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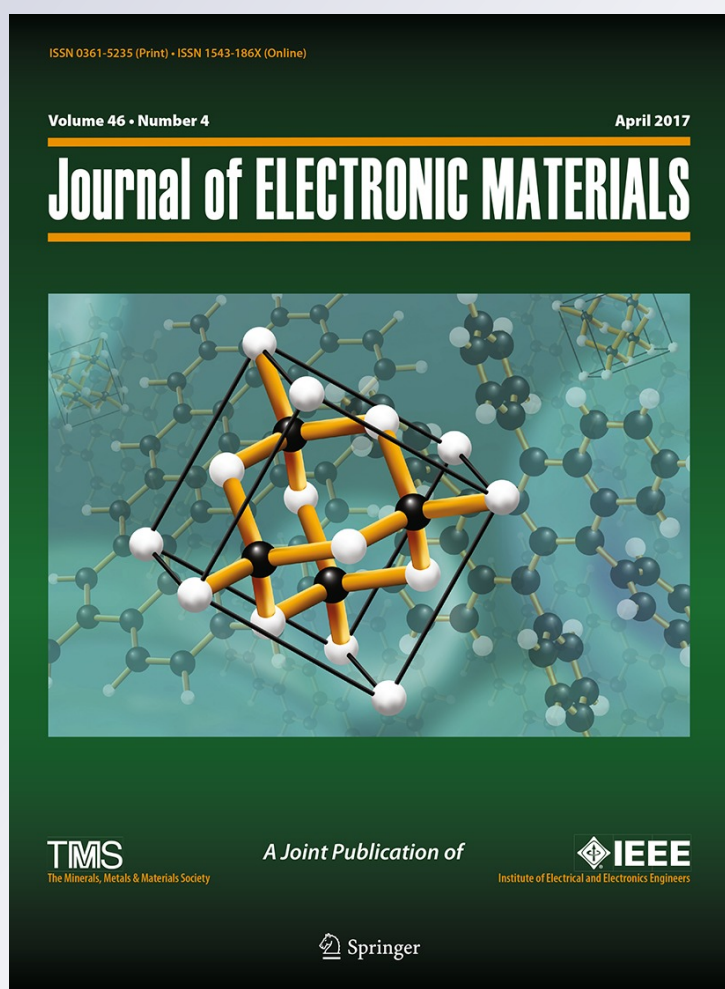
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Thermodynamic Properties of Compressed CuX (X = Cl, Br) Compounds: *Ab Initio* Study

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A pseudopotential plane wave method based on the density functional theory has been employed to study some thermodynamic properties of copper chloride (CuCl) and copper bromide (CuBr) compounds under the effect of temperature and pressure. The phase transition pressure, the unit cell volume, the isothermal bulk modulus, the constant volume heat capacity, the entropy, the Debye temperature, the Grüneisen parameter and the volumetric thermal expansion coefficient are studied in the pressure range 0–10 GPa, and for temperatures ranging from 0 K up to 650 K and 750 K for CuCl and CuBr, respectively. The phase transition pressure is found to be around 7.8 and 6.95 GPa for CuCl and CuBr, respectively. These values are respectively in reasonably good agreement with the experimental ones of 8.2 GPa and 6.8 GPa reported in the literature. Moreover, at room temperature and zero pressure, the heat capacity at constant volume and the Grüneisen parameter of both compounds of interest are found to be in good agreement with the available experimental and theoretical data. The information gathered from the present investigation may be useful for the study of the behavior of the fundamental properties of CuCl and CuBr under the influence of high temperature and pressure.

Key words: *Ab initio*, thermal properties, copper halide materials, temperature, pressure

INTRODUCTION

The thermodynamic parameters, namely, the heat capacity, entropy, Debye temperature, thermal expansion, and Grüneisen parameter, of semiconductor materials play an important role at high pressure and high temperature in the physics of solid-state matter.^{1,2} This is due to the fact that they are linked directly with other physical properties such as the elastic and mechanical properties. Thus, an accurate knowledge of thermodynamic properties is very important not only from a physical point of view, but also for the fabrication and application of advanced semiconducting materials.

The superionic conductors¹ of copper halide CuX (X = Cl, Br, and I) compounds have attracted increasing research interest in the last few years. They present many remarkable behaviors compared to other III–V and II–VI compounds, such as large band gaps³ and small values of phase-transition pressure.⁴ Copper (I) chloride with the chemical formula CuCl is the lower chloride of copper. The substance is very soluble in concentrated hydrochloric acid. CuCl is used as a precursor to the fungicide copper oxychloride and as a catalyst in atom transfer radical polymerization. Copper (I) bromide with the chemical formula CuBr is a diamagnetic solid which adopts a polymeric structure akin to that of zinc sulfide. It is insoluble in most solvents and is widely used in the synthesis of organic compounds.

The study of thermodynamic properties of semiconducting materials is important from several

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points of views. It lets us extend our knowledge on their specific behaviors when undergoing several constraints such as high temperatures and pressures. Experimentally, the pressure of the phase transition of copper chloride and copper bromide has been obtained by several techniques. In the CuCl compound, the phase transition from a fourfold coordinated zinc-blende (B3) structure to the sixfold coordinated ionic rock salt (B1) structure is found at about 10 GPa.^{5,6} Other works reported that the copper halides CuX (X = Cl, Br, and I) undergo a number of structural phase transitions with lower symmetry before attaining the ionic rock salt structure.^{4,7-9}

The phase diagrams for evaluating the volume changes and high-pressure elastic behavior of copper halides has been studied by Singh and Gupta.⁹ For the copper chloride compound, the first phase transition from the B3 phase to the tetragonal phase appears at a pressure in the range 5.0–5.5 GPa,^{4,7,10} and the second phase transition from the tetragonal phase to the rock salt phase appears at a pressure in the range of 9–14.25 GPa.^{4,7,10,11}

In the present work, we report on first principle calculations of the influence of pressure and temperature on several thermodynamic quantities of copper chloride and copper bromide compounds in their B3 structure using the pseudopotential plane wave method in the framework of the density functional theory (DFT)¹² in the local density approximation (LDA).¹³ The objective of the present contribution is the investigation of the thermal properties of CuCl and CuBr compound semiconductors, with emphasis on their dependence on temperature and hydrostatic pressure. The zinc-blende structure referred to as B3 has been adopted for both materials of interest.

FORMALISM

The nonequilibrium Gibbs function, $G^*(V, P, T)$, which is considerably related to the two thermodynamic quantities (pressure and temperature), can be given by the following expression¹⁴:

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

Here, V is the volume, P is the pressure, T is the temperature, and $E(V)$ is the total energy, which is obtained directly from the *ab initio* calculation, PV is a quantity which corresponds to the constant hydrostatic pressure condition, F_{vib} is the contribution of the lattice vibrational to the free energy (the vibrational Helmholtz free energy), and $\theta(V)$ is the Debye temperature.

In the quasi-harmonic Debye model,¹⁴ the vibrational Helmholtz free energy term F_{vib} can be given by the following expression:

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

where n is the number of atoms per primitive cell, k is the Boltzmann's constant, T is the temperature, θ_D is the Debye temperature, and $D(\theta_D/T)$ represents the Debye integral.

For an isotropic solid, the quasi-harmonic Debye temperature θ_D can be given by the following expression¹⁴:

$$\theta_D = \frac{\hbar}{k} (6\pi^2 V^{0.5} n)^{1/3} f(\sigma) (B_s/M)^{1/2} \quad (3)$$

where \hbar is the reduced Planck constant, k is the Boltzmann constant, M is the molecular mass per primitive cell, B_s is the adiabatic bulk modulus, and $f(\sigma)$ is the functional of the other quantity σ which is the Poisson ratio.

The adiabatic bulk modulus is approximately given by the static compressibility, which is given by the following expression¹⁴:

$$B_s \approx B(V) = V(d^2 E(V)/dV^2) \quad (4)$$

where V is the volume and $E(V)$ is the total energy.

METHOD OF CALCULATION

Several thermodynamic quantities of any system made of electrons and nuclei (periodic solids for example) can be obtained through the first principles calculations with help of several different thermal models. In order to obtain the pressure and temperature influence on the thermodynamic properties of (B3) CuCl and CuBr compounds, the Debye model¹⁴ is applied; our calculations are implemented through the Gibbs code.¹⁵ The Gibbs code is used to obtain many thermodynamic quantities from the minimization of energy–volume (E, V) data. Gibbs implements several models for the inclusion of temperature effects to the results of an *ab initio* calculation. The Debye model requires only the input of the static energy–volume (E, V) data and optionally the experimental Poisson ratio.¹⁵ So, through the Debye model, one could calculate several thermodynamic quantities including the equilibrium volume $V(p, T)$, isothermal bulk modulus B_T , etc.

The energy–volume (E, V) data are obtained firstly by using the ABINIT code¹⁶ which is based on the plane-wave pseudopotential approach in the framework of DFT.¹² More details can be found in Ref. 17.

In the context of the LDA as parameterized in Ref. 13 which reproduces the Perdew and Wang¹⁸ correlation scheme, the Trouiller–Martins¹⁹ norm-conserving nonlocal pseudopotentials are used in the computation. Well-converged total energy and geometrical configurations are obtained using a cutoff energy of 70 Hartree. Integrations in the Brillouin zone are performed using special k points generated with $8 \times 8 \times 8$ Monkhorst–Pack

meshes.²⁰ These parameters have been carefully tested to ensure that they lead to well-converged total energy and geometrical configurations.

RESULTS AND DISCUSSION

Phase Transition Pressure

To study the structural stability under pressure from a thermodynamic perspective, the Gibbs free energy has usually been calculated. In the present work, all geometry optimizations are performed at zero temperature, and, consequently, the Gibbs free energy becomes the enthalpy. The curves of the total energies and relative volumes of both zinc-blende and rock salt phases can be used to predict the phase transition pressure. The pressure of phase transition is the gradient of the common tangent which can be given as²¹

$$P_t = -\frac{\Delta E}{\Delta V} = \frac{E_1 - E_2}{V_2 - V_1} \quad (5)$$

where E is the energy and V is the volume.

Figure 1 shows the relative volume dependence of the total energies of both zinc-blende and rock salt phases of CuCl and CuBr compound semiconductors. Accordingly, we observe that the B3 structure is the most energetically favorable phase at low pressure, and, consequently, it is the ground-state phase for both CuCl and CuBr materials. The phase transition pressures suggested by these curves are around 7.8 GPa and 6.95 GPa for CuCl and CuBr, respectively. As regards CuCl compound, our computed value of transition pressure deviates by less than 5% from the experimental one of 8.2 GPa reported in Ref. 8. Moreover, it agrees to within 1% with the theoretical value of 7.7 GPa calculated by Hsueh et al.²² In the case of CuBr compound, the deviation between the present calculated value and the experimental one of 6.8 GPa obtained from x-ray measurements²³ is less than 3%. Moreover, our calculated value deviates only by less than 6% from the measured one of 6.6 GPa reported in Ref. 24. Besides, it lies in the transition pressure range of 6.8–8.7 GPa quoted in Ref. 25 where a mixed-phase of tetragonal and NaCl structures was observed in the pressure range of 6.8–7.7 GPa, and only an NaCl structure was seen in the pressure range of 7.7–8.7 GPa.

Thermodynamic Properties

Figure 2 displays the pressure dependence of the equilibrium volume (V) at various temperatures for both CuCl and CuBr compounds. Note that for both compounds of interest, the equilibrium volume decreases with increasing pressure at all temperatures of interest. At any given pressure, the V increases with raising the temperature. The behavior of the equilibrium volume with pressure is expected since applied pressure makes the atoms closer to each other and, hence, it reduces the lattice

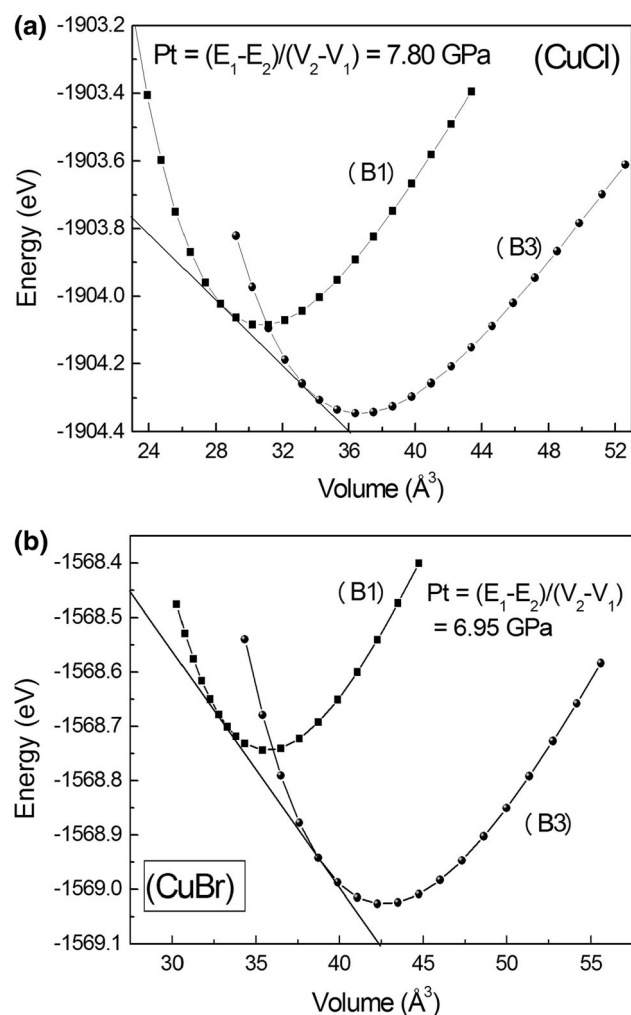


Fig. 1. Total energy versus volume for zinc-blende and rock salt phases of (a) CuCl and (b) CuBr materials.

parameter which in turn leads to the decrease of the volume. On the other hand, when the temperature increases, there will be a dilatation of the lattice parameter thus leading to the increase of the volume of the crystal of interest.

The isothermal bulk modulus B_T is given by the following expression¹⁵,

$$B_T = -V(dp/dV)_T = V(d^2F/dV^2)_T \quad (6)$$

where V is the volume, P is the pressure, T is the temperature, and F is the vibrational Helmholtz free energy.

Figure 3 displays the pressure dependence of the isothermal bulk modulus at various temperatures for CuCl and CuBr compounds. We observe that the isothermal bulk modulus increases with increasing pressure at all temperatures considered in the present work. The behavior is monotonic for both semiconductor compounds of interest. It should be noted also that for each given pressure, the isothermal bulk modulus decreases with raising the temperature up to 650 K for CuCl and 750 K for CuBr.

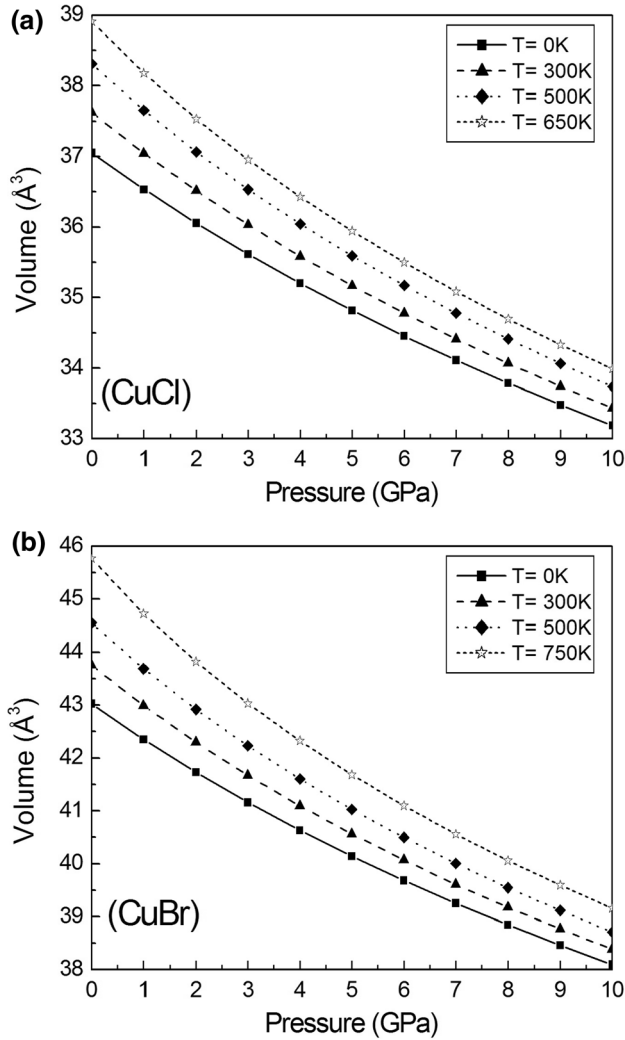


Fig. 2. Variation of the equilibrium volume as a function of pressure at different temperatures for (a) CuCl (b) CuBr.

One may thus conclude that both materials under study become harder when increasing pressure or decreasing temperature. At zero pressure and zero temperature, the obtained isothermal bulk modulus values of CuCl and CuBr materials are 68.5 GPa and 60.3 GPa, respectively. It decreases almost linearly with increasing temperature. For CuCl material, the discrepancy between our computed value and the experimental one of 65.4 GPa measured by Hoshino et al.²⁶ is less than 5%. In addition, our value agrees to within 4% with the theoretical one of 66 GPa calculated by Kremer and Weyrich²⁷ using a full-potential linear muffin-tin orbital method.

The heat capacity at constant volume C_V is obtained using the expression

$$C_V = (dU/dT)_V \quad (7)$$

where V is the volume, T is the temperature, and U is the total internal energy.

Figure 4 shows the calculated heat capacity at constant volume C_V for different pressures as a

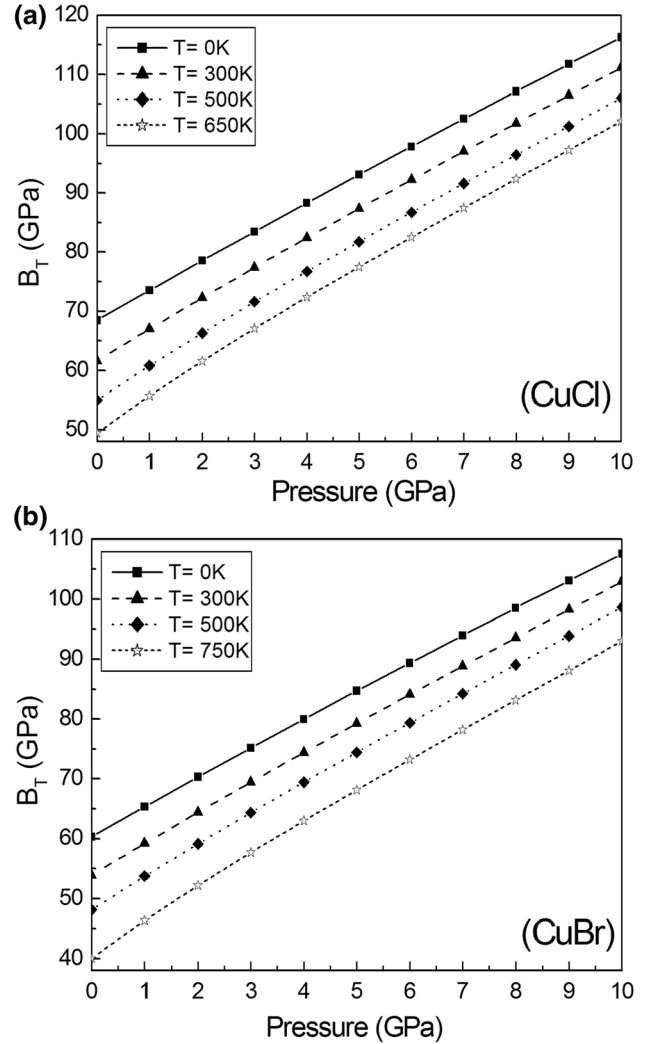


Fig. 3. Variation of the isothermal bulk modulus as a function of pressure at various temperatures for (a) CuCl (b) CuBr.

function of the temperature for CuCl and CuBr materials. It can be seen from Fig. 4 that the heat capacity C_V increases exponentially with the temperature for $T < 300$ K. Nevertheless, beyond the temperature of 300 K, it follows naturally the Debye model and approaches the Dulong–Petit limit indicating that at high temperature, all phonon modes are excited by the thermal energy.²⁸ Similar qualitative behavior has been reported for C_V versus temperature for CdSe, CdSe_{0.5}Te_{0.5}, and CdTe semiconductor materials.²⁹

In the Debye model,¹⁴ the entropy S is given by the following expression,^{14,15}

$$S = nk \left[4D(\theta_D/T) - 3 \ln(1 - e^{-\theta_D/T}) \right] \quad (8)$$

where n is the number of atoms per formula unit, k is the Boltzmann's constant, D is the Debye integral, T is the temperature, and θ_D is the Debye temperature.

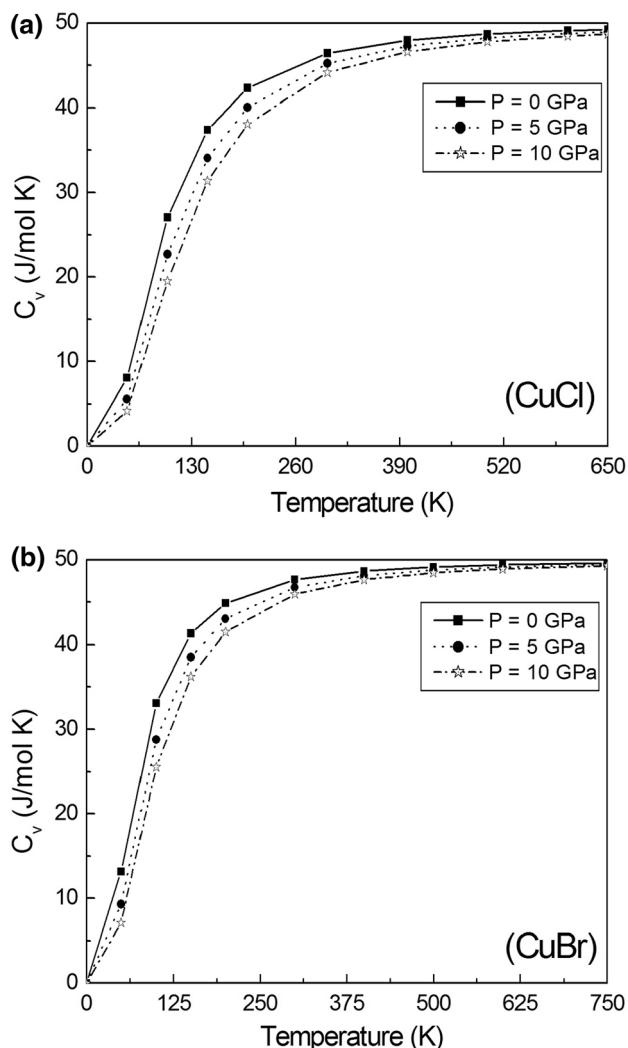


Fig. 4. Variation of the constant volume heat capacity as a function of temperature at various pressures for (a) CuCl (b) CuBr.

The effect of temperature and pressure on the entropy S is presented in Fig. 5. At low temperature and zero pressure, one can note that the entropy increases quickly with raising the temperature T ; then, the behavior of the entropy as a function of temperature becomes more like a sublinear behavior. By increasing pressure from 0 GPa up to 10 GPa, the behavior of the entropy versus temperature remains qualitatively almost the same. However, from the quantitative point of view, the entropy seems to decrease slightly in magnitude with increasing pressure for both CuCl and CuBr semiconducting compounds. The trend is similar to that of the entropy versus temperature in rock salt InN^2 . The decrease of the entropy with increasing pressure for any fixed temperature means that applied pressure reduces the molecular disorder within a macroscopic system of interest.

Figure 6 shows the calculated Debye temperature θ_D as a function of pressure at various temperatures. It can be seen from Fig. 6 that the Debye temperature

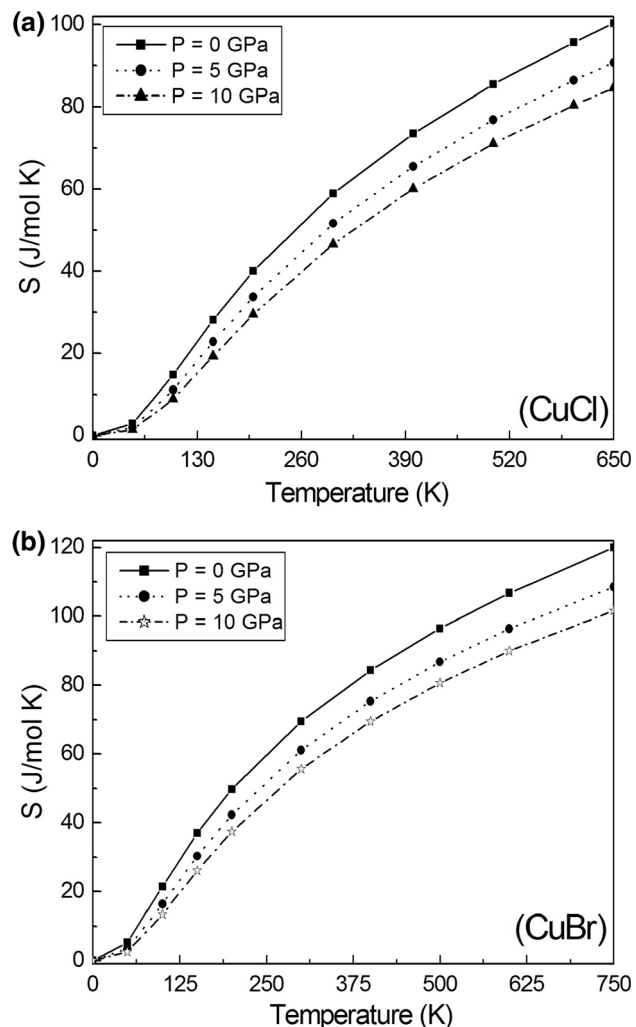


Fig. 5. Variation of the entropy as a function of temperature at different pressures for (a) CuCl (b) CuBr.

increases monotonically with increasing pressure. At a fixed pressure, the Debye temperature decreases with increased temperature for both CuCl and CuBr materials. It is worth noting that at zero pressure and zero temperature, the Debye temperature of CuCl is larger than that of CuBr. It has been reported in the literature that in $\text{A}^{\text{NB}^{8-\text{N}}}$ semiconductors, the high Debye temperature reflects low atomic mass, and, hence, short interatomic bond length.^{30,31} This is consistent with the present case since the bond length of CuCl ($d = 2.29$ Å) is smaller than that of CuBr ($d = 2.40$ Å).

The Grüneisen parameter is a quantity which describes the alteration in a crystal lattice's vibration frequency.^{32,33} This quantity can be reasonably used to predict the anharmonic properties of a solid, such as the temperature dependence of phonon frequencies and lattice volume.³³

The Grüneisen parameter of any system having a total internal energy U is given by the following formula¹⁵: $\gamma = V(dP/dU)_V$ where V is the volume, P

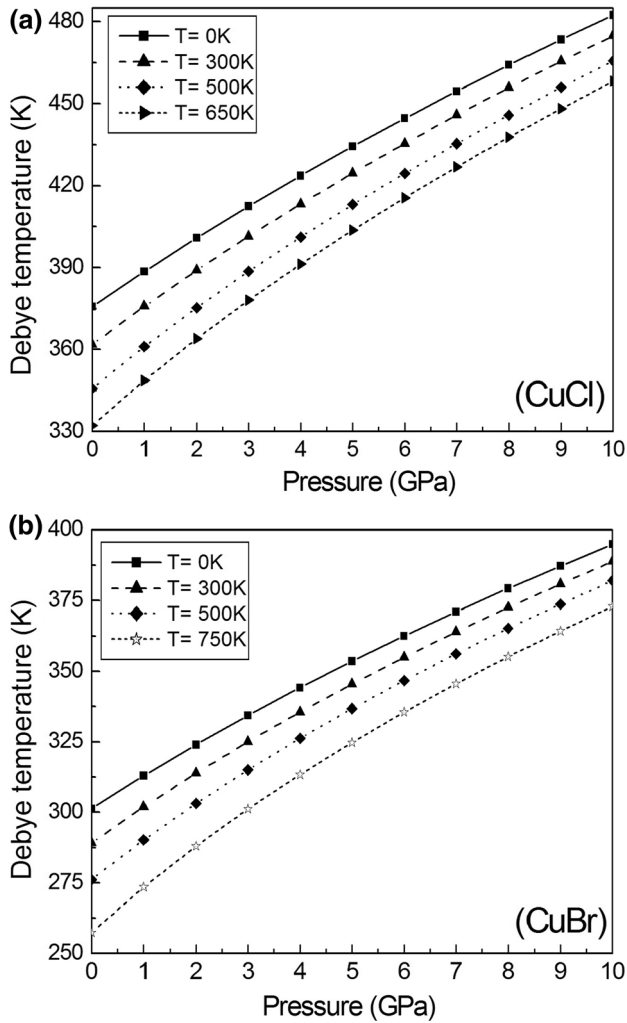


Fig. 6. Variation of the Debye temperature as a function of pressure at various temperatures for (a) CuCl (b) CuBr.

is the pressure, and T is the temperature. The derivative is to be evaluated at constant volume. The Grüneisen parameter γ is also given by the following expression¹⁴:

$$\gamma = -d \ln \theta_D(V) / d \ln V \quad (9)$$

where $\theta_D(V)$ is the Debye temperature and V is the volume.

At zero pressure and zero temperature, the determined γ in the present calculations is found to be ≈ 2.43 for both materials of interest. This value is in very good agreement with that of 2.4 measured by Shand et al.³⁴ for CuCl and Hochheimer et al.³⁵ for CuBr, where the discrepancy is found to be less than 2%.

Figure 7 displays the pressure dependence of the Grüneisen parameter γ at different temperatures. As can be seen from Fig. 7, the Grüneisen parameter for both materials of interest decreases with increasing pressure. The decrease is monotonic. Nevertheless, the opposite can be seen as regards

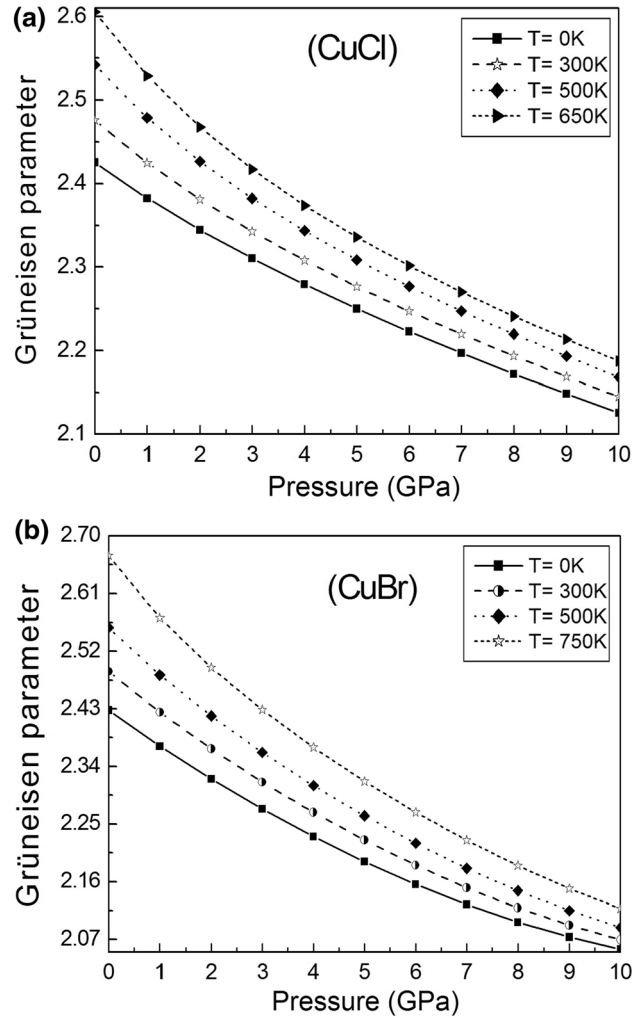


Fig. 7. Variation of the gamma Grüneisen parameter as a function of pressure at various temperatures for (a) CuCl (b) CuBr.

the temperature where the Grüneisen parameter increases by raising the temperature in the range 0–650 K for CuCl, and 0–750 K for CuBr, for any given pressure of interest. The obtained results indicated that the restoring force acting on an atom displaced from its equilibrium position is nonlinear in the atom's displacement. Applied pressure reduces the Grüneisen parameter for both materials of interest, reflecting, thus, the alteration of the vibration frequencies (phonons) within a crystal with changing volume. On the other hand, the increase of the temperature increases the Grüneisen parameter of both CuCl and CuBr compound semiconductors which is a consequence of the change of the size or dynamics of the lattice.

The volumetric thermal expansion coefficient α is a quantity which describes how the size of an object changes with a change in temperature.³³ α and the gamma Grüneisen parameter γ are related by the following formula^{14,15}:

$$\alpha = \gamma C_V / B_T V \quad (10)$$

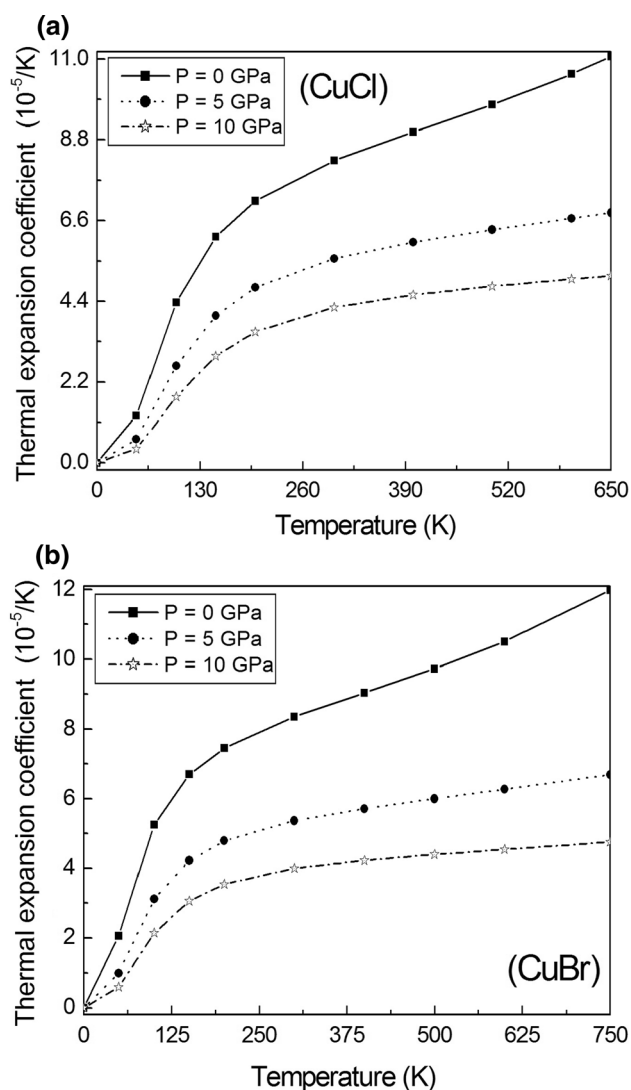


Fig. 8. Variation of volumetric thermal expansion coefficient as a function of temperature at different pressures for (a) CuCl (b) CuBr.

where C_V is the heat capacity at constant volume, B_T is the isothermal bulk modulus, and V is the volume.

In Fig. 8, we plot α as a function of temperature at various pressures for CuCl and CuBr semiconductor compounds. The behavior of this quantity is similar to that observed for the constant volume heat capacity and the entropy. Our calculations show that α increases monotonically with increasing the temperature. Nevertheless, for a fixed temperature, α decreases with increasing pressure for both CuCl and CuBr compounds. As a matter of fact, the increase of α with increasing temperature results from the increase of the heat transfer. On the other hand, the decrease of α with increasing pressure for a given temperature can be traced back to the increase of the bond energy, which also has an effect on the melting point of solids.

CONCLUSION

In conclusion, the thermal properties of CuCl and CuBr semiconducting compounds in the zinc-blende phase at different pressures and temperatures have been investigated using *ab initio* pseudopotential plane wave method, based on the DFT in the LDA approach. It is found that pressure influences all thermodynamic parameters of interest in a manner opposite to that of temperature. The phase transition pressure was found to be around 7.8 GPa and 6.95 GPa for CuCl and CuBr, respectively. At zero pressure and zero temperature, the isothermal bulk modulus was found to be 68.5 GPa and 60.3 GPa for CuCl and CuBr, respectively. The Debye temperature of CuCl was found to be larger than that of CuBr, thus suggesting that CuCl has shorter interatomic bond length as compared to CuBr. All features of interest were found to vary monotonically with either temperature or pressure. Generally, our results were found to be in good agreement with the available experimental and previous theoretical data published in the literature. In any case, our findings are predictions and might be useful for future investigations.

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