

Density Functional Study of the Structural Properties of Copper Iodide: LDA vs GGA Calculations

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Abstract. We have performed first principles total energy calculations to investigate the structural properties of copper iodide (CuI) in its sodium chloride, cesium chloride, zincblende and wurtzite structures. Calculations are done using the density functional theory. We employ the full potential linearized augmented plane wave method as implemented in the wien2k code. The exchange and correlation potential energies are treated in the generalized gradient approximation (GGA), and the local density approximation (LDA). Optical absorption experiments and x-ray diffraction measurements have shown that zincblende is the ground state of CuI. Our calculations find that in the GGA formalism wurtzite and zincblende have similar total energies, while in the LDA formalism the lowest minimum corresponds to zincblende. Results show that the energy difference between the wurtzite and the zincblende structures, as calculated within the GGA formalism is 2 meV, and within the LDA formalism, is 31 meV. These results may suggest a coexistence of both wurtzite and zincblende structures in the ground state of CuI. Structural parameters are correctly reproduced by the GGA calculations. We obtain that under the application of external pressure the atomic configuration may transform into the NaCl structure. At higher pressures it is possible to have a phase transition to the CsCl geometry.

Introduction

There is a continuous interest in the study of the structural and electronic properties of copper iodide (CuI), due to its importance in electronic devices such as solar cells [1]. Also, CuI thin films have been used in electrophotography and thermoelectric devices as well as photographic materials [2]. The atomic structure of CuI and its phase transitions have been investigated experimentally. Optical absorption measurements [3] and high resolution x-ray diffraction [4] have shown that the ground state of CuI is the zincblende structure (ZB). Under the application of external pressure CuI may transform into the rocksalt phase (NaCl) [3], but at high temperatures the atomic configuration converts into the hexagonal phase [5] before reaching the rocksalt structure. Up to date a few theoretical efforts have been made to understand completely the atomic structure of CuI and its transitions to other phases. Vashista et al. [6] have predicted a direct transition from the ZB to NaCl without intermediate phases. On the other hand, theoretical calculations have been performed in the zincblende and rocksalt structures to determine the band structure [3] of CuI.

In this paper, we report first principles total energy calculations to investigate the structural properties of CuI. The calculations are done within the periodic density functional theory (DFT), using the local density approximation (LDA) and the generalized gradient approximation (GGA).

Calculated structural parameters, obtained employing the GGA approximation, are in good agreement with the experimental results of Ken and Hull [4].

Computational Technique

We performed first principles total energy calculations to study the atomic configuration of CuI in four geometries: NaCl, CsCl, zincblende and wurtzite. Calculations are done within the DFT formalism. We apply the full potential linearized augmented plane wave (LAPW) approach as developed in the wien2k code [7]. The exchange and correlation potential energies are treated within the generalized gradient approximation (GGA) [8], within the Perdew, Burke, and Ernzerhof (PBE) parameterization, and the local density approximation (LDA) using the Perdew and Zunger [9] fit to the Monte-Carlo simulations of Ceperley and Alder [10]. The number of the integrating points over the irreducible part of the first Brillouin zone, that we have used are 72, 84, 91 and 70 k-points for the rock-salt, cesium chloride, zincblende and wurtzite structures, respectively. We have carefully tested the convergence of the k-points and larger number of k-points made negligible differences.

Results

In Fig. 1 we show the calculated total energy as function of volume, $E=E(V)$, for the rocksalt (stars), CsCl (circles), wurtzite (triangles) and zincblende (asterisks) phases of CuI, within the LDA formalism for the exchange and correlation potential. Energies and volumes are per single CuI formula unit; the wurtzite unit cell contains two and the others only one atom. Moreover we calculated the energies of the isolated neutral atoms of both Cu and I, and then added them to obtain the energy reference. Once the energy reference is defined, this is subtracted from the total energy obtained for each phase, to finally get the energy used in the graphs. This in turn defines the minimum energy as the cohesive energy of each configuration. Calculated data were fitted to the Murnaghan [11] equation of state for each phase obtaining the solid curves shown in the same figure. From the minimum of each curve we can obtain the structural parameters, like equilibrium lattice parameter and bulk modulus. The lowest minimum energy corresponds to the zincblende phase with $a=5.82$ Å, $B_0=59.73$ GPa, and cohesive energy $E_0=7.63$ eV, while the reported [5] experimental data are $a=6.0521$ - 6.103 Å and $a=6.043$ Å [12]. However, we note that the energies of both zincblende and wurtzite phases are similar, being the wurtzite structure higher by 31 meV ($a=4.04$ Å, $c/a=1.67$, $B_0=54.63$ GPa, $E_0=7.60$ eV). The energy of rock-salt is 0.39 eV higher, while the CsCl total energy is even higher (1.52 eV).

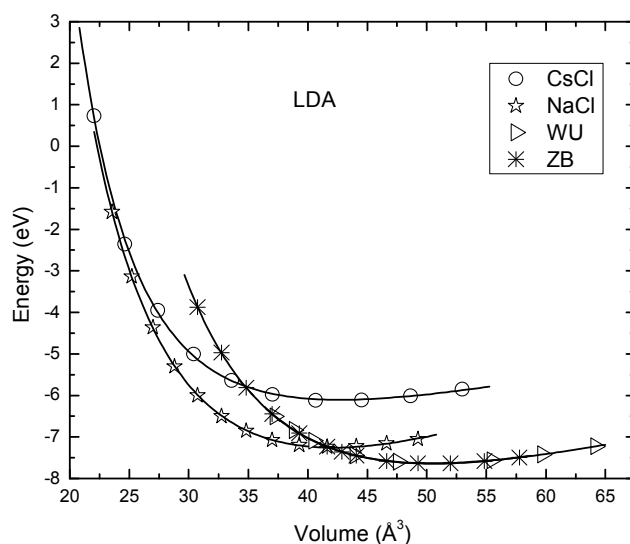
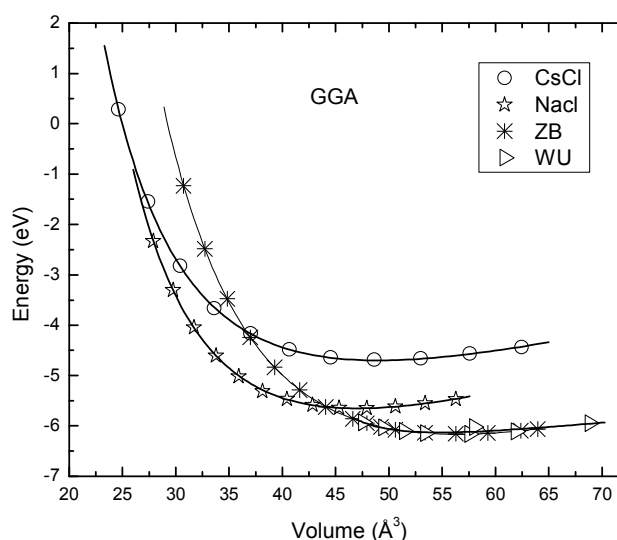


Figure 1. Total energies per single CuI formula unit as function of volume using the LDA approximation; the wurtzite unit cell contains two and the others only one atom.

Fig. 2 presents the results for total energy as function of volume, $E=E(V)$, obtained within the GGA approximation. Solid curves are the fittings while symbols represent the calculated energies. In this case, as in the LDA calculations, zincblende and wurtzite phases have very similar total energies. For wurtzite, the equilibrium structural parameters are $a=4.30$ Å, $c/a=1.67$, $B_0=34.99$ GPa, $E_0=6.16$ eV. We shall mention that the wurtzite phase has the lowest minimum total energy. The difference of the energy minimum between the wurtzite and zincblende phases is only 2 meV, within the accuracy of our calculations. This small energy difference suggests the possible coexistence of both wurtzite and zincblende phases in the ground state of CuI. Table 1 summarizes the calculated structural parameters of CuI in different phases, using the two exchange and correlation energy approximations. It is observed that the calculated parameters in the GGA scheme are in better agreement with the experiment than those obtained by LDA calculations. LDA calculations overestimate the bonding, yielding larger cohesive energies and shorter lattice parameters. On the other hand, GGA underestimates the bonding and yields smaller cohesive energies and larger lattice parameters.

Figure 2. Total energies per single CuI formula unit as function of volume using the GGA approximation; the wurtzite unit cell contains two and the others only one atom.



From Figs. 1 and 2 we see that the zincblende/wurtzite curves cross the curve corresponding to the rock-salt phase, predicting a phase transition to the rocksalt structure. The calculated transition pressure is 9.38 GPa while using LDA, and 9.7 GPa while using GGA. The zincblende/wurtzite curves also cross the curve corresponding to the CsCl phase, predicting a phase transition to the CsCl structure. According to the experiment of Ves et al. [3] the zincblende phase changes to an intermediate rhombohedral structure at 1.4 GPa, and then at 4 GPa it changes to a tetragonal geometry. At pressures above 10 GPa the NaCl structure is stable. Our calculated value for the transition pressure is in good agreement with the experimental one in the case of NaCl. As in the present work we are not considering the intermediate phases, we cannot compare directly with the experiment.

First principles total energy studies have been performed by Palomino et al. [14] to investigate the atomic structure and phase transitions of silver iodide (AgI). It was found that both GGA and LDA calculations yield the same ground state for the coexistence of the wurtzite and zincblende structures. In our studies we have obtained similar results. In the GGA calculations, the energy difference is only 2 meV between the wurtzite and zincblende atomic geometries, while in the LDA calculations it is 31 meV. The LDA results agree with experiments, which favor the zincblende as the ground state of CuI.

Table1. Calculated structural parameters for CuI.

Structure	NaCl		CsCl		Zincblende			Wurtzite	
	GGA	LDA	GGA	LDA	GGA	LDA	Exp.	GGA	LDA
a(Å)	5.77	5.50	3.65	3.44	6.08	5.82	6.0521 6.103 ^a 6.043 ^b 6.054 ^c	4.30	4.04
c/a								1.67	1.67
u								0.37	0.37
V(Å ³)	47.93	41.63	48.63	40.65	56.29	49.26	55.42- 56.83 ^a	57.56	47.59
B ₀ (GPa)	46.45	75.66	35.18	44.83	42.36	59.73		34.99	54.63
E ₀ (eV)	5.65	7.24	4.69	6.12	6.16	7.63		6.16	7.60

^a Ref. 5

^b Ref. 12

^c Ref. 13

The band structure and the corresponding density of states for the wurtzite structure of CuI are presented in Figs. 3 and 4, respectively. The calculations are done within the GGA approximation, using the optimized lattice parameter. In Fig. 3 we show the band structure, which displays the characteristics of a semiconductor with direct gap transitions. Fig. 4 shows the total and partial density of states (DOS); the top panel is for the total DOS and the lower panels are for the partial DOS. The total DOS has contributions of the Cu-3d and the I-5p orbitals. Only the orbitals of large contributions to the total DOS are reported. The description of the total DOS has been divided in several regions. The first one corresponds to the interval -6, to -4 eV, which has a strong I-p character. There is gap between -4.3 and -3 eV. The next region has been assigned to the range -3, to 0 eV, presenting principally Cu-d contribution. From 0 to 2 eV, there is a gap indicating that the CuI behaves as a semiconductor. Finally, in the last region [in between 2 and 5 eV], the main contribution is due to the I-p orbital. Similar results are obtained in the LDA case.

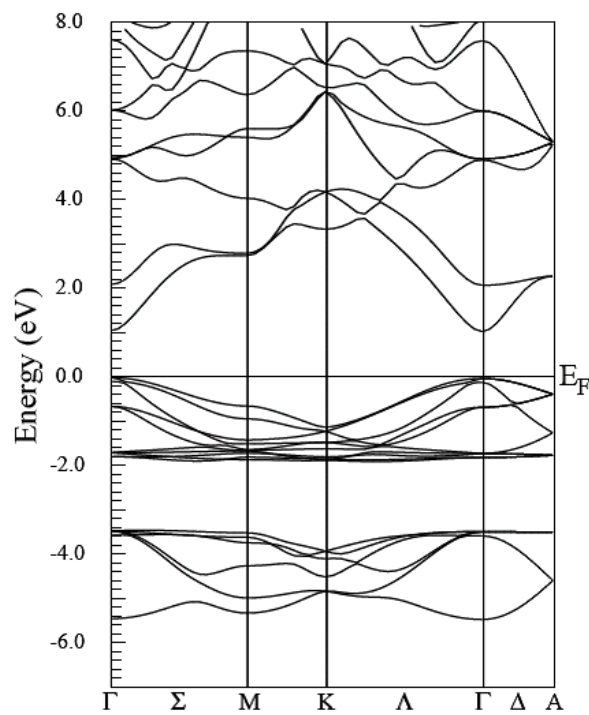


Figure 3. Electronic band structure of CuI for the wurtzite phase in the GGA approximation.

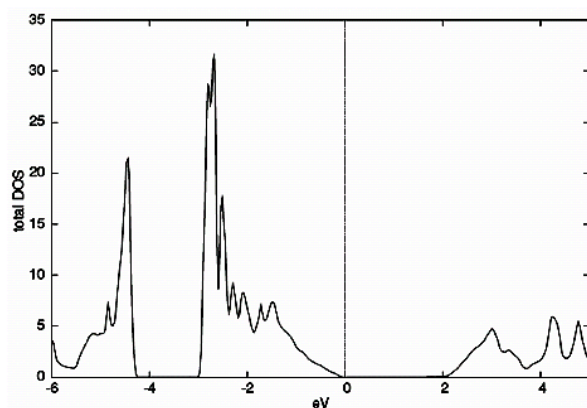
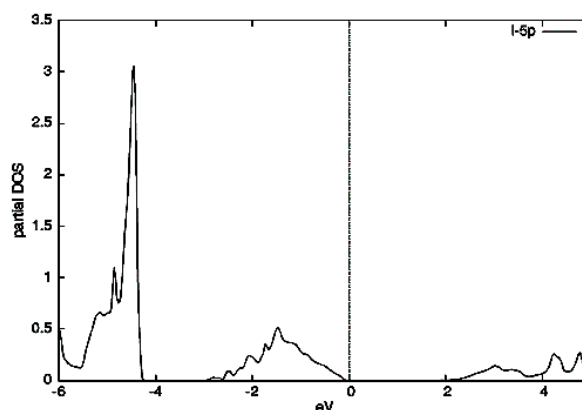
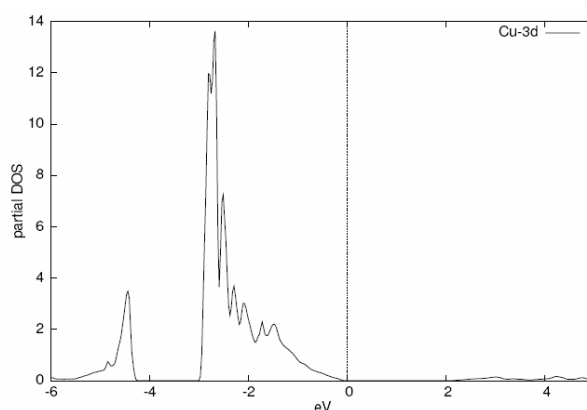


Figure 4. Total DOS and principal partial contributions of Cu and I of the CuI in the GGA approximation.



Conclusions

We have presented first principles total energy calculations to investigate the stability of several phases of copper iodide. Studies were carried out within the density functional theory (DFT) using the full potential linearized augmented plane wave (FP-LAPW) method as implemented in the wien2k code. Two approximations for the exchange and correlation energies have been employed: the generalized gradient approximation (GGA), and the local density approximation (LDA). Four phases have been considered, NaCl, CsCl, wurtzite and zincblende. Results show that the energy difference between the wurtzite and the zincblende structures, as calculated within the GGA formalism is 2 meV, and within the LDA formalism, is 31 meV. These energy differences are quite small, which may suggest a possible coexistence of both wurtzite and zincblende structures in the ground state of CuI. Structural parameters are correctly reproduced by the GGA calculations. Our calculations predict that under the application of external pressure the atomic configuration may transform into the NaCl structure. At higher pressures it is possible to have a phase transition to the CsCl geometry. The total density of states, in the wurtzite phase, is mainly due to the Cu-d and I-p contributions. Moreover the band diagram characteristic of CuI in the wurtzite phase corresponds to a semiconductor.

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References

- [1] M. Rusop, T. Soga, T. Jimbo, and M. Umeno, *Surf. Rev. and Lett.* Vol. 11 (2004), p. 577
- [2] T. K. Chaudhuri, P. K. Basu, A. B. Patra, R. S. Saraswat, and H. N. Acharya, *Jpn. J. Appl. Phys.* Vol. 29 (1990), p. L352
- [3] S. Ves, D. Glotzel, M. Cardona, and H. Overhof, *Phys. Rev. B* Vol. 24 (1981), p. 3073
- [4] D. A. Keen and S. Hull, *J. Phys.: Condens. Matter* Vol. 6 (1994), p. 1637
- [5] D. A. Keen and S. Hull, *J. Phys.: Condens. Matter* Vol. 7 (1995), p. 5793
- [6] P. Vashista, and A. Rahman, *Fast Ion Transport in solids*, edited by P Vashista, J. N. Mundy and G. K. Shenoy, North Holland, New York (1979).
- [7] P. Blaha, K. Schwarz, G.K.H. Madsen, D. Kvasnicka, and J. Luitz, WIEN2K: An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties (Karlheinz Schwarz, Techn. Universität Wien, Austria), 2001. ISBN: 3-9501031-1-2.
- [8] J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* Vol. 77 (1996), p. 3865
- [9] J.P. Perdew and A. Zunger, *Phys. Rev. B* Vol. 23 (1981), p. 5048
- [10] D. M. Ceperley and B.J. Alder, *Phys. Rev. Lett.* Vol. 45 (1980), p. 566
- [11] F. D. Murnaghan, *Proc. Natl. Acad. Sci. USA* Vol. 3 (1944), p. 244
- [12] R. W. Wyckoff, *Crystal Structures*, 2nd Ed. Vol. 1 Wiley (1963)
- [13] M. Yashima, Q. Xu, A. Yoshiasa, and S. Wada, *J. Mat. Chem.* Vol. 16 (2006), p. 4393
- [14] L. A. Palomino-Rojas, M. López-Fuentes, Gregorio H. Cocoltzi, Gabriel Murrieta, Romeo de Coss, and Noboru Takeuchi, doi:10.1016/j.solidstatesciences.2007.11.022.

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10.4028/www.scientific.net/JNanoR.5.25

DOI References

- [1] M. Rusop, T. Soga, T. Jimbo, and M. Umeno, Surf. Rev. and Lett. Vol. 11 (2004), p. 577
10.1016/j.diamond.2004.07.008
- [2] T. K. Chaudhuri, P. K. Basu, A. B. Patra, R. S. Saraswat, and H. N. Acharya, Jpn. J. Appl. Phys. Vol. 29 (1990), p. L352
10.1007/BF00582474
- [3] S. Ves, D. Glotzel, M. Cardona, and H. Overhof, Phys. Rev. B Vol. 24 (1981), p. 3073
10.1103/PhysRevB.24.3073
- [4] D. A. Keen and S. Hull, J. Phys.: Condens. Matter Vol. 6 (1994), p. 1637
10.1088/0953-8984/6/9/006
- [5] D. A. Keen and S. Hull, J. Phys.: Condens. Matter Vol. 7 (1995), p. 5793
10.1080/08957959508200910
- [8] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. Vol. 77 (1996), p. 3865
10.1063/1.472933
- [9] J.P. Perdew and A. Zunger, Phys. Rev. B Vol. 23 (1981), p. 5048
10.1103/PhysRevA.23.2785
- [10] D. M. Ceperley and B.J. Alder, Phys. Rev. Lett. Vol. 45 (1980), p. 566
10.1051/jphyscol:1980744
- [13] M. Yashima, Q. Xu, A. Yoshiasa, and S. Wada, J. Mat. Chem. Vol. 16 (2006), p. 4393
10.1039/b610127e
- [14] L. A. Palomino-Rojas, M. Lpez-Fuentes, Gregorio H. Coccoletzi, Gabriel Murrieta, Romeo de Coss, and Noboru Takeuchi,
10.1016/j.solidstatesciences.2007.11.022.