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First principles calculations of mechanical, electronic, thermoelectric and thermal properties of ZnCu

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Abstract

The structural, elastic, electronic, thermoelectric, and thermal properties of ZnCu were investigated using Density Functional Theory (DFT). The Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional within the Generalized Gradient Approximation (GGA) was employed in the Quantum ESPRESSO package for the purpose. The ZnCu compound was found to be both mechanically and dynamically stable. Analysis of its elastic and electronic properties reveals that ZnCu is mechanically stable, anisotropic, and exhibits metallic behavior. Furthermore, thermoelectric property analysis indicates that ZnCu achieves its highest power factor at 300 K. The study of thermodynamic properties suggests that ZnCu retains mechanical stability at elevated temperatures. Additionally, the specific heat capacity shows a significant increase at low temperatures and approaches a constant value at high temperatures, consistent with phonon excitation behavior.

Keywords

ZnCu compound, Quantum Espresso, electronic properties, phonopy, thermoelectric properties.

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1 Introduction

Alloying materials serve an important role in improving the qualities of materials for a variety of applications by increasing their strength, durability, and corrosion resistance. The material can be alloyed to achieve the qualities that alloy components lack for practical application [1]. There are enormous possibilities for alloying the material, but copper alloy has gained its own importance in the fields of machinery, electrical industry, and construction over the past year [2, 3]. Among the different possible alloys of copper, the ZnCu alloy stands out due to its potential application in diverse domains. The unique combination of zinc and copper provides promising characteristics [4–8].

Different research has been conducted to study the properties of the ZnCu alloy. For example, Iwaoka and Hirosawa used first principles method to calculate elastic properties of three different complex of Cu-Zn system to improve the stiffness of aluminum alloy [4]. Similarly, Liu et al. studied the structural, elastic, and electronic properties of Cu-X (X = Al, Be, Mg, Sn, Zn, and Zr) by the first-principles calculations [8]. Furthermore, Tang et al. used a mod-

ified quasi-chemical model (MQM) to describe the Gibbs energy of the liquid phase [9]. Despite significant progress in material science, comprehensive studies that integrate structural, electronic, elastic, thermoelectric, and thermal properties of ZnCu crystal structure are still sparse. Therefore, this work attempts to explain these properties of the ZnCu compound using the first principles calculations employing Quantum Esspresso codes [10].

2 Computational Details

The first principles calculation of ZnCu structure was performed using the Quantum Espresso software package [10]. The crystal structure was first optimized by performing the VC-relax calculation using Perdew-Burke-Ernzerhof (PBE) of scalar relativistic exchange-correlation functional and ionic potentials described by ultrasoft pseudopotential (USPP) for Zn and Cu downloaded from the material cloud website [11]. The plane wave cutoff energy was set to 40 Ry and 320 Ry was set for the wave function and charge density. The Brillouin zone was determined using Monkhorst-Pack for self-consistent field calculation and for density of state (DOS) calculation. The electronic band structure was calculated along the high-symmetry point in the Brillouin zone using the path $\Gamma - X - M - \Gamma - R - X|R - M$.

The bulk modulus was calculated using the Murnaghan equation of state using the ev.x utility of Quantum Espresso [12]. Furthermore, the Thermopw [13] postprocessing tool was used to calculate the elastic constant, which allowed for the calculation of mechanical properties such as bulk modulus, young modulus, shear modulus, and Poisson ratio of the material. Electronic transport properties were calculated with the help of the Boltztrap code [12, 14]. The output information of non-self-consistent field calculation was used as input for boltztrap software, which solves the Boltzmann transport equation to determine electrical conductivity, Seebeck coefficient, and thermal conductivity. The phonon calculation was executed in the Phonopy package [15] using the finite displacement method on a supercell. Finally, thermal properties such as heat capacity at constant volume, free energy, and entropy were calculated.

3 Results and Discussion

3.1 Structural properties

Figure 1 shows the ZnCu structure it is a tetraauricupride cubic structure in space group $Pm\bar{3}m$ with all bond lengths of 2.53 Å. Zn is bonded with eight Cu atoms in body centered geometry [16].

Using the first principles calculations in Quantum Espresso software, the total energies were minimized as a function of the lattice parameter for ZnCu crystal structure. The lattice parameter, bulk modulus $\left(B_0 = -V\frac{\partial P}{\partial V}\right)$, and pressure derivative (B') of the ZnCu crystal structure are derived by fitting the Murnaghan equation of state [**?**] as

$$P(V) = \frac{B_0}{B'}\left[\left(\frac{V_0}{V}\right)^{B'} - 1\right] \quad (1)$$

where V_0 is the equilibrium volume and $B' = dB/dP$.

The Murnaghan equation of state is fitted using the `ev.x` tool of Quantum Espresso to calculate total energy as a function of unit cell volume. The obtained value of the lattice parameter is 2.96628 Å, which is consistent with the experimental value of 2.959 Å [**?**]. Similarly, bulk modulus (B_0) and pressure derivative (B') are found to be 115.00 GPa and 5.02, respectively. The obtained value of bulk modulus is in good agreement with the value in the materials project database, which is 116.00 GPa. Thus, these results validate the present calculation approaches.

4 Vibrational properties

The phonon serves as a medium for transmitting vibrational energy. Utilizing the `phonopy` algorithm, the phonon frequency of ZnCu was calculated. A $2\times2\times2$ supercell ws created to collect force sets for analyzing the phonon band structure and phonon density of states (DOS). The phonon dispersion curves and the corresponding phonon density of states (DOS) of ZnCu are shown in Figure ZZZ. These calculations were performed to assess the dynamical stability and lattice vibrational behavior of the compound.

The phonon dispersion displays the vibrational frequencies along high-symmetry directions in the Brillouin zone, Figure ZZ. Importantly, no imaginary frequencies (i.e., frequencies below zero) are observed throughout the entire Brillouin zone, indicating that the ZnCu structure is dynamically stable in its equilibrium configuration. The phonon spectrum features both acoustic and optical branches. The acoustic modes originate from the Γ- point and extend up to about 4 THz, while the optical modes span from about 4 THz to over 6.5 THz. The separation between the acoustic and optical branches suggests a moderate mass difference between Zn and Cu atoms and indicates potential phonon scattering behavior relevant to thermal transport. The phonon density of state (DOS) exhibits multiple sharp peaks, especially in the high-frequency region (5–7 THz), corresponding to localized optical modes. The lower-frequency region

shows a more gradual increase in DOS, associated with acoustic phonons. This distribution of vibrational states implies that optical phonons significantly contribute to the vibrational properties, while acoustic phonons dominate low-temperature specific heat and thermal conductivity. he phonon DOS achieved is consistent with the findings of a previous study by Peter et al. for β-ZnCu [**?**].

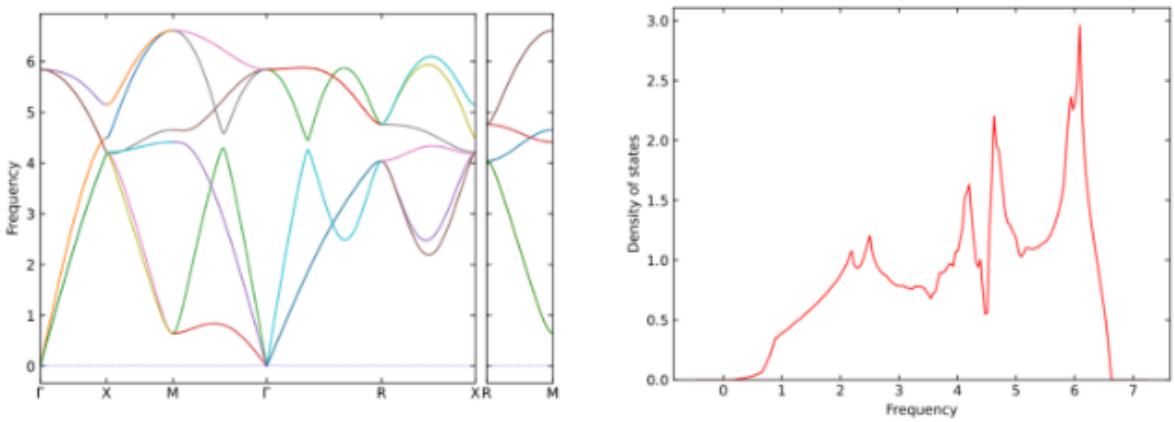

Figure 2: Phonon band structure and phonon DOS of ZnCu complex

4.1 Elastic properties

The elastic constant matrices (C_{ij}) were calculated using `Thermo_pw` utility of Quantum Espresso. Three independent elastic constants; C_{11}, C_{12}, and C_{44} for cubic structure of ZnCu were obtained. These elastic constants were further used to calculate the elastic property through Voigt–Reuss–Hill (VRH) methods [**?**]. The relation of shear modulus (G) and bulk modulus (B) are as

$$G_V = \frac{C_{11} - C_{12} + 3C_{44}}{5} \tag{2}$$

$$G_R = \frac{5C_{44}(C_{11} + C_{12})}{4C_{44} + 3(C_{11} - C_{12})} \tag{3}$$

$$G = \frac{G_V + G_R}{2} \tag{4}$$

$$B_V = B_R = \frac{C_{11} + 2C_{12}}{3} \tag{5}$$

$$B = \frac{B_V + B_R}{2} \tag{6}$$

Similarly, Young's modulus (Y), Poisson's ratio (ν), and universal elastic anisotropy index (A^U) can be calculated using the relations as

$$Y = \frac{9BG}{3B + G} \tag{7}$$

$$\nu = \frac{3B - 2G}{2(3B + G)} \tag{8}$$

$$A^U = 5\left(\frac{G_V}{G_R}\right) + \left(\frac{B_V}{B_R}\right) - 6 \tag{9}$$

Table shows the calculated value of these elastic parameters. Born criteria for mechanical stability of the cubic system, i.e., $C_{11} > 0$, $C_{44} \geq 0$, $C_{11} \geq |C_{12}|$ and $C_{11} + 2C_{12} \geq 0$ are satisfied by the calculated value of elastic constants [**?**]. This shows that ZnCu crystal is mechanically stable. Furthermore, the value of bulk modulus (B_0) calculated using Murnaghan equation of state in Section 3.1 and Voigt-Reuss-Hill methods using Equation (6) are comparable with the value of bulk modulus in material project database [**?**]. The small discrepancy in the calculated values of elastic parameters with material project database may be due to the use of different pseudopotentials. We have used PBE type pseudopotential whereas material project used PBESol type pseudopotential.

Table 1: Calculated values of elastic parameters for ZnCu complex

Parameter	This work	Material project	Other [?]
C_{11} (GPa)	152.692	134.8	–
C_{12} (GPa)	102.697	104.7	–
C_{44} (GPa)	96.992	75.4	–
B (GPa)	119.362	116	117.4
G (GPa)	56.632	46	40.1
Y (GPa)	145.975	107.7	–
ν	0.295	0.33	0.34
A^U	2.565	3.57	3.87

5 Electronic properties

The electronic properties of ZnCu were investigated using Density Functional Theory (DFT) within the PBE scalar relativistic approximation. The electronic band structure, density of states (DOS), and partial density of states (PDOS) are presented in Figure 4(a,b).

The band structure of ZnCu shows multiple bands crossing the Fermi level (E_F), consistent with its metallic character, as shown in Figure 4(a). Notably, several highly dispersive bands are observed near E_F along the Γ-X, R-X, and M–Γ directions, indicating the presence of high carrier mobility in these directions. In contrast, the presence of relatively flat bands around −3 eV to −2 eV corresponds to localized Cu-d states, as supported by the PDOS in Figure 4(b). The absence of a band gap and the significant overlap of conduction and valence bands near E_F suggest that ZnCu can exhibit good electrical conductivity. The availability of partially filled conduction states also implies the possibility of tuning thermoelectric performance through appropriate doping or carrier concentration adjustment.

The PDOS plot reveals that the Cu-3d orbitals dominate the valence region, particularly within the energy range from approximately −4 eV to −2 eV, as shown in Figure 4(b). The Zn-3d states contribute mainly at deeper energies (−6 eV to −3 eV), whereas the s and p orbitals of both Zn and Cu exhibit relatively minor contributions. The non-zero density of states at the Fermi level confirms the metallic nature of ZnCu, which further supports the results of the band structure.

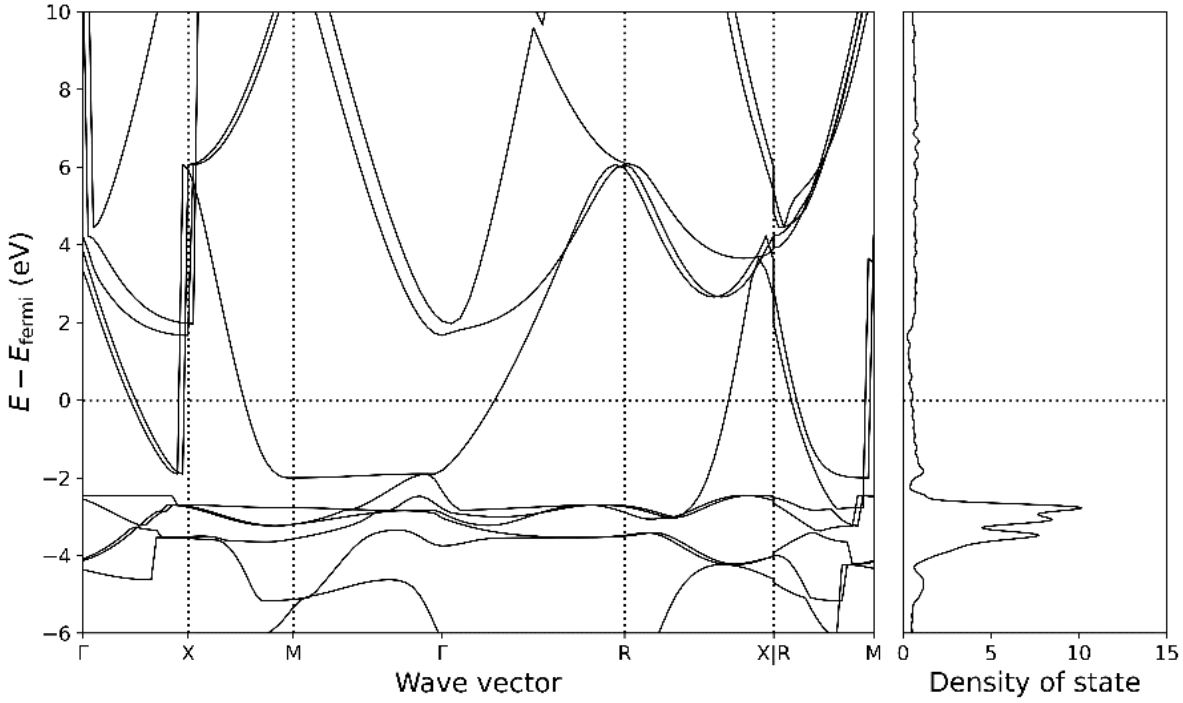

Figure 3: Caption

5.1 Thermoelectric properties

The thermoelectric properties of the ZnCu crystal structure were investigated, focusing on the Seebeck coefficient (S), electrical conductivity (σ/τ), thermal conductivity (k/τ), and power factor ($PF = S^2\sigma/\tau$). The calculated values of these parameters are plotted as a function of temperature in Figure 5(a–d). The Seebeck coefficient exhibits a nonlinear trend, reaching its peak value at 200 K and its lowest point at 300 K. The electrical conductivity decreases as the temperature rises, while thermal conductivity shows a linear increase with temperature.

Moreover, the power factor is at its maximum at 300 K. The reduction in electrical conductivity and the rise in thermal conductivity with increasing temperature could be attributed to electron–phonon interaction. Although the electrical conductivity is not particularly high at 300 K, it is adequate to yield the maximum power factor due to the significantly negative Seebeck coefficient value.

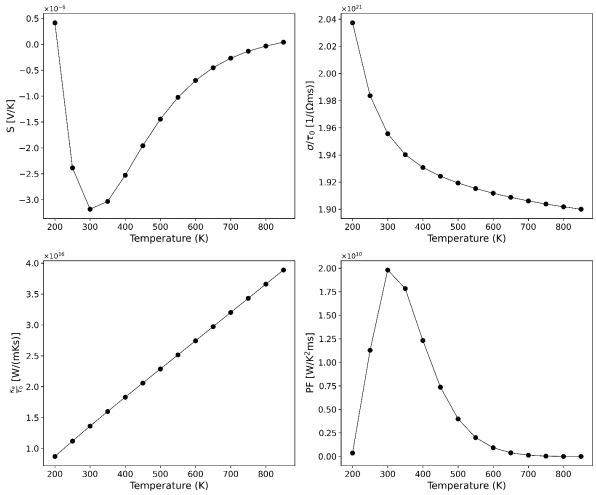

Figure 4: Caption

6 Phonon and thermal properties

The thermodynamic assessment of ZnCu, presented in Fig. (vii), indicates a reduction in free energy as temperature increases, suggesting mechanical stability at higher temperatures. The entropy also rises with temperature, reflecting an increase in system disorder, and the specific heat capacity C_V exhibits a sharp rise at low temperatures and becomes constant at high temperature indicating phonon excitation.

7 Conclusions

Structural properties, elastic properties, electronic properties, thermoelectric properties, and phonon and thermal properties of ZnCu were studied in this work. The following conclusions are drawn from this study:

1. **Structural and electronic properties** were investigated using Density Functional Theory (DFT) implemented in the Quantum ESPRESSO software. The calculated values of lattice constant and bulk modulus are in good agreement with experimental results and other theoretical studies.

2. **Elastic properties** such as bulk modulus, Young's modulus, shear modulus, Poisson's ratio, and universal elastic anisotropy index were studied using the Thermo_pw code. The calculated values show good agreement with those available in the Materials Project database. The obtained universal anisotropy index of 2.565 indicates that ZnCu is anisotropic in nature.

3. **Thermoelectric properties** of ZnCu were studied using the BoltzTraP code. The study reveals that the material exhibits its maximum power factor at 300 K.

4. **Phonon and thermal properties** were analyzed using the Phonopy code. The phonon density of states (DOS) obtained aligns well with those reported by Peter *et al.*. The results show that the free energy decreases and entropy increases with temperature. More-

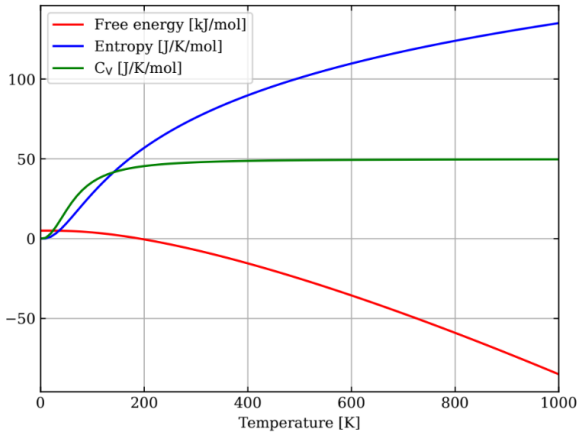

Figure 5: Caption

over, the heat capacity at constant volume (C_V) increases sharply at low temperatures and saturates at higher temperatures.

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