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Elastic properties and zone centre frequencies of Cu_2O by LCAO method

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The elastic properties and the phonon frequencies at the Brillouin zone centre have been investigated for the cubic cuprous oxide. The calculations under the framework of density functional theory have been carried out by deploying the periodic linear combination of atomic orbitals method. After settling the crystal structure the elastic constants have been determined. The absolute values of elastic constants are well in agreement with the experimental reports. The vibrational frequencies at the centre of the Brillouin zone are classified as the Raman and Infrared active modes and compared with the available experimental data. The contribution of vibrational modes to the Gibbs free energy, entropy and heat capacity has also been found.

Keywords: LCAO method, Elastic properties, Vibration frequencies, Cuprous oxide

1 Introduction

The quantum mechanical studies using state of art first-principles methods enable to design and tune properties of materials. Especially the consistency and order of accuracy in calculations have evolved immensely in last few years which are mandatory for the elastic and vibrational properties. Cuprous oxide has received considerable attention because copper is very important in technological applications and readily available[1]. This is one of the oldest and very important semiconductor but its elastic, thermal and vibration properties are less well understood[2,3]. Elastic properties can give information in terms of acoustic behavior and a detailed picture of the chemical bonding. Earlier experimental studies of elastic properties revealed unusual temperature dependence[4]. A discrepancy in the compressibility is found and crystal instability, impending phase transformation at higher pressure are suggested[5,6]. The lattice dynamics of Cu_2O has been studied experimentally by infrared (IR) and Raman spectroscopy, excitation luminescence, and inelastic neutron scattering[7-10]. On the theoretical side, first-principles calculations are reported[11]. Some discrepancies in the phonon bands are also pointed out by Linnera and Karttunen[12]. These studies helped to gain understanding of the nature of the electron-phonon interaction. Moreover, information about the spin‒phonon interaction is also discussed[13,14]. The vibrational properties of solids are directly associated with the phonon dispersion which is very insightful in understanding the phase transition. In this work, we study elastic constants and give the phonon dispersion within the framework of density functional theory (DFT). For this, we have applied the periodic linear combination of atomic orbitals (LCAO) method embodied in the CRYSTAL14 package[15].

2 Crystal Structure and Computational Method

The space group of cubic cuprous oxide is Pn3m. The unit cell of cuprous oxide consists of two formula units. The BCC sublattice is formed by two oxygen atoms and each oxygen atom is surrounded by a tetrahedron of copper atoms whereas an FCC sublattice is formed by copper atoms which are linearly coordinated with two oxygen atoms. In the pressure range 10-12 GPa, the experimental and theoretical studies show that, the cubic cuprite phase transforms into the hexagonal CdI_2-like phase[16-19].

The first-principles periodic LCAO method is applied. The salient features can be found in our earlier work[15,20]. The Gaussian basis sets proposed for Cu and O are directly taken[21,22]. The Perdew-Burke-Ernzerhof (PBE) ansatz based on the generalized gradient approximation (GGA) is applied to treat the exchange and correlation (XC) part of the Kohn-Sham Hamiltonian [23]. The Monkhorst and Pack[24] net of 16×16×16 is taken for the self - consistent calculations. The structure is optimized with an iterative method based on the total energy gradients

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*Corresponding author (E-mail: vijaymaurya2414@gmail.com) calculated analytically with respect to the nuclear coordinates and numerically with respect to the lattice constants. For exact treatment of the Coulomb and exchange terms of the total energy operator, computation of integrals over an infinite series is mandatory. To achieve it in practice, each infinite series needs to be truncated beyond preset threshold (T) values. These values ensure that beyond cutoff limits (10^{-T}) the contribution to the total sum is neglected. In current calculations, five tolerances of the order of 10^{-7}, 10^{-7}, 10^{-7}, 10^{-7} and 10^{-12} were set to truncate Coulomb and exchange sum. The SCF process is stopped when two successive cycles differ in energy by less than 10^{-8} Hartree in geometry optimization and 10^{-12} Hartree in force calculations. The convergence is checked from the root-mean-square and absolute value of the largest component of the gradients and displacements. The thresholds (in a u) for the maximum and the root-mean-square forces were set to 4.5×10^{-4} and 3.0×10^{-4} and for displacements the thresholds were 1.8×10^{-3}, 1.2×10^{-4}, respectively. The complete optimization was ensured when the four conditions are simultaneously satisfied for the fractional coordinates and cell parameters. The elastic constants and strain dependence are determined by applying the Hellmann Feynman forces within $0.01 eV/Å$ and the maximum stress with 0.02 GPa[15,25].

As for crystals with cubic symmetry, the 21 independent elements of the elastic tensor C_{ij} reduce to 3, (i.e., C_{11}, C_{12}, and C_{44}). An automated scheme for the calculation of C is used[25]. Using elastic constants a few mechanical constants can also be computed using the suitable formulae[26].

By diagonalising the mass weighted Hessian matrix, the phonon vibration frequencies at the centre of Brillouin zone (BZ) are calculated within the harmonic approximation[25-28]. For each k- point in the Brillouin zone, the mass weighted Hessian matrix can be written as:

$$W_{ij}(k) = \sum_{\underline{G}} exp\left[ik.\underline{G}\right] \frac{H_{ij}^{0\underline{G}}}{\sqrt{M_i M_j}} \quad \cdots (1)$$

where, $\underline{G}$ represents the reciprocal lattice vectors and $H_{ij}^{0\underline{G}}$ is the second derivative of V(**x**) at equilibrium with respect to displacement coordinates. In harmonic approximation V(x) takes the form:

$$V(0) = \frac{1}{2}\langle u|H|u\rangle \quad \cdots (2)$$

where, $|u\rangle$ represents the displacement of i^{th} Cartesian coordinate and H is the Hessian matrix. At the centre of Brillouin zone [Γ = (0, 0, 0)] above equation reduces to:

$$W_{ij}(0) = \sum_{\underline{G}} \frac{H_{ij}^{0\underline{G}}}{\sqrt{M_i M_j}}. \quad \cdots (3)$$

Frequencies at the centre of Brillouin zone are evaluated using set of SCF calculations of the unit cell which are performed at the equilibrium geometry and improving each of the 3N nuclear coordinates in turn by u. These calculations are implemented deploying the crystalline-orbital program package CRYSTAL14[15].

3 Results and Discussion

3.1 Elastic properties

The mechanical properties of a material are closely related to the elastic constants. The mechanical constants are deduced from the elastic constants C_{ij} following the formulation of Wu *et al.*[26] Three elastic constants, bulk modulus (B), shear modulus (G) and Poisson's ratio (σ) are listed in Table 1. The C_{12} and C_{44} show maximum deviation with the experiments. The bulk modulus calculated by us is slightly higher

Table 1 – Comparison elastic constants and bulk properties of Cu$_2$O. All quantities are in GPa except sigma and (B/G), which are dimensionless. The experimental data are taken from the inelastic neutron scattering (INS) and ultrasonic measurement (UM). The planewave pseudopotential (PW-PP) calculations are performed using CASTEP.

Properties	This work	Experiment		Theoretical	
		INS [34]	UM [5]	PW-PP [34]	VASP [35]
C_{11}	125.78	116	121	127.46	127.2
C_{12}	135.19	105	105	107.07	105.4
C_{44}	17.32	11	10.9	9.21	6.3
B	132.05	112	105.7	113.87	112.7
G	8.43	-	10.3	9.59	-
σ	0.469	-	0.454	0.459	-
B/G	15.65	-		11.87	-

whereas the shear modulus is slightly smaller than the other two predicted values. All constant are overall in good agreement with the experimental values as well as other theoretical values. While studying the elastic properties of a substance, the role of ductility and brittleness becomes important. Ductile materials can be easily pressed into desirable shapes and are more resistant to catastrophic failure whereas brittle materials are susceptible to sudden failure under critical mechanical stress conditions. There is no standalone criterion to measure ductility or brittleness of a material purely on the basis of elastic constants [29]. Nevertheless, the B/G ratio can reasonably predict such behavior[30]. A high B/G ratio is associated with ductility and the low value indicates brittleness. The critical value 1.75 separates ductile and brittle nature. The high value of B/G by all calculations shows the ductile nature of Cu_2O.

Using elastic constants the compressional (V_t), shear (V_l) and the mean wave velocity (V_m) in crystals can be calculated. The values of these quantities for Cu_2O are 4.487, 1.665 and 1.89 km/s respectively. The corresponding experimental values reported by Manghnani *et al.*[6] are 4.493, 1.418 and 1.485 km/s. The compressional wave velocity agrees very well with the experiment whereas, some deviation can be seen in the shear velocity. It may probably be due to the fact that calculations are done at 0 K while the measurements are at ~300 K. Fine *et al.* have given an empirical relation to calculate melting point (in Kelvin) of a crystal from elastic constant using the relation[31,32]:

$$T_m = 553 + 5.91\, C_{11} \pm 300 \quad \cdots (4)$$

where, C_{11} is in GPa and ± 300 is the standard error with 68 % confidence level. It gives that the melting point of Cu_2O is 1296.3 K. The experimental value of C_{11} is 1508 K[33]. The deviation, well within the suggested error, implies a good agreement.

We note that the three born stability criteria of cubic phase viz $C_{11} > 0$, $C_{44} > 0$ and $(C_{11} + 2C_{12}) > 0$ are well satisfied[26]. However, the criterion $(C_{11}-C_{12}) > 0$ is missed by 9 GPa. The low values of C_{44} and $C^{/} = (C_{11} - C_{12})/2$ emphasize weakness of the crystal to resist shear. This marginal instability is also mentioned by Kun *et al.*[36] Moreover, the temperature dependent studies of $C^{/}$ and C_{44} have also pointed out instability[5] in Cu_2O. Further, anomalous behavior in the pressure dependent elastic constants is found and instability in the crystal structure is suggested[6]. Some of the workers have ascribed it to the specific characteristic of the Cu-Cu metallic bond in Cu_2O[37,38]. The cations are close packed and suggest the metal–metal bonding. Such a behavior despite the usual nd^{10} configurations has been explained in terms of the participation of the higher s and p orbitals in bonding accompanied by the creation of d–orbitals holes on the metal atoms theoretically as well as experimentally[37,39,40]. Further, calculation of elastic constants requires very precise total energy calculations. The basis sets of the constituent atoms affect the total energy of the crystal. The basis sets used by us are slightly different from the TZVT basis sets describe by Linnera and Karttunen[12]. This may also be a reason for the residual difference.

3.2 Zone centre phonon frequencies and thermodynamic functions

On the basis of group theoretical symmetry analysis the vibration phonon modes can be classified in the irreducible Brillouin zone representations. The classification enables comparison with the Raman, infrared, and inelastic neutron scattering measurements. The symmetry decomposition of phonon branches at the Γ- point is:

$$\Gamma = 3F_{2g} \oplus B_u \oplus 2E_u \oplus 6F_{1u} \oplus 3F_{2u} \quad \cdots (5)$$

Excluding the three translational acoustic modes belonging to the F_{1u} representation, there are three Raman active ($3F_{2g}$) modes vibrating at 548.76 cm^{-1}. Out of the six IR active ($6F_{1u}$) optic modes, three vibrate at 123.7 and other three at 662.27 cm^{-1}. One B_u, two E_u and three F_{2u} modes are both Raman and IR inactive originating from the Cu atoms. All these modes and corresponding frequencies at the Γ- point are listed in Table 2. Our results agree with the experiment better than that of Mittal *et al.* and Sanson[8,41]. However, low frequency modes show some deviation with the experimental results. Our results are nearly equal to the PBE calculations of Linnera and Karttunen[12]. The agreement improves for the high frequency modes. It is worth noticing that the PBE and PBE0 calculations mentioned in the Table 2 are also done using LCAO method used in the current work. The results from PBE0 are closest to the experiment. The high frequency modes from current calculations and the PBE0 show nearly identical deviation from the experiment. The two calculations differ in one way. The basis sets of the Cu and O are different in the two calculations. The TZVT basis sets are undertaken by Linnera and Karttunen. These are

Table 2 – Phonon frequencies in cm^{-1} at the Γ- point of the Brillouin zone of Cu_2O. The lattice dynamic model (LDM) calculations and the LSD-Perdew-Wang (LSD-PW) are also included for comparison.

Mode	This work			LCAO method		LSD-PW [41]	LDM [8]	Expt [44, 45]
	Frequency	IR	Raman	PBE [12]	PBE0[12]			
F_{2u}	42.83	Inactive	Inactive	64	86	67	101	86-88
E_u	86.96	Inactive	Inactive	79	108	119	150	109-110
F_{1u}	123.70	Active	Inactive	133	144	142	115	146-153
B_u	365.36	Inactive	Inactive	334	340	350	328	350
F_{2g}	548.76	Inactive	Active	491	497	515	515	515
F_{1u}	662.27	Active	Inactive	603	619	635	578	609-640

all-electron, triple-ζ –valence Gaussian-type basis sets optimized at the polarization level. It affects the total energy of the crystal and the dynamical matrix elements. The polarized basis sets affect the dipole moment on the atoms and hence the vibration frequencies. All these factors give rise to the difference in the calculated frequencies. In view of this current results are overall in agreement with other data.

One can split the frequency spectrum of the vibration modes in two parts. One spans from 0 to 365 cm^{-1} and other from 549 to 662 cm^{-1}. There is a gap of 284 cm^{-1} between the two parts. Such a gap has also been reported by other workers[42,43]. It is also mentioned that the optical modes of oxygen constitute the high-frequency states while the acoustic modes and optical modes associated with Cu constitute the low-frequency states.

The vibrational frequencies contribute to the total energy of the crystal and a few thermodynamic quantities like Gibbs free energy, entropy etc. can be calculated. Consequently, it is also possible to find entropy. To get enthalpy the PV contribution is added. The vibrational partition function enables to find its contribution to the free energy as:

$$F_{vib}(T) = k_B T \sum_{q\lambda} ln \left\llbracket 2 sinh \frac{\hbar w_{q\lambda}}{2k_B T} \right\rrbracket \quad \ldots (6)$$

where, qλ designates a vibration mode. Values of these functions at the 298.15 K and 1.013 kPa are given in Table 3. In the Einstein model, the free energy is calculated taking the vibrational modes contribution only at the Γ-point. Calculations have shown that the Einstein model introduces errors of 20 % and hence not a good approximation to study thermal expansion[42] in Cu_2O. We have included the phonon frequencies at a few other symmetry points and so the free energy is lower than that reported by other workers. The heat capacity 56.36 J/(mol.K) is very near to the experimental data[46].

Table 3 – A few thermodynamic functions of Cu_2O.

S (meV/(cell.K))	F_{vib} (meV/cell)	F_{vib}+pV-TS (eV/cell)
1.899	242.10	-323.91

4 Conclusions

In this paper, we have applied the periodic LCAO method to study elastic properties and the phonon frequencies at the Γ-point of the Brillouin zone of the cubic cuprous oxide. The absolute values of most of the elastic constants are well in agreement with other results. The instability features proposed by earlier workers are also seen in current calculations. The residual difference may probably be reduced by taking improved basis sets of the constituent atoms at the polarization level. We have reported the vibrational frequencies at the centre of the Brillouin zone with classifications as the Raman and Infrared active modes. These are compared with the available experimental data and overall a good agreement is found. The contribution of vibrational modes to the Gibbs free energy, entropy and heat capacity is determined including the contribution of the vibration frequencies at other symmetry points. The results follow the general trend.

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References

1 Singh J & Rawat M, *J Bioelectron Nanotechnol*, 1 (2016) 9.

2 Meyer B K, Polity A, Reppin D, Becker M, Hering P, Kramm B, Klar P J, Sander T, Reindl C, Heiliger C, Heinmann M, Müller C & Ronning C, Chapter VI in *semiconductors and semimetals*, Vol 88, (Eds.) Svensson B G, Pearton S J, Jagadish C (Academic Press, Oxford), (2013) 201.

3 Meyer B K, Polity A, Reppin D, Becker M, Hering P, Klar P J, Sander T, Reindl C, Benz J, Eickhoff M,

Heiliger C, Heinmann M, Bläsing J, Krist A, Shokovets S, Müller C & Ronning C, *Phys Stat Sol B*, 1 (2012) 23.
4 Zuckerwar A, *Bull Am Phys Soc*, 14 (1969) 392.
5 Hallberg J & Hanson R C, *Phys Stat Sol*, 42 (1970) 305.
6 Manghnani M H, Brower W S & Parker H S, *Phys Stat Sol (A)*, 25 (1974) 69.
7 Beg M M & Shapiro S M, *Phys Rev B*, 13 (1976) 1728.
8 Mittal R, Chaplot S L, Mishra S K & Bose P P, *Phys Rev B*, 75 (2007) 174303.
9 Reichardt W, Gompf F, Aïn M & Wanklyn B M, *Z Phys B-Condensed Matter*, 81 (1990) 19.
10 Dar M A, Ahsanulhaq Q, Kim Y S, Sohn J M, Kim W B & Shin H S, *Appl Surf Sci*, 255 (2009) 6279.
11 Debbichi L, Marco de Lucas M C, Pierson J F & Krüger P, *J Phys Chem C*, 116 (2012) 10232.
12 Linnera J & Karttunen A J, *Phys Rev B*, 96 (2017) 014304.
13 Kuz'menko A B, Marel D V D, Bentum P J M, Tishchenko E A, Presura C & Bush A A, *Phys Rev B*, 63 (2001) 09430.
14 Chen X K, Irwin J C & Franck J P, *Phys Rev B*, 52 (1995) 13130.
15 Dovesi R, Saunders V R, Roetti C, Orlando R, Zicovich-Wilson M, Pascale F, Civalleri D, Doll K, Harrison N M, Bush J, D'Arco Ph, Llunell M. Causà M, & Noël Y, *CRYSTAL14 User's Manual, University of Torino*, Torino (2014).
16 Rai B P, *Solar Cells*, 25 (1988) 265.
17 Nandy S, Banerjee A N, Fortunato E & Martins R A, *Rev Adv Sci Eng*, 2 (2013) 273.
18 Zemzemi M, Elghoul N, Khirouni K & Alaya S, *JETP,* 118 (2014) 235.
19 Kalliomaki M, Meisalo V & Laisaar A, *Phys Stat Sol (A)*, 56 (1979) K127.
20 Paliwal U & Joshi K B, *J Phys D:Appl Phys,* 44 (2011) 255501.
21 Ru E, Liunell M & Alemany P, *J Solid State Chem*, 176 (2003) 400.
22 Heifets E, Kotomin E A, Bagatinyants A A & Maier J, *J Phys Chem Lett*, 6 (2015) 2897.
23 Perdew J P, Burke K & Ernzerhof M, *Phys Rev Lett,* 77 (1996) 3865.
24 Monkhorst H J & Pack J D, *Phys Rev B*, 13 (1976) 5188.
25 Perger W F, Criswell J, Civalleri B & Dovesi R, *Comput Phys Commun*, 180 (2009) 1753.
26 Wu Z J, Ghao E J, Xiang H P, Hao X F, Liu X J, & Meng J, *Phys Rev B*, 76 (2007) 054115.
27 Evarestov R A, Quantum Chemistry of Solids: The LCAO first principles treatment of crystals, (Springer Verlag: Heidelberg), (2007) 153.
28 Pascale F, Zicovich-Wilson C M, Lopez F, Civalleri B, Orlando R & Dovesi R, *J Comput Chem*, 25 (2004) 888.
29 Pugh S F, *Phil Mag*, 54 (1954) 823.
30 Nakamura M, Matsumoto S & Hirano T, *J Mater Sci*, 25 (1990) 3309.
31 Fine M E, Brown L D & Marcus H L, *Scr Metall*, 18 (1984) 951.
32 Ustundag M, Aslan M & Yalcin B G, *Comput Mater Sci*, 81 (2014) 471.
33 Young J A, *J Chem Edu*, 80 (2003) 257.
34 Liu N, Sun J & Wu D, *Adv Mater Res*, 335 (2011) 328.
35 Gupta M K, Mittal R, Chaplot S L & Rols S, *J Appl Phys*, 115 (2014) 093507.
36 Kun L, Yi-Feng D, Dong L V, Hong-Bo W, Li-Xia Q, Li-Wei S & Gang T, *Chin Phys Lett*, 31 (2014) 117701.
37 Zuo J M, Kim M, O'Keeffe & Spence J C H, *Nature*, 401 (1999) 49.
38 Maurya V & Joshi K B, *J Phys Chem A*, 123 (2019) 1999.
39 Marksteiner P, Blaha P & Schwarz K, *Phys B – Conden Matt*, 64 (1986) 119.
40 Humphreys C J, *Nature*, 401 (1999) 21.
41 Sanson A, *Solid State Comm*, 151 (2011) 1452.
42 Bohnen K P & Heid H, *Phys Rev B*, 80 (2009) 134304.
43 Kugel G E, Carbatos C & Kress W, *Ab Initio calculation of phonon spectra*, (Ed.) J T Devreese, (Plenum Press: New York), (1983) 101.
44 Petroff Y, Yu P Y & Shen Y R, *Phys Rev B*, 12 (1975) 2488.
45 Ivanda M, Waasmier D, Endriss A, Ihringer J, Kirfel A & Kiefer W, *J Raman Spectrosc*, 24 (1997) 487.
46 Chase M W, NIST – *JANAF Thermochemical Tables Part II*, Cr – Zr, (AIP Pub New york), 4th Edn, (1998).