Pressure-induced polymorphism in CuCl: An *ab initio* study

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We report the results of pseudopotential and full-potential linear augmented plane-wave (FP-LAPW) calculations on high-pressure phases of copper chloride. It is found that nonlocal ionic pseudopotentials accurately describe the bonding in these strongly hybridized compounds over a wide range of densities. Successive transitions from CuCl-II (zinc blende) to CuCl-IV (binary analog of the metastable BC8 structure found in Si and Ge) and then to CuCl-V (rocksalt) are predicted by both *ab initio* methods. Both these transitions have been observed in recent neutron powder diffraction experiments. The structural properties and electronic energy band structure of zinc blende and NaCl structure CuCl as determined by the pseudopotential and FP-LAPW methods are compared and the band structure of CuCl-IV is reported.

I. INTRODUCTION

The copper halides (CuCl,CuBr,CuI) are the most ionic of the zinc-blende structure (tetrahedral) semiconductors. Their ionicity approaches 0.7 according to the Phillips scale and this is close to the value at which the zinc-blende structure becomes unstable with respect to the more closely packed structures, wurtzite or rocksalt, due to the electrostatic interactions. As a result of this near structural instability, a large number of pressure- or temperature-induced polymorphs are possible. The vibrational properties of copper halides also show anomalies which have motivated intense theoretical and experimental study. For example, these materials exhibit extreme anharmonicity in addition to unexpectedly large negative thermal expansion and anomalies in the first-order Raman spectrum.[1–3] In addition to the structural behavior and unusual vibrational properties of these materials,[4] the electronic properties have also been of sustained interest for many years.[5–8] The copper halides are distinct from their III-V or II-VI counterparts in that the copper $3d$ electrons hybridize strongly with the halogen p states. This admixture of Cu $3d$ states and halogen $2p$ levels is also the origin of the anomalously low deformation potentials in the copper halides. This issue has been discussed in detail elsewhere.[7]

The main point for the present discussion is that the ten $3d$ electrons of copper cannot be treated as being part of an inert core and the number of valence electrons per formula unit becomes 18 rather than 8 as it is for the other members of the tetrahedral semiconductor family.

This situation has presented a serious computational obstacle to the application of the pseudopotential method in the study of the electronic properties or structural stability of these materials. Successful electronic structure calculations on the ambient-pressure zinc-blende structure of CuCl have been reported using Korringa-Kohn-Rostoker[5] (KKR) and linear muffin-tin orbital[6] (LMTO) techniques. Relative structural stability of the zinc-blende and rocksalt phases as well as high-pressure elastic behavior of copper halides has been investigated by Singh and Gupta[9] using a three-body potential model. However, no structural stability calculations have been performed on copper halides using *ab initio* methods, to our knowledge.

The high-pressure structural, chemical and electrical properties of the copper halides (copper chloride, in particular) have been the subject of extensive experimental study.[10,11] Under normal conditions, CuCl is found in the zinc-blende structure (CuCl-II, space group $F\bar{4}3m$). At elevated temperatures and ambient pressure it is reported to exist in the wurtzite structure (CuCl-I) and at even higher temperatures, in a structure related to that adopted by β-AgI. High-pressure x-ray-diffraction measurements were reported by Meisalo and Kalliomäki[13] and these suggested that the structure of CuCl-IV was tetragonal although no atomic positions could be assigned.

More recently an extensive high-pressure powder neutron study was carried out on the copper halides by Hull and Keen[14] up to pressures of 10 GPa at room temperature. A transition from zinc blende to the octahedrally

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coordinated rocksalt structure was observed in both CuCl and CuBr up to this pressure. Unlike III-V and group-IV semiconductors which are observed to transform directly from diamond or zinc-blende structures to six- or eight-fold coordinated metallic modifications, the zinc blende to rocksalt transition in CuCl and CuBr was observed to proceed via intermediate tetrahedrally coordinated structures. One intermediate phase was identified in CuCl and was denoted as CuCl-IV and two were observed in CuBr (CuBr-IV and CuBrV). The structure of CuCl-IV and CuBr-IV was determined to be the binary analog of the BC8 structure[17]adopted by Si-III and Ge-IV when depressurized from metallic phases.[12] This is in contrast to the structural solution for this phase reported in Ref. 13. This binary version of the BC8 structure is simple cubic with 16 atoms per unit cell and is denoted as SC16.[15] The pressure-induced polymorphism in the copper halides was therefore found to be very different from that observed in more covalent systems such as the III-V and group-IV materials.

Earlier total energy calculations,[15] however, predicted that the SC16 modification is a stable high-pressure polymorph of several III-V semiconductors including GaAs, AlAs, and InAs although the structure has never been observed experimentally in these compounds. It was proposed that the formation of this structure was inhibited in the III-V materials because of geometric considerations concerning the nature of the phase transitions. Specifically, it was suggested that pressure-induced transitions between zinc blende and SC16 (two topologically distinct covalent network structures) would encounter a substantial kinetic barrier. It has very recently been reported that the β-Sn to Si-III (BC8 structure) transition proceeds via an intermediate phase characterized by odd-membered rings. This would certainly be an unfavorable transition route in compounds.[16]

In view of the predicted stability of SC16-structure III-V compounds and the experimental observation of SC16-structure I-VII compounds, it now appears that the relative energetics of high-pressure phases in these two (most and least ionic) compound semiconductor families may not be nearly as dissimilar as they first appeared. It is therefore of particular importance to make a thorough computational study of the structural stability of high-pressure phases in copper halides. This is the objective of the present work in which we apply both pseudopotential and all-electron methods to study the structural and electronic properties of CuCl under high pressure.

This paper is organized as follows. In Sec. II we describe the essential structural information of CuCl-IV. In Sec. III the computational details of the two *ab initio* total energy methods employed in this study are outlined. We then present the results of our calculations with emphasis on structural and electronic properties of CuCl in its ambient- and high-pressure forms as calculated using the two methods.

II. STRUCTURAL DETAILS OF CuCl-IV

The structure of CuCl-IV has spacegroup $Pa\bar{3}$ and represents the ordered binary analog of the BC8 structure which is known as a dense metastable polymorph of both silicon and germanium.[17] The BC8 structure is body-centered cubic containing 16 atoms per conventional cell and 8 atoms per primitive cell. The binary analog is simple cubic with a basis of 16 atoms and is generally referred to as the SC16 structure. An illustration of the SC16 structure is shown in Fig. 1. This structure contains eight CuCl formula units and is fully specified by a single unit cell parameter and two free atomic positional parameters (one for each species). We define these positional parameters as x_{Cu} and x_{Cl}. Atom positions are then located at the 8*c* sites of the $Pa\bar{3}$ spacegroup. At a pressure of 55.2 kbar these two positional parameters have been determined by structural refinement of neutron powder data to be x_{Cu} =0.6297(3) and x_{Cl} = 0.1527(3), with a corresponding lattice parameter of 6.416 Å.[14] These values for the positional parameters give a Cu^{+}-Cl^{-} contact distance of 2.4 Å which is similar to that found in the zinc-blende phase. The variation of x_{Cu} with pressure is insignificant, being within quoted experimental errors, whereas the value of x_{Cl} appears to increase slightly to 0.1540(3) at a pressure of 92.4 kbar. This structure reduces to the body-centered $Ia\bar{3}$ structure of Si-III and Ge-IV in the special case for which the anion and cation are identical and $x_{\mathrm{Cu}} - x_{\mathrm{Cl}} = 1/2$.

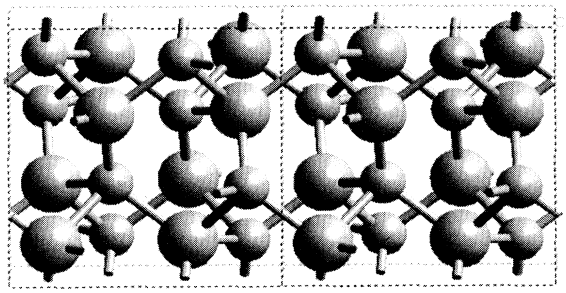

FIG. 1. Three-dimensional illustration of the SC16 structure containing two unit cells. The Cu atoms are denoted as the smaller spheres.

III. COMPUTATIONAL TECHNIQUES

A. Pseudopotential plane-wave method

Nonlocal, norm-conserving ionic pseudopotentials for Cu were generated according to the scheme described in Refs. 18 and 19. The Cl pseudopotential was optimized according to the scheme given by Rappe *et al.*[19] The separation method of Klienman and Bylander[20] is used in both cases to handle the nonlocal pseudopotential.

For chlorine, the electronic configuration was $3s^{2.00}$ $3p^{5.00}$ for *s* and *p* potentials and $3s^{1.00}$ $3p^{3.75}$ $3d^{0.25}$ for the *d* potential. The cutoff radius was 0.9 Å.

The electronic configuration used to generate the pseudopotential for copper was $3d^{9.00}$ $4s^{0.75}$ $4p^{0.25}$ for all *s*, *p*, and *d* potentials. Two Cu pseudopotentials were generated initially having core radii of 1.06 and 1.27 Å, respectively. The latter potential, being softer, allowed for a far

smaller plane-wave energy cutoff. However, the Cu-Cl contact distances in the zinc-blende and SC16 structures were also very small (2.33 and 2.36 Å, respectively). This led to near core overlap if the Cu pseudopotential having $r_c = 1.27$ Å was used. We therefore consider the Cu pseudopotential having $r_c = 1.06$ Å to be more reliable. However, we used the softer pseudopotential to demonstrate the insensitivity of the atomic positional parameters to pressure. The tuning parameters for this potential as defined in Refs. 18 and 19 were $q_c(s) = 0.8$, $q_c(p) = 1.0$, and $q_c(d) = 1.175$. A plot of this Cu pseudopotential is shown in Fig. 2. Tests of this Cu pseudopotential were performed for metallic copper using an $8 \times 8 \times 8$ Monkhorst special k-point grid with a face-centered-cubic unit cell containing four atoms. Calculations were performed at plane-wave cutoff energies of 1000 and 650 eV. The lattice constant of metallic copper was found to differ by less than 0.3% and the bulk modulus was found to differ by 1.8%. The absolute energy was found to be converged to 0.01 eV for the 1000 eV cutoff and to 0.1 eV for the 650 eV cutoff. In view of the compute-intensive nature of calculations on the SC16 structure of CuCl we have chosen to perform all pseudopotential calculations with a 650-eV plane-wave cutoff. For SC16 CuCl, this value of the energy cutoff corresponds to approximately 10 800 plane waves per band per k point. Thus the determination of the ground state energy corresponds to a minimization problem in over 3×10^6 variables. Electronic degrees of freedom were relaxed using a preconditioned conjugate-gradient algorithm.[21] In the SC16 calculations, the equilibrium atomic positions were optimized at every volume. Sets of ten, four, and ten special k points were used in the total energy calculations of the zinc-blende, SC16, and NaCl structures, respectively. The Perdew-Zunger[22] parametrization of the Cepperley-Alder[23] exchange-correlation potential was used.

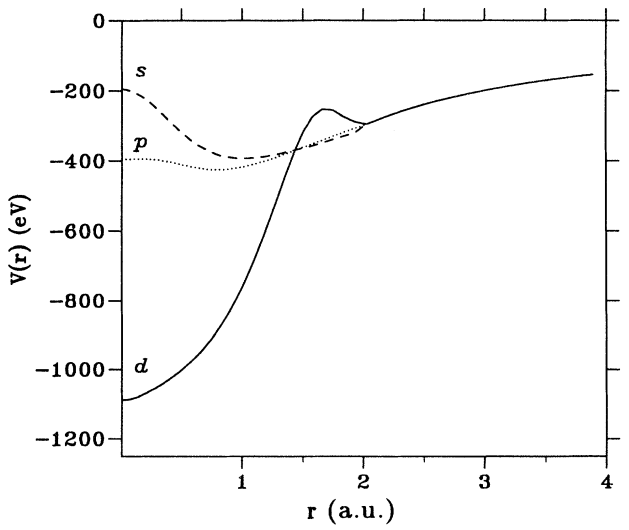

FIG. 2. Optimized nonlocal Cu pseudopotential. The core radius is 1.06 Å.

B. Full-potential linear augmented-plane-wave method

The theory and implementation of the full-potential linear augmented-plane-wave (FP-LAPW) method have also been described fully elsewhere.[25] Nevertheless, the FP-LAPW code of Ref. 25 has been extended to treat systems without inversion symmetry (and therefore complex wave functions) such as the zinc-blende structure.[26] Our FP-LAPW calculations were performed using the Vosko-Wilk-Nusair[24] form for the exchange and correlation potential. Brillouin zone sampling for the zinc-blende, SC16, and NaCl structures involved sets of 10, 4, and 56 special k points. The core electrons are treated full relativistically by solving the Dirac equation for the spherical part of the potential. The valence electrons are treated scalar relativistically.

The muffin-tin sphere radii were 1.06 Å for both Cu and Cl. Inside the muffin-tin spheres the wave functions, charge densities, and potential are expanded in spherical harmonics up to an angular momentum cutoff of $L_{\max} = 12$ for the wave functions and of $L_{\max} = 6$ for the charge densities and potentials.

Relaxation of atom positions under Hellmann-Feynman forces was not implemented in our FP-LAPW calculations. We therefore optimized the two atomic positional parameters in the SC16 structure only at our calculated equilibrium volume. These values varied from the experimental ones only in the third decimal place for Cu and the fourth decimal place for Cl. These were then fixed for subsequent volumes. Given the insensitivity of the positional parameters to pressure, we believe that neglect of the relaxation does not give rise to appreciable error, due to the small differences found from the pseudopotential calculations.

IV. RESULTS AND DISCUSSION

A. Structural stability

In Fig. 3 is shown the total energy as a function of unit cell volume for CuCl in the zinc-blende, SC16, and NaCl structures as determined from the FP-LAPW calculations. The results for these three different phases as determined by the pseudopotential method are shown in Fig. 4. We discuss first the results for the zinc-blende and NaCl structures with a view to comparing the structural properties as calculated using the two methods. We will discuss the electronic properties later in this section.

The equilibrium atomic volumes for the zinc-blende phase as determined from the pseudopotential and the FP-LAPW calculations are individually 4% and 8% smaller than the experimental value of 19.947 Å^3/atom. For the NaCl phase, the FP-LAPW method gives an equilibrium volume approximately 2% smaller than the experimental value of 14.967 Å^3/atom, as would be expected from a local density approximation (LDA) calculation, whereas the pseudopotential calculation predicted this value to be 6% larger than experiment. The calculated and experimental equilibrium lattice parameters, bulk modulii, and transition pressures for all three phases

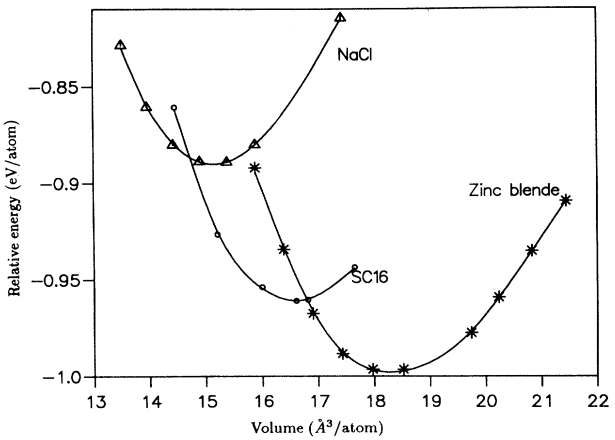

FIG. 3. Total energy as a function of unit cell volume for the zinc-blende, SC16, and NaCl structures of CuCl as determined from full-potential linear augmented-plane-wave calculations. All energies are relative to −28 732 eV.

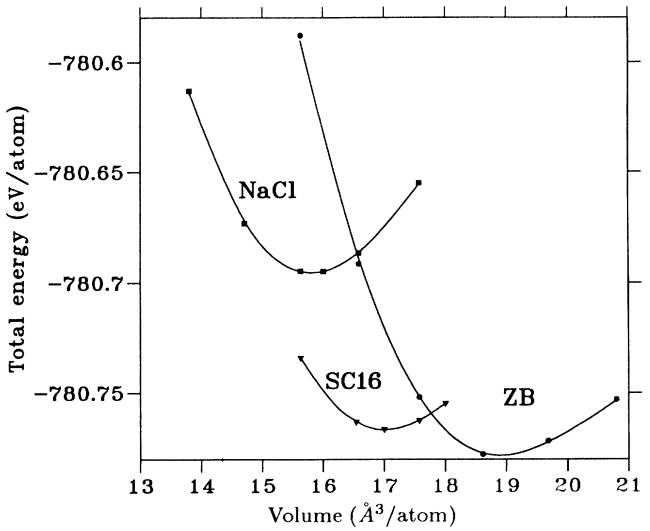

FIG. 4. Total energy as a function of unit cell volume for the zinc-blende, SC-16, and NaCl structures of CuCl as determined from pseudopotential calculations.

are given in Table I, with the experimental values taken from the recently published results by Hull and Keen.[14]

According to our FP-LAPW calculations, the zinc-blende structure of CuCl first transforms to the SC16 structure at a pressure of 37 kbar, which remains stable until a pressure of 87 kbar is reached. At this point, the NaCl-type structure becomes the most energetically favorable. The transition pressures obtained from this set of data are in good agreement with those collected experimentally by Hull and Keen using neutron powder diffraction techniques.[14] They observed the zinc-blende structure to transform to SC-16 at 55 kbar, which then transformed to the NaCl-type structure at 106 kbar.

The pseudopotential calculations suggest that the zinc-blende structure of CuCl will remain stable up to a pressure of approximately 12 kbar at which point it becomes unstable with respect to SC16. These calculations further suggest that the stability of the SC16 structure of CuCl will persist up to a pressure of 77 kbar where a transition to NaCl is expected. These calculations were repeated using the Cu pseudopotential having $r_c = 1.27$ Å. For this case we found that equilibrium volumes for the zinc-blende and SC16 phases increased slightly but that the energy differences between phases were substantially underestimated relative to the calculation based on $r_c = 1.06$ Å.

Thus we find that the structural properties and relative stability of these three phases of CuCl are fairly well described by both pseudopotential and FP-LAPW methods. However, both calculation methods lead to transition pressures between zinc-blende and SC16 and between SC16 and NaCl which are somewhat lower than those found experimentally. It is possible that hysteresis effects in the experiment could lead to an overestimate of the transition pressure upon upstroke. No data are currently available on the transition pressure as measured during decompression. It is unlikely that hysteresis effects will be as pronounced in highly ionic materials such as the copper halides as they are in covalent network solids such as InSb (Refs. 26, 27) and GaAs (Ref. 28) and we do not believe that hysteresis effects can account entirely for the discrepancy between the experimental and calculated transition pressures.

It is also possible that local regions of SC16 form at pressures lower than those at which long-range order of this structure can be observed in diffraction measurements. In fact Hull and Keen identified SC16 (CuCl-IV) as a minority phase at a pressure of 49.8 kbar and it may be that the zinc-blende structure of CuCl becomes

TABLE I. Calculated structural parameters for the zinc-blende, rocksalt, and SC16 phases of CuCl as determined using the pseudopotential (pseudo.) and FP-LAPW (LAPW) methods. Experimental results (Expt.) are also shown for comparison and are taken from the results given in Ref. 14. The units for lattice constant, bulk modulus, and transition pressure are in angstroms, Mbars, and kbars, respectively.

Description	a_0			B_0			P_t		
	LAPW	pseudo.	Expt.	LAPW	pseudo.	Expt.	LAPW	pseudo.	Expt.
zinc-blende	5.273	5.343	5.424	0.756	0.619	0.650	-	-	-
SC-16	6.421	6.483	6.418	0.839	0.636	0.66	37	12	55
rocksalt	4.893	5.021	4.929	0.927	0.803	-	87	77	105

unstable at pressures even lower than this. It would be particularly interesting to investigate specifically the pressure-induced short-range structural changes in CuCl through techniques such as x-ray-absorption fine structure (EXAFS) but bond lengths in the SC16 and zinc-blende structures are not easily distinguished.

We believe that the dominant cause of the smaller transition pressure values is the strongly temperature-dependent elastic properties of CuCl. Our *ab initio* total energy calculations correspond to zero-temperature conditions. Our values for the zero-temperature transition pressures are consistent with the *P-T* phase diagrams published by Rapoport *et al.*,[29] and references therein, which suggests that the transition pressure between CuCl-II (zinc blende) and CuCl-IV decreases substantially with decreasing temperature. Very recent experimental studies on two-photon absorption in CuCl indicate that the luminescence peak from CuCl-IV can be observed at pressures at least as low as 40 kbar at a temperature of 6 K,[30] which is in close agreement with our FP-LAPW calculations. In this work the high-pressure phase was denoted as having a tetragonal crystal structure though it now appears that it was, in fact, the signal from the SC16 structure which was being observed.

B. Electronic properties

Electronic band structures for the zinc-blende and NaCl phases of CuCl using both pseudopotential and all-electron methods are shown in Figs. 5(a) and 5(b), and the band structure of CuCl-IV as calculated by the FP-LAPW method is given in Fig. 6.

The two methods produce very similar band structures for the zinc-blende and NaCl phases along the directions studied. Both methods calculate the lowest-energy band gaps to be direct in the zinc-blende phase and indirect in the NaCl phase. CuCl-IV is also calculated to have a direct band gap. All three phases are shown to be insulating, with no evidence of band overlap in the Brillouin zone directions studied. These results are in good agreement with optical experiments carried out by Müller *et al.*[31] who predicted the same types of band gaps for the three phases from the sharpness and definition of absorption edges, and electrical studies performed by Batlogg *et al.*[32] showing no evidence of a metallic phase under the effect of pressure up to 120 kbar. The calculated lowest-energy band gaps for all three phases are given in Table II, which also includes results by Ves *et al.*[33] using a self-consistent scalar-relativistic LMTO method.

The agreement between the pseudopotential and FP-LAPW methods is shown by comparing the bandwidths. In the zinc-blende phase, the pseudopotential method gives band widths around 1% larger than the FP-LAPW method, but the main difference is the position of the lowest conduction band at the Γ point, which accounts for the inequivalent band gaps between the two methods. It should be noted that the band structure calculations were performed at the minimum energy lattice constant as given by each of our two methods. As shown in Table I, the equilibrium lattice constants differ by 0.07 Å. The resulting differences in the calculated band structures are

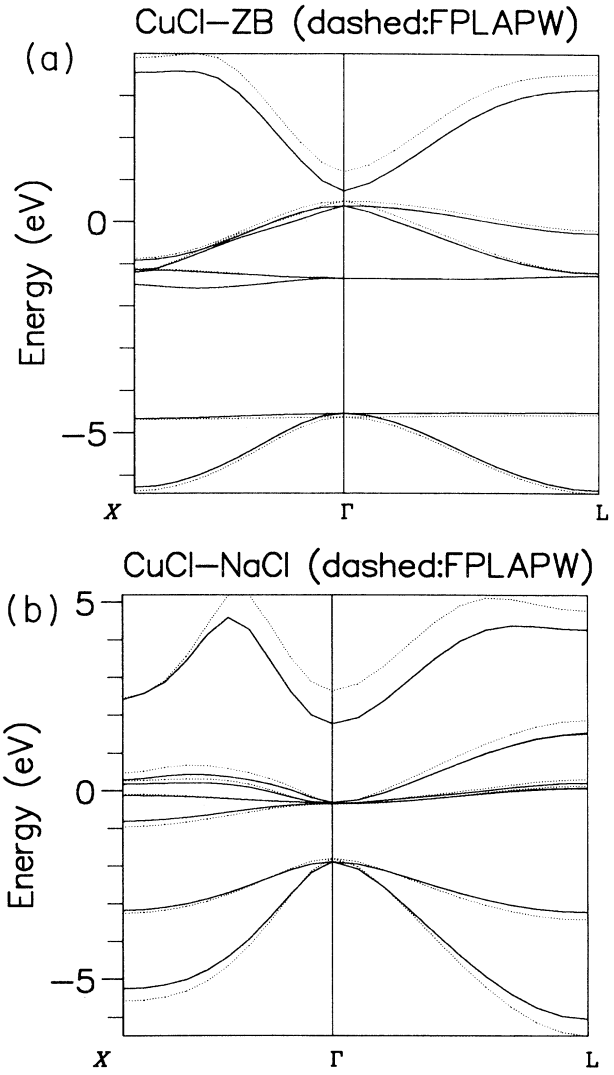

FIG. 5. Band structure of CuCl in the zinc-blende (a) and NaCl (b) structures as determined from all-electron (dashed line) and pseudopotential (solid line) methods.

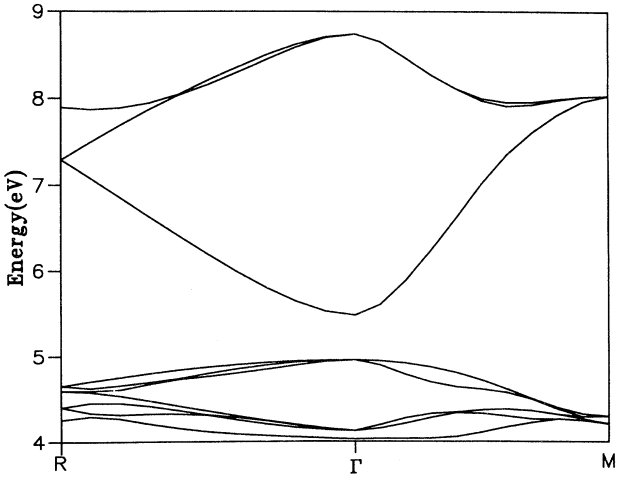

FIG. 6. Band structure of CuCl-IV (SC16) as determined from all-electron calculations.

TABLE II. The direct energy gaps calculated by pseudopotential and FP-LAPW methods for the zinc-blende (ZB) and NaCl phases are shown, as is the direct energy gap for CuCl-IV(SC16) calculated only by the FP-LAPW method. Results for zinc-blende and NaCl phases as calculated by Ves *et al.* (Ref. 33) using a scalar-relativistic LMTO method are also given for comparison.

Structure	Psuedopotential	FP-LAPW method	LMTO method
ZB direct gap (eV)	0.351	0.707	0.5
SC16 direct gap (eV)	-	0.526	-
NaCl indirect gap (eV)	0.224	0.577	0.6

found to be consistent with the deformation potentials of CuCl in this structure.[33] A different situation is seen in the NaCl phase, with the bandwidths varying by around 10% between the two structures. The FP-LAPW method calculates larger valence-band widths than the pseudopotential method, but a smaller conduction-band width. Also, upon close inspection, the FP-LAPW method predicts the lowest-energy indirect band gap to be between points L and X in the Brillouin zone, whereas the pseudopotential has the indirect gap between the L and Γ points. This was also the case for Ves *et al.*,[33] where they found their self-consistent local density calculations predicting the L to X indirect transition. However, they concluded that the actual transition would be from L to Γ, as calculated by a non-self-consistent superposition of atomic potentials, since the energy gap and corresponding deformation potential were closer to experimental values. Again, the difference in the equilibrium lattice constants accounts (through the sign of the deformation potentials) for the calculated differences in the band gap of NaCl structure CuCl.

V. SUMMARY AND CONCLUSIONS

We have applied first principles total energy calculations in order to explore pressure-induced polymorphism and the consequent changes in the electronic structure of CuCl. Results from calculations employing nonlocal ionic pseudopotentials were found to be comparable to those obtained from the full-potential LAPW method. Both calculation methods successfully account for the observed pressure-induced phase transition sequence observed experimentally in this material. First principles calculations have now demonstrated that the SC16 structure is a stable high-pressure polymorph of both III-V and I-VII binary semiconductors though it appears that kinetic factors preclude its formation in the III-V family. The observed differences in structure adoption therefore appear to depend sensitively on the details of the transition mechanisms.

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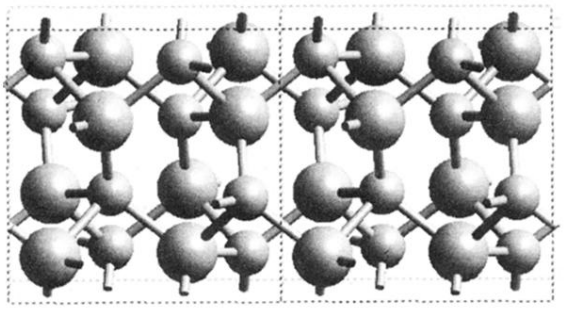

FIG. 1. Three-dimensional illustration of the SC16 structure containing two unit cells. The Cu atoms are denoted as the smaller spheres.