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Energy bands and effective masses of CuCl

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We have made the first self-consistent energy-band calculation of CuCl with sufficient variational freedom to calculate the effective masses accurately. The conduction-band mass agrees with experiment whereas the valence-band mass is much less than any of the experimental values, indicating that the hole forms a small polaron. The calculation was repeated for a reduced lattice constant. The indirect gap proposed by Rusakov to explain the high-temperature "superconductivity" anomaly does not exist and the direct gap widens with pressure.

Using a spherical potential, Song[1] has calculated the energy bands and some effective masses of CuCl using only Cl 3*s* and 3*p* and Cu 3*d* atomic orbitals for the valence bands and three to six orthogonalized plane waves for the conduction bands. Using Song's bands Kahn[2] calculated a few more effective masses. Calabrese and Fowler[3] used a mixed-basis set for both bands and calculated the electron effective mass (see Table I). Zunger and Cohen[4] performed the first self-consistent calculation using an optimized set of atomic orbitals through Cu 4*p* and Cl 3*p* supplemented with Slater Cl 3*d* and 4*s* orbitals but reported no effective masses. We believe that except for the non-self-consistent calculation of Calabrese and Fowler none of these calculations had sufficient variational freedom to obtain the conduction bands or any of the effective masses with great accuracy. We have made a self-consistent calculation expanding in 15 *s*, 3 × 13 *p*, and 5 × 8 *d* Cu and 14 *s*, 3 × 11 *p*, and 5 × 4 *d* Cl Gaussian orbitals. At each iteration we fit the electronic charge at 1137 points in the $\frac{1}{24}$th irreducible unit cell using[5] two $(\beta/\pi)(\beta r^2-0.5)e^{-\beta r^2}/r$, thirty three $(\beta/\pi)(1.5-\beta r^2)e^{-\beta r^2}$, seven $(\beta/\pi)(4.5-\beta r^2)xyze^{-\beta r^2}$, and four

$$(\beta/\pi)(5.5-\beta r^2)(x^4+y^4+z^4-\tfrac{3}{5}r^4)e^{-\beta r^2}$$

functions on each site which yield Coulomb potentials of the form $(1-e^{-\beta r^2})/r$, $e^{-\beta r^2}$,$xyze^{-\beta r^2}$, and $(x^4+y^4+z^4-\frac{3}{5}r^4)\,e^{-\beta r^2}$ functions on each atom. All Hamiltonian and overlap matrix elements are calculated in real space including all neighbors with contributions greater than 10^{-9} a.u. In order to test the accuracy of our convergence and fitting procedure in Table II we list Fourier transforms (FT) of several charge densities. WF(out) represents the FT calculated directly from our final wave functions at the two special Brillouin-zone points of Cohen and Chadi.[6] WF(in) represents the same thing for the preceding iteration (the last from which a potential was calculated). Fit represents the FT of our Gaussian fit to the charge density calculated from the WF(in) wave functions. Although the error in the fit can be seen to be an order of magnitude worse than the convergence, the largest error it leads to in any Coulomb FT is less than 0.002 eV. The Slater exchange potential cannot be calculated exactly but because it is both smaller than and smoother than the Coulomb potential, it is fit with even greater accuracy than the Coulomb potential. SFit represents a fit using only the spherical functions. It is seen to be as good as the regular fit except for the (222)2 and (311)1 FT. RWF(out) is the same as WF(out) except that the eigenfunctions were calculated from a constricted set of basis functions consisting of all the core functions plus two Cu *s*, two Cu *p*, three Cu *d*, two Cl *s*, two Cl *p*, and one Cl *d* optimized valence-conduction orbitals.[7] In spite of the fact that this set has more variational freedom than those sets used by other workers, we see that the discrepancy between RWF(out) and WF(out) is an order of magnitude

TABLE I. Electron and hole effective masses of CuCl. The last column indicates whether the reference is experimental or theoretical except for this work where it indicates lattice constant. The $m_h^*(\Gamma_8)$ of Ref. 2 are $\partial^2E/\partial k_x^2$; the $m_h^*(\Gamma_8)$ of this work are [111] cyclotron masses.

$m_e^*(\Gamma_6)$	$m_h^*(\Gamma_7)$	$m_h^*(\Gamma_8)$	Ref.
0.415	20.4	···	12(exp)
0.44	3.6	···	14(exp)
0.43	4.2	···	13(exp)
0.25	13	···	1(theor)
···	13.5	3–13.7	2(theor)
0.48	···	···	3(theor)
0.417	1.477	0.969–3.101	a_0
0.401	0.913	0.611–1.808	$0.88a_0$

TABLE II. Comparison of various charge-density Fourier transforms described in the text. Here $(ijk)1=\frac{1}{2}[V(ijk)+V(\overline{ijk})]$ and $(ijk)2=[V(ijk)-V(\overline{ijk})]/2i$ with the origin on a Cu atom. The units are electrons per unit cell.

FT	WF(out)	WF(in)	Fit	SFit	RWF(out)
(111)1	25.1940	25.1943	25.1938	25.1827	25.2063
(111)2	13.6555	13.6553	13.6501	13.6533	13.6319
(200)	11.5004	11.5010	11.5016	11.5003	11.5387
(220)	32.1432	32.1437	32.1501	32.1444	32.1807
(311)1	19.9356	19.9362	19.9362	19.9561	19.9680
(311)2	−9.6187	−9.6186	−9.6249	−9.6175	−9.6439
(222)1	10.1183	10.1190	10.1118	10.1205	10.1213
(222)2	0.0592	0.0592	0.0544	0.0000	0.0336
(400)	26.4433	26.4438	26.4456	26.4436	26.4886

worse than the discrepancy between Fit and WF(in), thus justifying the added work in using a large Gaussian basis set. Finally, although not shown in Table II, we compared some FT's from the two special BZ point sample with a four-point (ΓXLW) sample and the eight-point sample which samples equal $\frac{1}{64}$th of the full BZ. The two-point sample agreed with the eight much better than did the four. In fact the discrepancy between the two- and eight-point samples was much less than that between Fit and WF(in).

In Fig. 1 we display the energy bands of CuCl calculated with a lattice constant $a_0=10.2153$ a.u. The direct gap is 3.09 eV in fair agreement with the experimental value[8] of 3.4 eV. There is no indirect gap as proposed by Rusakov[9] to explain the high-temperature "superconductivity" (superdiamagnetism). Using an $X\alpha$ exchange potential with $\alpha=0.82$ we obtained a direct gap of about[10] 1.7 eV. Using exchange and correlation approximately equivalent to $\alpha=0.8$ Zunger and Cohen obtained a direct gap of 2.0 eV. We believe their gap would be slightly smaller had they sufficient variational freedom. (Dropping our longest-range s and p Gaussian basis function with $\beta=0.08$ Bohr^{-2} caused the conduction band to rise $\frac{1}{2}$ eV with almost no change in the valence band.) From exciton spin-orbit splitting the top of the valence-band Γ_{15} level is estimated[9] to be 25% Cl 3p and 75% Cu 3d. In Fig. 2 we display the bonding and antibonding Γ_{15} eigenfunctions along the [111] direction. Comparing the squares of the Cu d peaks we estimate the antibonding function to be 71% Cu 3d and the bonding function to be 29% Cu 3d.

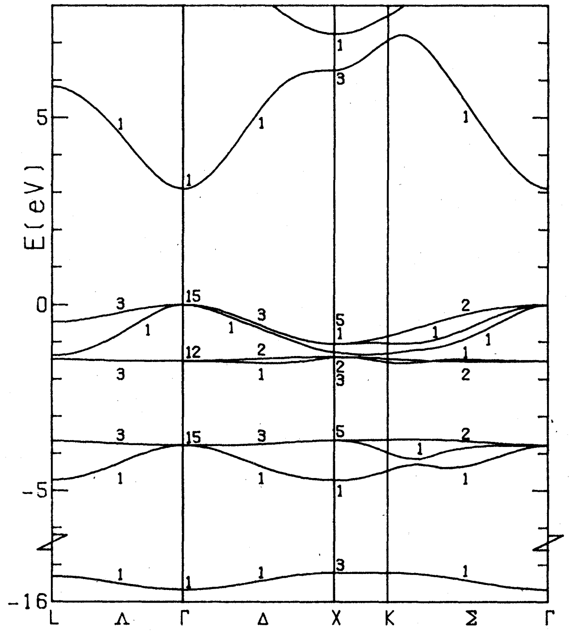

FIG. 1. Energy bands of CuCl.

We have calculated the effective masses at Γ by calculating the energies at Δ and Λ, 5% of the way to the X and L points and fitting with $E=k^2/2m^*$. The Γ_1 conduction-band effective mass is 0.41669 or 0.41672 depending on whether Δ or Λ is used. This negligible difference is an indication of the numerical accuracy of our calculation. We obtain the valence-band effective-mass parameters $L=-1.9466$ and $M=-1.5424$ from[11] $1+L=-1/m^*(\Delta_1)$ and $1+M=-1/m^*(\Delta_3)$. Then from[11] $1+\frac{1}{3}L+\frac{2}{3}M-\frac{1}{3}N=-1/m^*(\Lambda_3)$ we obtain $N=-1.2066$ or from $1+\frac{1}{3}L+\frac{2}{3}M+\frac{2}{3}N=-1/m^*(\Lambda_1)$ we obtain $N=1.2057$. Thus we obtain for the spin-orbit effective-mass parameters,[11]

$$A=\tfrac{1}{3}(L+2M)+1=-0.6771\ ,$$

$$B=\tfrac{1}{3}(L-M)=-0.1347$$

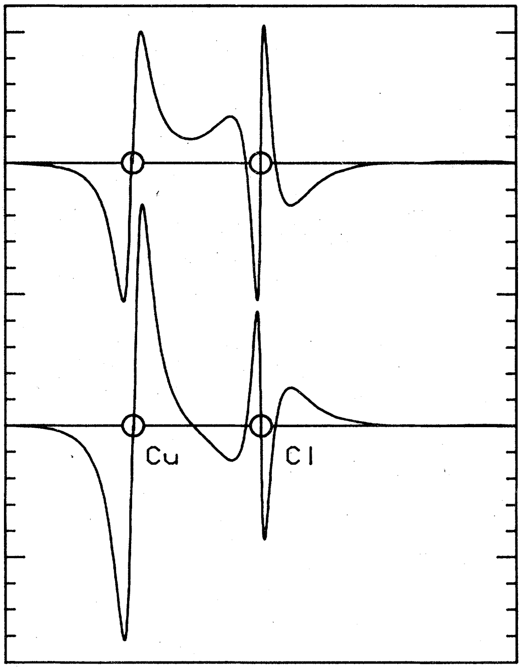

FIG. 2. Bonding and antibonding Cu d–Cl p Γ_{15} wave functions along the [111] direction. Note when comparing the size of the d and p contributions that the d cubic harmonic is $(\frac{5}{3})^{1/2}$ times as large as the p along [111].

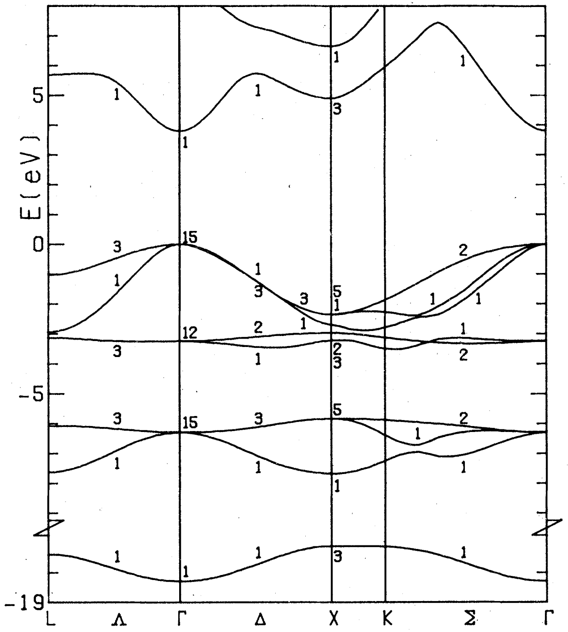

FIG. 3. Energy bands of CuCl with lattice constant reduced by 12%.

and

$$C^2=\tfrac{1}{3}[N^2-(L-M)^2]=0.4305 \ .$$

Because d spin-orbit splitting is of opposite sign to p, CuCl, unlike all other zinc-blende crystals, has the doublet Γ_7 at the top of the valence band. In Table I we list $m_h^*(\Gamma_7)=-1/A$ and the [111] cyclotron masses

$$m_h^*(\Gamma_8)=-1/[A\pm(B^2+\tfrac{1}{4}C^2)^{1/2}]$$

together with other theoretical effective masses and experimental effective masses determined from hyperfine contributions to the exciton spectrum,[12] exciton-free electron interactions,[13] and exciton-exciton interactions.[14] The latter two determinations use the hydrogenic exciton reduced mass (0.39). Because $m_e^*(\Gamma_6)$ is not much larger than the reduced mass, small changes in $m_e^*(\Gamma_6)$ require large changes in $m_h^*(\Gamma_7)$. Thus the large discrepancies in the experimental values of $m_h^*(\Gamma_7)$ are more apparent than real. Our calculated $m_e^*(\Gamma_6)$ is seen to be in perfect agreement with experiment whereas our $m_h^*(\Gamma_7)$ which is even more accurately calculated (the valence bands are less sensitive to the choice of Gaussian basis functions) is much smaller than any of the experimental values. This we believe is due to the hole forming a small polaron; it is known that this band will not support low-mass p-type doping.[15]

Besides the superdiamagnetic anomaly[16,17] which occurs at pressures as low as 5 kbar, CuCl also shows an increase in conductivity by a factor as large as 10^7 at 40 kbar. Chu *et al.*[15] associate this with an isostructural phase transition.[18] Extrapolation of the volume versus pressure curves of Rusakov *et al.*[19] to 40 kbar indicates that the lattice constant at 40 kbar may be reduced by as much as 12%. Thus we repeated our band calculation with $0.88a_0=8.9895$ a.u. The results are shown in Fig. 3 and Table I. We note that the direct gap widens to 3.79 eV and the valence bands broaden, becoming more semiconductorlike. There are no major band crossings so the bands at lower pressure will be intermediate to those of Figs. 1 and 3. Thus the superdiamagnetic anomaly cannot be accounted for within the zinc-blende band structure. Note that the hole effective masses are much reduced at 40 kbar. It is possible that at the phase transition acceptor states become delocalized which would account for the large increase in conductivity.

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