

Ground State Structural Anomalies in Cuprous Halides: CuCl

C. H. Park and D. J. Chadi

NEC Research Institute, 4 Independence Way, Princeton, New Jersey 08540

(Received 29 December 1995)

We have examined structural instabilities and elastic anomalies in CuCl via first-principles calculations and find that its crystal structure is not ideal zinc blende but that correlated displacements of groups of *four* Cu atoms lead to a more stable configuration. About 20% of the Cu atoms are estimated to be affected. The Cu-Cu distance in the Cu₄ complex shrinks from 3.82 to 2.72 Å, close to that of metallic Cu. The energetics of defect formation are examined also for CuBr and CuI.

PACS numbers: 61.50.Ah, 61.66.Fn, 61.72.Ji, 62.20.Dc

Cuprous halides are the most ionic crystals with a zinc blende lattice structure. Their ionicities are near the critical threshold above which cubic binary compounds prefer either the NaCl or the CsCl structure [1]. Among the cuprous halides CuCl is the most puzzling and exhibits the greatest number of anomalies. Infrared and Raman experiments show that the phonon spectrum is highly unusual in that two distinct sets of TO and LO phonon modes [2–10] are seen (even at temperatures as low as 2 K) where only one set is expected [11]. The Lyddane-Sachs-Teller relation is not obeyed, unless both sets of phonons are taken into account [2,3]. Another anomaly first pointed out by Martin [12] is that in comparison with other zinc blende compounds the values of the bulk and shear moduli for CuCl deviate strongly from a simple d^{-4} scaling with bond length. In particular, the bulk modulus of CuCl is only 60% as large as its expected value.

It is well known that CuCl is a superionic material at temperatures above about 450 °C. At lower temperatures, e.g., room temperature, x-ray and neutron diffraction studies show that CuCl is structurally disordered [5,13,14] with the Cu ions having large displacements away from their tetrahedral sites. Several models [3–6,13,15] have been suggested to explain the phonon anomalies and disorder in CuCl. Vardeny and Brafman [6] proposed the existence of low energy secondary minima along the four [111] antibonding directions for Cu. The model received strong support from the first-principles calculations of Wei, Zhang, and Zunger who verified the existence of such minima with a formation energy of 0.1 eV [16].

The (111) soft modes can manifest themselves in two different ways. The displaced Cu atoms can occupy the various (111) minima randomly, giving a statistically disordered distribution; or if the energy barriers are small (as indicated by the calculations), the potential experienced by a Cu ion would be strongly anharmonic and the Cu atoms would sample the four minima dynamically [6,13]. Most experimental data on CuCl have been interpreted in terms of either the statically disordered or the anharmonic model. Schreurs, Mueller, and Schwartz [14] pointed out many years ago that the two models could be ex-

perimentally distinguished via neutron scattering experiments. They suggested that for the anharmonic model all diffuse scattering would be inelastic while for the disordered model there would be an elastic component. The results of their experiments showed that (50–70)% of diffuse neutron scattering was elastic thus favoring the disorder model. They concluded, however, that a random statistical distribution of Cu atoms could not explain the k dependence of the diffuse background intensity and that “more complex models, probably with correlated displacements, must be considered.”

In this Letter, we pursue the question of low energy structural metastabilities in CuCl through first-principles calculations similar to those of Wei, Zhang, and Zunger [16]. The main difference between the two calculations is the size of the unit cell used in the simulations. We find that cell size affects the sign of the formation energy for some primary defects associated with displaced Cu ions. The formation of these defects becomes suppressed for small 16 atom unit cells where the elastic strain energy around the defects cannot be fully relaxed but the defects become exothermic for a 32 atom cell.

The total energy was calculated using a first-principles pseudopotential method [17] within the local density approximation [18]. Norm-conserving nonlocal pseudopotentials [19] were generated by the scheme of Troullier and Martins [20], and Kleinman-Bylander type of fully separable pseudopotentials were constructed [21]. The Cu d states are critical in understanding the unusual properties of CuCl. They strongly hybridize with Cl-derived p states and were included in the calculations. Supercells containing 16 and 32 atoms and a kinetic energy cutoff of 40 Ry for the plane-wave expansions were used. The Brillouin zone summations were done with two special k points for a 32 atom cell [22]. For the 16 atom cell we used k -point samplings equivalent in accuracy to ten special k points for the bulk zinc blende lattice [22]. Energy minimization was achieved by the iterative Davidson method [23].

In previous theoretical work [16] Wei, Zhang, and Zunger examined the variation of the total energy when a single Cu atom in a 16 atom cell is displaced along

an antibonding $[\bar{1}\bar{1}\bar{1}]$ direction. We will refer to this defect as Cu_1 where the subscript denotes the number of displaced Cu atoms. We find, in good agreement with Wei, Zhang, and Zunger, that for a 16 atom cell the total energy of Cu_1 initially increases as the Cu atom is moved away from its tetrahedral site, but then decreases to give a metastable state with an energy of 0.1 eV.

For a larger 32 atom cell the Cu_1 defect is found (i) to become exothermic, and (ii) to evolve into the more extended Cu_4 defect shown in Fig. 1. The defect forms when the four second-neighbor Cu atoms surrounding a tetrahedral interstitial site move along their respective antibonding directions by 0.69 Å towards this site. The displacements are along the four equivalent antibonding (111) axes and the Cu_4 structure has T_d symmetry locally. The total energy is lowered by a relatively large 0.13 eV per Cu_4 complex. The separation between the Cu atoms in Cu_4 is drastically reduced from 3.82 to 2.72 Å, not much larger than the bond length of 2.56 Å in metallic Cu. We find that Cu_4 is not rigid but floppy, i.e., the excitation energies into the Cu_1 , Cu_2 , or Cu_3 states are very small (≤ 0.05 eV) and at room temperature these modes are easily excited. For a smaller 16 atom cell, the Cu_4 complex is found to be unstable as a result of the strain induced repulsive interaction between such complexes when they get too close to each other. This suggests that not all the Cu atoms in CuCl undergo a large distortion and that the motions of the displaced Cu atoms are correlated.

From the results of the calculations for 16 and 32 atomic cells it is possible to estimate the fraction of displaced Cu atoms in a CuCl crystal. Assuming that the formation energy $E(n)$ of a *single* Cu_4 center in an n atom cell is inversely proportional to n since the strain energy is distributed over n atoms, we have

$$E(n) = \frac{a}{n} - b, \quad (1)$$

where a and b are constants to be determined. The constant b gives the formation energy of a single fully relaxed Cu_4 center in an infinite cell. We find that $E(n)$ for 16 and 32 atom cells are approximately 0.10 and -0.13 eV, respectively [24]. This gives $a =$

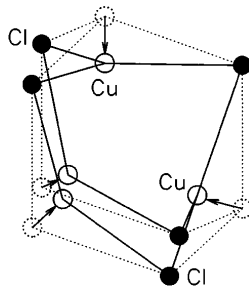


FIG. 1. A Cu_4 structure in which four Cu atoms are displaced into a common interstitial position, maintaining T_d symmetry is shown. The dashed circles show the initial position of the Cu atoms.

7.5 eV and $b = 0.36$ eV. The formation energy is, therefore, exothermic when

$$n > a/b, \quad (2)$$

i.e., when the unit cell contains more than about 21 atoms.

Assuming that the crystal contains N_{total} atoms and that on average every n atom region contains a Cu_4 center, the total energy relative to CuCl in the ideal zinc blende state is given by

$$E_{\text{total}}(n) = \frac{N_{\text{total}}}{n} E(n) = \frac{N_{\text{total}}}{n} \left(\frac{a}{n} - b \right). \quad (3)$$

The minimum of E_{total} occurs at $n = 2a/b$ or $n \approx 42$ atoms. We have considered other models and find that this estimate remains largely unchanged. Since only half the atoms in CuCl are Cu atoms and Cu_4 involves the motion of four Cu atoms, we are led to an estimate of about 20% for the percentage of Cu atoms undergoing displacement at equilibrium. From Eq. (3) we estimate that the formation of the Cu_4 complex is exothermic by 0.18 eV per complex at equilibrium where there is approximately one complex for every 42 atoms.

As mentioned above, Raman and neutron scattering data on CuCl show two sets of TO phonon peaks. These are a narrow $\text{TO}(\gamma)$ mode from the “normal” zinc blende lattice and a broader $\text{TO}(\beta)$ mode that persists to temperatures near absolute zero [3,6]. The stability of the Cu_4 defect is consistent with the temperature dependence of the intensity of the anomalous $\text{TO}(\beta)$ mode. As the temperature increases, the oscillator strength of the $\text{TO}(\beta)$ mode is observed to gradually decrease relative to that from the $\text{TO}(\gamma)$ mode [3,6,8]. This can be explained most simply when the formation energy of the “defect” is exothermic since in this case an increase in temperature decreases the density of these centers. If this energy is assumed to be endothermic [6] then the formation energy acquires an unexplained temperature dependence.

We find that the Cu_4 structure becomes more stable under pressure (see Fig. 2). This indicates that the bulk modulus of CuCl, when Cu_4 complexes are taken into account, should be smaller than that of the ideal zinc blende phase. For the *ideal zinc blende lattice*, our calculated bulk modulus of 0.66 Mbar is significantly larger than the experimental value of 0.4 Mbar [25,26], but is close to the value of 0.6 Mbar given by the d^{-4} or $d^{-3.5}$ scaling relationship [12,27]. On the other hand, using a 32 atom cell containing a Cu_4 center, the bulk modulus is calculated to be 0.49 Mbar. This value is much closer to the experimental value of 0.4 Mbar.

We have estimated the pressure dependence of the a and b parameters in Eq. (3) and find that the concentration of Cu_4 centers should gradually increase with pressure. This may account for the experimental observation that the elastic constants of CuCl decrease with pressure [28].

We have examined the Cu_4 type lattice instability for CuBr and CuI. For CuBr, the formation energy of the Cu_4

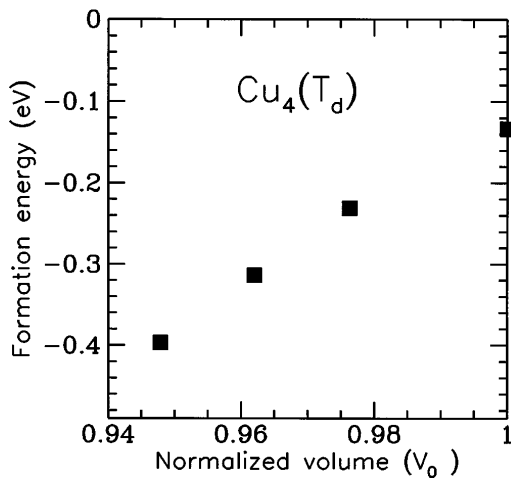


FIG. 2. Calculated formation energy of a $\text{Cu}_4(T_d)$ center is shown as a function of volume. V_0 is the equilibrium volume of the ideal zinc blende lattice.

center is calculated to be nearly zero (0.0 ± 0.05 eV), while for CuI, Cu_4 is found to be unstable. These results are consistent with experimental observations that the anomalous $\text{TO}(\beta)$ phonon mode in CuBr is seen at temperatures above 80 K [2,8], indicating a low energy metastable state, but that for CuI no anomalous phonon mode is seen [7,8]. The results are also consistent with a smaller (35%) deviation of the bulk modulus in CuBr from its expected value (as compared to 40% in CuCl) and the closeness of the measured and theoretical values for CuI [12,25,26].

What is the driving mechanism for Cu_4 complex formation in CuCl? The states near the valence band maximum (VBM) of CuCl consist of *antibonding* combinations of Cu 3*d* orbitals and Cl *p* orbitals. Bond breaking decreases the electronic energy of these states and at the same time transforms them into states with a strong hybridization of Cu *d* states as can be seen from Fig. 3. The state shown in this figure has an energy about 2.7 eV below the VBM. The decreased stability of a Cu_4 center in going from CuCl to CuBr to CuI is primarily correlated with an increase in the lattice constant from 5.41 to 5.69 to 6.04 Å, respectively, which decreases the Cu-Cu interactions.

Raman data indicate that the intensity of the $\text{TO}(\beta)$ mode in CuCl which we associate with the Cu_4 complex decreases with pressure [6,10]. Livescu and Brafman explained the data by assuming a decrease in the concentration of off-center atoms due to an increase in their formation energy [6]. From the results of our calculations, the concentration of the Cu_4 is expected to increase, not to decrease. The pressure phase diagram of CuCl is, however, complex [26,29]. At a pressure of around 5–25 kbar, a transition to a new phase was suggested by the observation of a strong Meissner-like flux exclusion [30]. It is possible that other structural instabilities can occur and these may account for the decrease of $\text{TO}(\beta)$

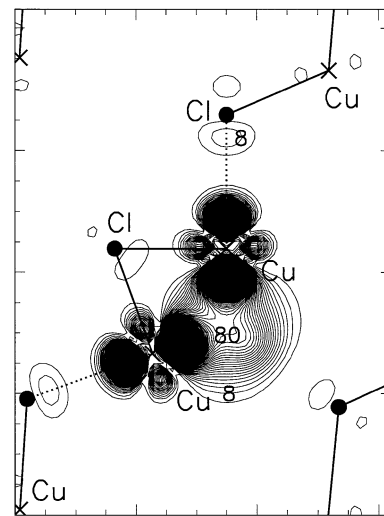


FIG. 3. Charge-density contours for a localized state around a Cu_4 center are shown in a (110) plane. The charge density is spread around the four Cu atoms of the complex two of which lie in the plane of the figure. The contour spacings are in units of 4 electrons per 32 atom cell.

intensity under pressure. We have identified one such lattice instability for CuCl, which becomes stabilized with pressure. A C_{2v} symmetric [100]-axis displacement of a Cu atom is found to give a local minimum in the total energy with an activation energy of 0.02 eV. At a pressure of about 14 kbar, this $\text{Cu}_1(C_{2v})$ structure becomes more stable than the on-site geometry. We have used the experimental bulk modulus for the pressure estimation. In this displacement, the Cu atom moves by 0.44 Å along the cubic [100] axis but the relaxation of the surrounding Cl atoms maintains the fourfold coordination. The resulting bond-length changes are small, but bond angle variations are relatively large. One bond angle around the displaced Cu atom goes from 109.5° to 90°. We suggest that the deep *p*(Cl)-*d*(Cu) hybridized bonding states (at ~5 eV below the VBM at the Γ point of the Brillouin zone) are responsible for the C_{2v} lattice instability. The Cu *d* bonding orbitals favor a bond angle of 90° around Cu. As the Cu and Cl hybridization is changed by Cu ion displacements the increase of the *p-d* coupling can stabilize the C_{2v} state. The C_{2v} symmetric lattice instability may be related to the significant reduction of the $\text{TO}(\beta)$ intensity with pressure. More extensive calculations are required to consider the structural and elastic properties of CuCl under pressure with respect to both Cu_4 and $\text{Cu}_1(C_{2v})$ lattice instabilities.

It is also possible that the anomalies in the diamagnetic susceptibility of CuCl [30] are caused by internal transitions of Cu atoms between $\text{Cu}_1(C_{2v})$ and Cu_4 type complexes. Such a transition would cause very large changes in the coordination (from 4 to 6) and in the valence charge distribution of the Cu atoms and can easily affect the susceptibility. Another intriguing possibility is a metastable state in which Cu_4 complexes in different parts of a

crystal can become linked via single Cu-Cu "joints" thereby forming a meandering chain of Cu atoms.

In summary, through first-principles calculations, we have identified structural metastabilities which help explain some of the anomalous properties of CuCl and its intrinsically disordered nature. Stable Cu_4 complexes, in which four Cu atoms surrounding a common interstitial site are all displaced into their (111) off-center positions, spontaneously lower the energy of CuCl. We estimate that about 20% of the Cu ions in CuCl are displaced into off-center sites at low temperatures. The negative pressure coefficient of the formation energy of a Cu_4 complex explains the unexpectedly soft bulk modulus of CuCl.

-
- [1] J.C. Phillips, *Bonds and Bands in Semiconductors* (Academic Press, New York, 1973).
- [2] I.P. Kaminow and E.H. Turner, *Phys. Rev. B* **5**, 1564 (1972); E.H. Turner, I.P. Kaminow, and C. Schwab, *Phys. Rev. B* **9**, 2524 (1974).
- [3] J.E. Potts, R.C. Hanson, C.T. Walker, and C. Schwab, *Phys. Rev. B* **9**, 2711 (1974).
- [4] M. Krauzman, R.M. Pick, H. Poulet, G. Hamel, and B. Prevot, *Phys. Rev. Lett.* **33**, 528 (1974).
- [5] B. Prevot, B. Hennion, and B. Dorner, *J. Phys. C* **10**, 3999 (1977).
- [6] Z. Vardeny and O. Brafman, *Phys. Rev. B* **19**, 3276 (1979); G. Livescu and O. Brafman, *Phys. Rev. B* **34**, 4255 (1986).
- [7] T. Fukumoto, S. Nakashima, K. Tabuchi, and A. Mitsuishi, *Phys. Status Solidi B* **73**, 341 (1976).
- [8] Z. Vardeny and O. Brafman, *Phys. Rev. B* **21**, 2585 (1980).
- [9] T. Nanba, K. Hachisu, and M. Ikezawa, *J. Phys. Soc. Jpn.* **50**, 1579 (1981).
- [10] M.L. Stand, H.D. Hochheimer, M. Krauzman, J.E. Potts, R.C. Hanson, and C.T. Walker, *Phys. Rev. B* **14**, 4637 (1976); H.D. Hochheimer, M.L. Shand, J.E. Potts, R.C. Hanson, and C.T. Walker, *Phys. Rev. B* **14**, 4630 (1976).
- [11] C.-Z. Wang, R. Yu, and H. Krakauer, *Phys. Rev. Lett.* **72**, 368 (1994).
- [12] R.M. Martin, *Phys. Rev. B* **1**, 4005 (1970).
- [13] M. Sakata, S. Hoshino, and J. Harada, *Acta Crystallogr. Sect. A* **30**, 655 (1974); J.A. Wilson, *Philos. Mag. B* **38**, 427 (1978); S. Miyake, S. Hoshino, and T. Takenaka, *J. Phys. Soc. Jpn.* **7**, 19 (1952).
- [14] J. Schreurs, M.H. Mueller, and L.H. Schwartz, *Acta Crystallogr. Sect. A* **32**, 618 (1976).
- [15] J.B. Boyce, T.M. Hayes, and J.C. Mikkelsen, Jr., *Phys. Rev. B* **23**, 2876 (1981).
- [16] S.-H. Wei, S.B. Zhang, and A. Zunger, *Phys. Rev. Lett.* **70**, 1639 (1993).
- [17] M.L. Cohen, *Phys. Scr.* **T1**, 5 (1982); J. Ihm, A. Zunger, and M.L. Cohen, *J. Phys. C* **12**, 4409 (1979).
- [18] P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964); W. Kohn and L.J. Sham, *ibid.* **140**, A1133 (1965).
- [19] D.R. Hamann, M. Schlüter, and C. Chiang, *Phys. Rev. Lett.* **43**, 1494 (1979).
- [20] N. Troullier and J.L. Martins, *Phys. Rev. B* **43**, 1993 (1991).
- [21] L. Kleinman and D.M. Bylander, *Phys. Rev. Lett.* **48**, 1425 (1982).
- [22] D.J. Chadi and M.L. Cohen, *Phys. Rev. B* **8**, 5747 (1973).
- [23] C.H. Park, I.-H. Lee, and K.J. Chang, *Phys. Rev. B* **47**, 15996 (1993).
- [24] We take the formation energy of the $\text{Cu}_1(\text{C}_{3v})$ structure for $E(16)$, because $\text{Cu}_4(\text{T}_d)$ is unstable against the transition to the $\text{Cu}_1(\text{C}_{3v})$ in a 16 atom cell.
- [25] *Landolt-Börnstein Tables*, edited by O. Madelung, M. Schulz, and H. Weiss (Springer, Berlin, 1984), Vol. 17a, and references therein.
- [26] S. Hull and D.A. Keen, *Phys. Rev. B* **50**, 5868 (1994).
- [27] M.L. Cohen, *Phys. Rev. B* **32**, 7988 (1985); *Science* **261**, 307 (1993).
- [28] R.C. Hanson, K. Helliwell, and C. Schwab, *Phys. Rev. B* **9**, 2649 (1974).
- [29] W. Klement, Jr., and A. Jayaraman, *Prog. Solid State Chem.* **3**, 289 (1966).
- [30] C.W. Chu, S. Early, T.H. Geballe, A. Rusakov, and R.E. Schwall, *J. Phys. C* **8**, L241 (1975); N.R. Brandt, S. Kuvshinnikov, A. Rosakov, and M. Semyonov, *JETP Lett.* **27**, 37 (1978); G.C. Vezzoli and J. Bera, *Phys. Rev. B* **23**, 3022 (1981).