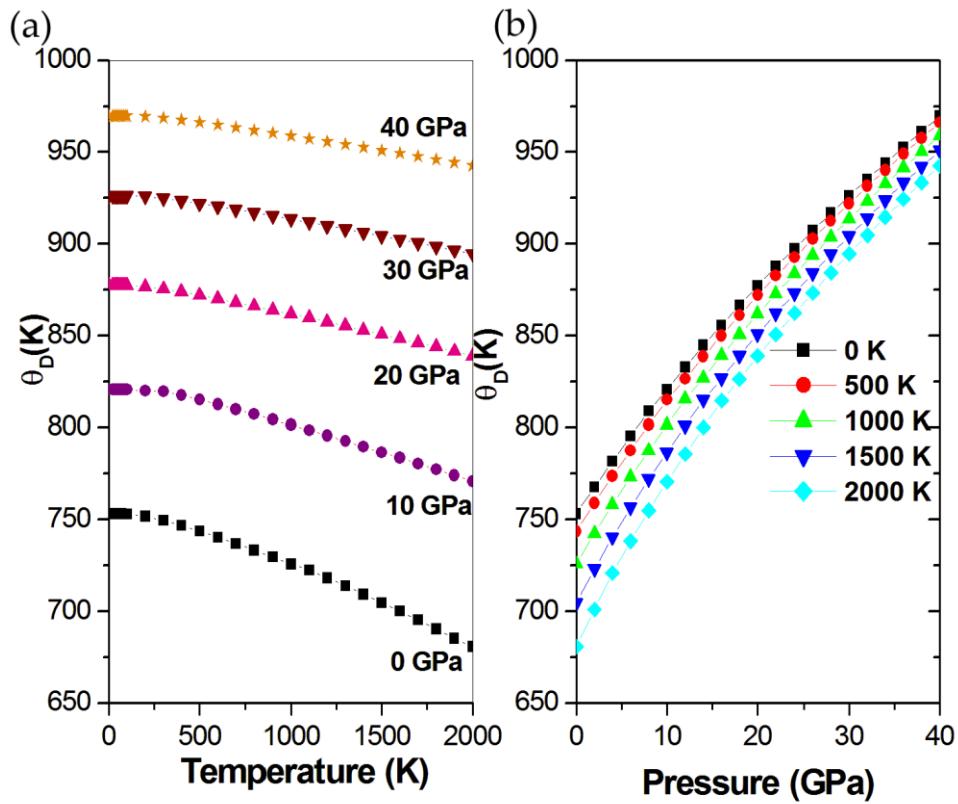


Figure S8. (a) The dependency of Debye temperature θ_D respect to temperature at different given pressures. (b) the dependency of Debye temperature θ_D respect to pressure at different given temperatures.

References

- Emery, A. A. & Wolverton, C. (2017). *Sci. Data.* **4**, 170153.
- Fischer, P., Schwarzenbach, D. & Rietveld, H. M. (1971). *J. Phys. Chem. Solids.* **32**, 543.
- Grzelak, A., Gawraczyński, J., Jaroń, T., Kurzydłowski, D., Mazej, Z., Leszczyński, P. J., Prakapenka, V. B., Derzsi, M., Struzhkin, V. V. & Grochala W. (2017). *Dalton Trans.* **46**, 14742.
- Jagau, T. C., Dao, D. B., Holtgrewe, N. S., Krylov, A. I. & Mabbs, R. (2015). *J. Phys. Chem. Lett.* **6**, 2786.
- Marchetti, A. P. & Bottger, G. L. (1971). *Phys. Rev. B* **3**, 2604.
- Romiszewski, J., Grochala, W. & Stolarczyk, L. Z. (2007). *J. Phys.: Condens. Matter* **19**, 116206.
- Vinichenko, D., Sensoy, M. G., Friend C.M. & Efthimios Kaxiras. (2017). *Phys. Rev. B* **95**, 235310.
- Zheng, Y., Zhang, P., Wu, S. Q., Wen Y. H. Zhu, Z. Z. & Yang, Y. (2012). *Solid. State. Commun.* **152**, 1703.
- Zhou, Z., Shi, J. & Guo L. (2016). *Comp. Mater. Sci.* **113**, 117.