

Self-consistent energy bands of Cu_2O

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We have used an expansion in Gaussian orbitals to make the first self-consistent calculation of the energy bands of Cu_2O . Although the ordering of the bands at Γ is identical to that calculated by Dahl and Switendick, there is considerable difference in the two sets of bands due to a much larger O $2p$ -Cu $3d$ hybridization in the self-consistent bands. Unlike Dahl and Switendick and in agreement with Elliott's interpretation of the excitonic data, we find that the spin-orbit splitting of the top of the valence band puts the $\Gamma_7^+(j=1/2)$ level above the $\Gamma_8^+(j=3/2)$.

I. INTRODUCTION

The excitonic structure of Cu_2O has been an area of continuing experimental study¹⁻⁸ for the past 30 years. Elliott⁹ points out that the extremely good hydrogenic properties of the yellow series implies that both the valence and conduction bands from which they are built have no more than double-Kramers degeneracy, i.e., they must have Γ_6^+ or Γ_7^+ symmetry. He further points out that the intensity of the weak $n=1$ line of the yellow series as a function of the electromagnetic polarization vector and wave-vector direction cosines establishes that the $n=1$ yellow exciton state has $\Gamma_{25'}$ symmetry. This can be so only if the valence- and conduction-band extrema contain both Γ_6 and Γ_7 symmetries of the same parity.⁹ Because the top of the valence band is Cu d , it is thought to be a Γ_7^+ state and because the bottom of the conduction band is Cu s , it is thought to be a Γ_6^+ state. Elliott also speculates that the second conduction band has Γ_2 symmetry at the center of the Brillouin zone (BZ). However, it appears that his only requirement for the state is that it be coupled to the top of the valence band by electric-dipole radiation. Dahl and Switendick¹⁰ (hereafter DS) have performed a non-self-consistent calculation of the energy bands of Cu_2O . Because the crystal contains six atoms per unit cell, the calculations are fairly time consuming and there have been no self-consistent calculations heretofore. (See Fig. 1 in DS for a picture of the unit cell.) DS found the second conduction-band level at Γ to have $\Gamma_{12'}$ symmetry which, although different from Elliott's Γ_2 , does satisfy his condition of coupling to the $\Gamma_{25'}$ valence band. They find the bottom of the conduction band to be Γ_1 whose double group representation is Γ_6^+ in agreement with Elliott. The top of the valence band they correctly find is a $\Gamma_{25'}$ state. They calculate the spin-orbit splitting to be 0.072 eV with the $\Gamma_8^+(j=3/2)$ level lying above the $\Gamma_7^+(j=1/2)$ level. Although an $n=1$ exciton of $\Gamma_{25'}$ symmetry can be built from Γ_8^+ and Γ_6^+ bands, the series

would not be expected to be hydrogenic.

In this paper, using an expansion in Gaussian orbitals, we perform the first self-consistent calculation of the energy bands of Cu_2O . We use the Slater¹¹ exchange potential as did DS and find bands that differ in some detail from theirs. We calculate the spin-orbit splitting of all four $\Gamma_{25'}$ valence-band levels, finding splittings of both signs. However, the top of the valence band splits with opposite sign to that calculated by DS in agreement with the excitonic data.

II. ENERGY-BAND CALCULATIONS

This calculation is similar to our recent CuCl calculation¹² except that, because of the large number of atoms per unit cell, we use a somewhat constricted basis set. We expand in Cu $1s$, $2s$, $3s$, $4s$, $2p$, $3p$, and $3d$ atomic orbitals together with three s , four p , and four d Gaussian orbitals for a total of 50 orbitals per Cu atom. Our oxygen orbitals are atomic $1s$, $2s$, and $2p$ with three s , three p , and one d Gaussians for a total of 22 orbitals per O giving a total of 244 orbitals per unit cell. The atomic orbitals are themselves expanded in as many as 15 Gaussians. Because there are only two atoms in the $\frac{1}{48}$ th irreducible unit cell, the fitting of the Cu_2O charge density is only slightly more difficult than was the CuCl. We calculate the charge density at 608 points on a uniform mesh in the $\frac{1}{48}$ th unit cell plus a radial mesh of 57 points in four directions about the oxygen at the center of the unit cell and another four directions about the Cu at $(\frac{1}{4}a)(1, 1, 1)$ for a total of 1064 points. The four radial meshes about each atoms are staggered so that 228 different radial values are included about each atom. The charge density is obtained by sampling the four special simple cubic BZ points of Chadi and Cohen.¹³ We fit the charge density using 62 Gaussians about the Cu and 44 about the O of various symmetry types as shown in Table I. Because of the low Cu site symmetry, the Cu quartic Gaussians are essential for a good fit, whereas the oxygen quartics are not. One

TABLE I. Gaussian orbitals centered on Cu and O atoms used in fit of crystal charge density.

Atom	Orbital
Cu, O	$(\alpha/\pi)(\alpha r^2 - \frac{1}{2})e^{-\alpha r^2}/r$
Cu, O	$(\alpha/\pi)(\frac{3}{2} - \alpha r^2)e^{-\alpha r^2}$
Cu	$(\alpha/\pi)(xy + xz + yz)(\frac{7}{2} - \alpha r^2)e^{-\alpha r^2}$
O	$(\alpha/\pi)xyz(\frac{9}{2} - \alpha r^2)e^{-\alpha r^2}$
Cu, O	$(\alpha/\pi)[(x^4 + y^4 + z^4) - 3(x^2y^2 + x^2z^2 + y^2z^2)](\frac{11}{2} - \alpha r^2)e^{-\alpha r^2}$
Cu	$(\alpha/\pi)[7xyz(x + y + z) - r^2(xy + yz + zx)](\frac{11}{2} - \alpha r^2)e^{-\alpha r^2}$

point which should have been obvious but which we did not realize when making the CuCl calculation¹² is that the directions chosen for the radial meshes must be such that all the $l \neq 0$ Gaussian harmonics average to zero over them.¹⁴ If this is not done, it looks to the fitting routine as though the $l \neq 0$ Gaussians contain charge, when in fact they do not, and the charge-containing Gaussians compensate for it, causing them to contain an incorrect charge.¹⁵ For¹² CuCl we compared Fourier transforms of the charge density obtained directly from the wave functions with Fourier transforms obtained from the fit to show that the fit gave Coulomb Fourier transforms accurate to within 0.002 eV. Because the rms error in the fit of the Cu₂O charge density is $\frac{2}{3}$ of that obtained in fitting CuCl, we do not think it necessary to make that comparison again. Applying Poisson's equation to the charge-density fit one immediately obtains an expansion of the Coulomb potential in Gaussians of the form $(1 - e^{-\alpha r^2})/r$, $e^{-\alpha r^2}$, $(xy + xz + yz)e^{-\alpha r^2}$, $xyz e^{-\alpha r^2}$, etc. The exchange potential is fit using all but the $1/r$ -type Coulomb Gaussians at the same 1064 points. All Hamiltonian and overlap matrix elements are calculated in real space including all neighbors with contributions greater than 10^{-9} a. u. except that integrals involving pairs of long range Gaussian Bloch functions are evaluated in reciprocal space.

The energy bands, iterated until they were stabilized to better than 0.01 eV, were calculated at seven points along each symmetry line in the BZ and are presented in Figs. 1 and 2. In Table II the energy levels are listed at the symmetry points in the BZ. We use the symmetry notation of Dahl.¹⁶ (DS apparently interchanged X_1 with X_3 and X_2 with X_4 and then were unable to distinguish their X_1 and X_2 both of which they labeled Δ_5 .) At Γ our ordering is identical to DS but at other points some of the levels are interchanged. The main difference between the two calculations seems to be that the ionic potential constructed by DS is not as ionic as the self-consistent potential. Their O 2s and

2p levels lie¹⁷ 2.5 and 1.6 eV below ours relative to the top of the valence band. Note that our unhybridized Γ_{15} O 2p level is practically degenerate with the Γ_1 Cu *d* level, whereas the DS O 2p bands are well split off from their Cu *d* bands. Our total integrated charge within an oxygen inscribed sphere is +0.1e and within a Cu is +5.5e. The remaining -22.4e per unit cell is heavily localized in the regions just outside the oxygen inscribed spheres. As a result of having the O 2p so close in energy to the Cu 3d we have a much larger amount of hybridization. Note that the splitting of the hybridizing $\Gamma_{25'}$ and nonhybridizing Γ_{15} O 2p levels is 3.62

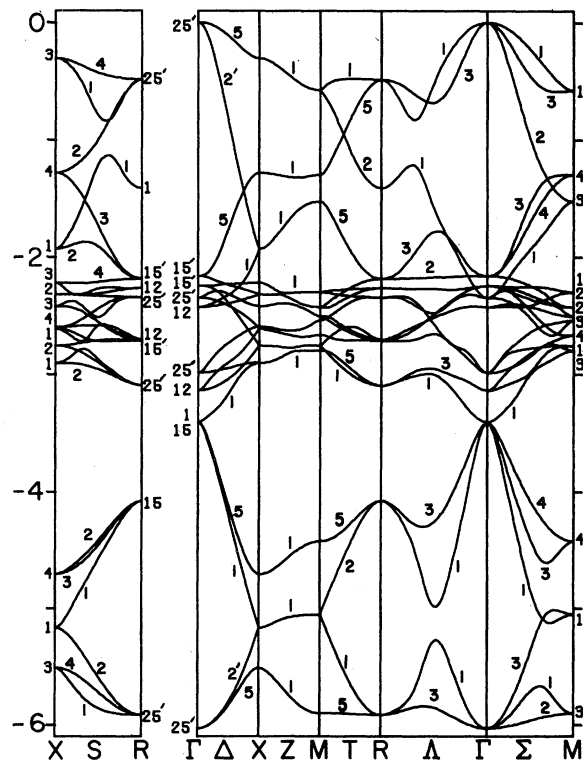
FIG. 1. Valence energy bands of Cu₂O (eV).

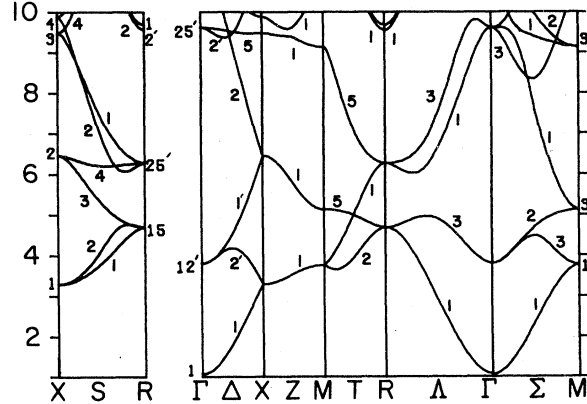
TABLE II. Energy levels (eV) at high-symmetry points of Cu_2O .

Γ_1	-18.85	X_1	-18.52	M_1	-18.51	R_1	-18.72
$\Gamma_{2'}$	-18.19	X_3	-5.51	M_3	-5.90	$R_{2'}$	-18.26
$\Gamma_{25'}$	-6.03	X_1	-5.16	M_1	-5.05	$R_{25'}$	-5.91
Γ_{15}	-3.41	X_4	-4.70	M_4	-4.43	R_{15}	-4.08
Γ_1	-3.40	X_1	-2.90	M_3	-2.80	$R_{25'}$	-3.09
Γ_{12}	-3.13	X_2	-2.76	M_4	-2.76	$R_{15'}$	-2.71
$\Gamma_{25'}$	-2.98	X_1	-2.61	M_4	-2.67	R_{12}	-2.70
Γ_{12}	-2.42	X_4	-2.59	M_3	-2.54	$R_{25'}$	-2.35
$\Gamma_{25'}$	-2.35	X_3	-2.42	M_2	-2.51	R_{12}	-2.26
$\Gamma_{15'}$	-2.24	X_2	-2.32	M_2	-2.43	$R_{15'}$	-2.18
$\Gamma_{15'}$	-2.16	X_3	-2.22	M_1	-2.30	R_1	-1.41
$\Gamma_{25'}$	0.00	X_1	-1.93	M_3	-1.53	$R_{25'}$	-0.49
Γ_1	1.07	X_4	-1.28	M_4	-1.30	R_{15}	4.68
$\Gamma_{12'}$	3.80	X_3	-0.31	M_1	-0.58	$R_{25'}$	6.27
$\Gamma_{25'}$	9.61	X_1	3.28	M_1	3.76	$R_{2'}$	9.55
		X_2	6.45	M_3	5.12	R_1	9.68
		X_3	9.48	M_3	9.13		
		X_4	9.87				

eV, whereas for DS it was only 1.49 eV. The amount of hybridization in the four valence band $\Gamma_{25'}$ levels can be estimated from the spin-orbit parameters listed in Table IV. $\zeta_{11} + 2\zeta_{22} + \zeta_{33}$ is a measure of the Cu 3d content of a wave function, whereas ζ_{55} is a measure of the O 2p content. We see that only the top and bottom of the valence band are strongly hybridized. This hybridization pushes up the top of the valence band and thus reduces the energy gap from DS's 1.77 to 1.07 eV. The experimental gap is⁸ 2.17 eV. We believe that this discrepancy is a consequence of the discrepancy of about 4.5 eV between the Slater¹⁸ and Hartree-Fock¹⁹ atomic 3d-4s splittings.²⁰ The Slater exchange is known²¹ to be a good approximation to the screened Hartree-Fock exchange potential appropriate for metals and semiconductors but should not be expected to give the relative positions accurately of the Cu 3d-O 2p bands and unoccupied nearly-free-electron bands in an ionic crystal. We believe that our valence bands are quite accurate. If it were not for the energy gained

TABLE III. Expansion of $\Gamma_{25'}$ wave functions in Kubic harmonics about the six atoms in the unit cell. Atoms 5 and 6 are oxygens at (0,0,0) and $(a/2)(1,1,1)$; atoms 1 through 4 are coppers at $(a/4)(1,1,1)$, $(a/4)(1,\bar{1},\bar{1})$, $(a/4)(\bar{1},1,\bar{1})$, and $(a/4)(\bar{1},\bar{1},1)$, respectively.

$$\begin{aligned} & \alpha(s_1 + s_2 - s_3 - s_4) + \beta(yz_1 + yz_2 + yz_3 + yz_4) + \gamma[(xy + xz)_1 - (xy + xz)_2 + (xy - xz)_3 - (xy - xz)_4] + \delta[(3x^2 - r^2)_1 + (3x^2 - r^2)_2 \\ & \quad - (3x^2 - r^2)_3 - (3x^2 - r^2)_4] + \mu(x_5 - x_6) + \nu(yz_5 + yz_6) \\ & \alpha(s_1 - s_2 + s_3 - s_4) + \beta(xz_1 + xz_2 + xz_3 + xz_4) + \gamma[(xy + yz)_1 + (xy - yz)_2 - (xy + yz)_3 - (xy - yz)_4] + \delta[(3y^2 - r^2)_1 - (3y^2 - r^2)_2 \\ & \quad + (3y^2 - r^2)_3 - (3y^2 - r^2)_4] + \mu(y_5 - y_6) + \nu(xz_5 + xz_6) \\ & \alpha(s_1 - s_2 - s_3 + s_4) + \beta(xy_1 + xy_2 + xy_3 + xy_4) + \gamma[(xz + yz)_1 + (xz - yz)_2 - (xz - yz)_3 - (xz + yz)_4] + \delta[(3z^2 - r^2)_1 - (3z^2 - r^2)_2 \\ & \quad - (3z^2 - r^2)_3 + (3z^2 - r^2)_4] + \mu(z_5 - z_6) + \nu(xy_5 + xy_6) \end{aligned}$$

FIG. 2. Conduction energy bands of Cu_2O (eV).

from the hybridization we have calculated (the strongly hybridizing $\Gamma_{25'}$ levels also contain a large amount of Cu 4s), there would be little reason to expect Cu_2O to crystallize in this highly unusual structure (shared only by Ag_2O and Pb_2O). Furthermore, the spin-orbit splitting we calculate in the next section is extremely sensitive to the $\Gamma_{25'}$ wave function (it varies between -1.27 and +1.06 eV for different $\Gamma_{25'}$). The agreement obtained between this calculation and experiment is a strong indication of the accuracy of the top of the valence band $\Gamma_{25'}$ wave function.

III. SPIN-ORBIT SPLITTING

We approximate the spin-orbit Hamiltonian by

$$H_{\text{so}} = \frac{1}{2} \alpha^2 \sum_{i=1}^6 \frac{1}{r_i} \frac{\partial U_i}{\partial r_i} \vec{L}_i \cdot \vec{S} \Theta(r_i - R_0), \quad (1)$$

where α is the fine structure constant, $\vec{r}_i = \vec{r} - \vec{R}_i$ with \vec{R}_i is the position of the i th atom in the unit cell, U_i is the spherically averaged potential, and \vec{L}_i is the angular-momentum operator about the i th atom. \vec{S} is the spin operator and $\Theta(r_i - R_0)$ is a step function with R_0 the inscribed sphere radius.

TABLE IV. ζ_{ij} and the spin-orbit splitting $\Delta = \frac{3}{2} \zeta$ for each of four $\Gamma_{25'}$ levels at the energies shown. A positive Δ indicates the fourfold level is above twofold. Band energies are in eV, ζ_{ij} and Δ in meV.

Energy	ζ_{11}	ζ_{22}	ζ_{33}	ζ_{32}	ζ_{55}	ζ_{66}	Δ
0.00	8.67	3.13	8.24	-5.08	3.85	0.00	-127.3
-2.35	7.15	11.80	1.18	3.74	0.06	0.00	105.8
-2.98	10.35	0.30	18.03	2.32	0.05	0.00	-11.93
-6.03	4.47	1.01	2.99	-1.74	5.75	0.00	-39.68

An expansion of the $\Gamma_{25'}$ wave functions about the six atoms in the unit cell is given in Table III. We write the wave function about atoms 1 (Cu) and 5 (O) as

$$\psi(\vec{r}_1) = \{yz\}f_1(r_1) + (\{xy\} + \{xz\})f_2(r_1) + \{3x^2 - r^2\}f_3(r_1) + f_4(r_1), \quad (2)$$

$$\psi(\vec{r}_5) = \{x\}f_5(r_5) + \{yz\}f_6(r_5), \quad (3)$$

where the $\{ \}$ are properly normalized Kubic harmonics, e.g., $\{xy\} = (15/4\pi)^{1/2}(xy/r^2)$. Then evaluating and diagonalizing the $6 \times 6 H_{so}$ matrix between the $\Gamma_{25'}$ function one finds

$$E_{so}(j = \frac{3}{2}) = \frac{1}{2}\zeta, \quad E_{so}(j = \frac{1}{2}) = -\zeta, \quad (4)$$

where

$$\zeta = 4(-\zeta_{11} + \zeta_{22} + 2\sqrt{3}\zeta_{32}) + 2(\zeta_{55} - \zeta_{66}) \quad (5)$$

and

$$\zeta_{ij} = \frac{1}{2}\alpha^2 \int_0^{R_0} \frac{\partial U}{\partial r} f_i(r) f_j(r) r dr. \quad (6)$$

Note that half the Cu ζ_{ij} 's cancel out in the sum over the four Cu atoms and do not appear in Eq. (5). Note also that the oxygens, which are at tetrahedral sites, give a contribution to the spin-orbit splitting similar to that in zinc-blende crystals, i.e., p functions positive and d functions negative, whereas the sign of the copper d -function contribution is variable.

Equation (6) is integrated numerically. The spherically averaged charge about each atom is obtained by averaging the charge along the four

radial directions used in the charge-density fit described in Sec. II. (Remember that these directions were chosen so that all Kubic harmonics with $l \leq 4$ in an expansion of the charge density about each atom average to zero in the four directions.) Then it is easy to show that

$$\frac{\partial U}{\partial r} = \frac{2}{r^2} [Z - z(r)] + \frac{1}{3} V_{ex}(r) \frac{\partial \ln \rho}{\partial r}. \quad (7)$$

Here Z is the nuclear charge, $z(r)$ is the total integrated electronic charge within a sphere of radius r , the factor 2 arises from Ry atomic units, V_{ex} is the Slater exchange potential, and ρ is the spherically averaged charge density. To evaluate $f_i(r)$, we obtain $\psi(\vec{r}_1)$ along four directions and $\psi(\vec{r}_5)$ along two directions and solve for $f_1(r_1)$, $f_2(r_1)$, $f_3(r_1)$, and $f_4(r_1)$ [see Eq. (2)] and for $f_5(r_5)$ and $f_6(r_5)$ [see Eq. (3)]. We chose several sets of four and two directions and obtained variations in the calculated values of the ζ 's of less than 0.1%.

In Table IV we list all the ζ_{ij} appearing in Eq. (5) (as well as ζ_{33}) together with the spin-orbit splitting for all four $\Gamma_{25'}$ valence states. We note that the spin-orbit splitting of the top of the valence band (-1027 cm^{-1}) is in near perfect agreement with Elliott's estimate of -1000 cm^{-1} and that the second $\Gamma_{25'}$ level has a spin-orbit splitting almost as large as that of the first but with opposite sign.

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