Semiempirical band structure and partial density of states of CuCl

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(Received 26 September 1986)

A mixed-basis band-structure interpolation scheme has been used to generate a semiempirical band structure of CuCl (zinc-blende structure). The pseudopotential parameters in the interpolation scheme were determined by fitting eigenvalues obtained from angle-resolved photoelectron spectroscopy data. Partial densities of states for CuCl were obtained by projecting $s$, $p$, and $d$-like components out of the mixed basis and compared with uv photoemission and x-ray emission data taken from the literature.

I. INTRODUCTION

A mixed-basis band-structure interpolation scheme (MBBESIS), which employs a combination of $d$-like orbitals and plane waves, is an extremely valuable computational tool for examining the electronic structure of the $d$-band metals. Benbow and Smith and various co-workers have developed a fcc $d$-band interpolation scheme over the past decade and applied it as an aid in interpreting photoemission data. In previous studies, the MBBESIS (Refs. 2 and 3) has been extended to obtain semiempirical band structures for fluorite- and rocksalt-structure compounds, as well as for fcc $d$-band metals. Applications of the MBBESIS have included mapping out the energy-versus-wave-vector dispersion relations of electronic states, plotting the total valence-band density of states (DOS), and calculating total and band-specific charge densities using the wave functions. In this paper, a MBBESIS is applied to the zinc-blende-structure compound CuCl to generate a semiempirical band structure based on recent angle-resolved photoelectron spectroscopy (ARPES) data, and also to calculate total $d$, $p$, and $s$-orbital projected DOSs using the mixed-basis eigenfunctions. The two major goals of this paper are to show that the MBBESIS can be used for $d$-band compounds with the zinc-blende structure as well as for compounds with inversion-center symmetry and that it can be used to calculate orbital-symmetry projected DOS's.

CuCl is a I-VII-type semiconductor that crystallizes in the zinc-blende structure. The valence bands of CuCl are derived from an $s^2p^6d^{10}$ valence electronic configuration, in contrast to III-V and II-VI compound semiconductors that have an $s^2p^6$ configuration. The Cu 3$d$ energy levels are energetically close to the Cl 3$p$ levels, and thus a strong hybridization between Cu 3$d$ and Cl 3$p$ orbitals occurs in the valence bands. This $p$-$d$ mixing would be expected to have a significant effect on the physical and chemical properties of CuCl, especially compared to III-V or II-VI group semiconductors, such as GaAs and ZnS.

Interesting anomalies occur in the CuCl electronic structure, such as the reversal of the spin-orbit splitting of the edge exciton from the normal zinc-blende materials. There has been some controversy over models to explain these unusual properties, and many theoretical and experimental investigations have been conducted in the past decade to clarify the situation. Studies of silver and copper halides before 1977 have been reviewed by Goldmann.

In order to understand the properties of CuCl information concerning the $p$-$d$ mixing in the valence bands is highly desirable. Soft x-ray-emission spectroscopy (SXES) or ultraviolet photoemission spectroscopy (UPS) techniques can be used experimentally to determine the partial DOS in solids. The SXES spectra represent symmetry-projected DOS, because x-ray emission obeys the dipole selection rule for the transitions from the initial states to the final core states. The strong dependence of photoionization cross sections on photon energy also enables the partial DOS to be determined from UPS spectra. These experimentally determined partial DOS's may be compared to those calculated from band structures in order to determine the quality of the calculation. The availability of a large data base for CuCl makes this an especially attractive compound for the present study.

In Sec. II the application of the MBBESIS to the zinc-blende structure and the calculation of partial DOS's are described. In Sec. III the band structure and the total, as well as the $d$, $p$, and $s$-projected, DOS's calculated by MBBESIS for CuCl, are presented and compared with the SXES and UPS spectra. Finally, in Sec. IV the conclusions of this study are presented.

II. INTERPOLATION SCHEME AND PARTIAL DENSITY OF STATES

The MBBESIS used in this investigation has been described in detail previously. In the application of this MBBESIS to the zinc-blende structures, the atom with $d$ orbitals is called $A$ and placed at the origin of the unit cell, whereas the nonmetal atom ($B$) is at position $r=(a/4)(1,1,1)$. The total local pseudopotential of the zinc-blende compound $(AB)$ can be written as follows:

$$V_{\text{G}}(AB) = V_{\text{G}}(A) + V_{\text{G}}(B)[\cos(G \cdot r') + i \sin(G \cdot r')] ,$$

where $G$ is in units of $2\pi/a$. When $G \cdot G$ is an odd number, the total pseudopotential is complex whereas for all

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the cases studied previously (e.g., Refs. 1–3) the pseudopotential was strictly real. Thus, the values of \( V_G \) for \( AB \) are complex or real, with

\[
V_G(AB) = \begin{cases} 
V_G(A) - V_G(B) & \text{for } |G| = 0, \sqrt{8} \\
V_G(A) - V_G(B) & \text{for } |G| = 2, \sqrt{12} \\
V_G(A) - iV_G(B) & \text{for } |G| = \sqrt{3} \\
V_G(A) + iV_G(B) & \text{for } |G| = \sqrt{11} .
\end{cases}
\]

(2)

For \( G = G \), the total pseudopotential is the sum or difference of the pseudopotential coefficients for atoms \( A \) and \( B \), which was also the case for the fluorite and rocksalt structures. Thus, \( V_G \) can be expressed as one pseudopotential parameter in the MBBSIS. For \( G = G \), odd, the total pseudopotential is the sum of a real pseudopotential term for atom \( A \) and an imaginary term for atom \( B \). Two different pseudopotential parameters are needed for \( V_G(AB) \), and a complex Hamiltonian must be diagonalized. However, in the case of CuCl, including the two parameters \( V_{111}(B) \) and \( V_{311}(B) \) in the MBBSIS did not improve the band structure compared to an approximate, strictly real Hamiltonian. The standard deviations of these two parameters calculated in the fitting procedure were much larger than the values of the parameters. Thus, \( V_{111}(B) \) and \( V_{311}(B) \), the imaginary components of the total pseudopotential, were negligible in the CuCl case. Therefore, the same interpolation scheme applied to the fluorite and rocksalt structures\(^2,3\) was used for CuCl in the calculations reported in this paper. The semiempirical energy bands of CuCl were obtained by fitting the MBBSIS eigenvalues to 30 energies at the \( L \), \( \Gamma \), and \( X \) symmetry points obtained from the ARPES spectra of Westphal and Goldmann\(^{10,11}\).

The MBBSIS eigenfunctions are linear combinations of 39 plane waves and 5 \( d \) wave functions. For a crystal with inversion symmetry, such as fcc metals, the eigenfunctions have pure \( l \)-orbital character at the \( \Gamma \) point of the Brillouin zone (BZ)\(^{12}\). The zinc-blende structure does not have inversion symmetry, but since the imaginary part of the Hamiltonian has been neglected for CuCl, the MBBSIS eigenfunctions will have pure \( l \)-orbital character at the \( \Gamma \) point. One can obtain the \( l \)-orbital partial DOS \( \langle N_l(E) \rangle \) by extracting the \( l \)-like component from the total density of states (TDOS) in calculating the weighted sum:

\[
N_l(E) = \sum_k \sum_m \sum_i C_i^l(\Gamma) C_m^l(k) A w(k) \times \exp(-E - E_k^m / \delta)^2 ,
\]

(3)

where the \( C_i^l(\Gamma) \) are coefficients of the eigenfunction for band \( i \) at the \( \Gamma \) point with \( l \)-orbital symmetry, \( C_m^l(k) \) are those of eigenfunction \( m \) at an arbitrary wave vector \( k \), \( A \) is a normalization factor for the Gaussian weighting function, \( w(k) \) is the weighting factor for each \( k \) point if the sum is over a restricted set of special \( k \) points, and the Gaussian is centered at the energy eigenvalue \( E_k^m \) with a width determined by \( \delta \). The Gaussian function is used to produce a continuous DOS if the number of \( k \) points used in the summation is relatively small and/or to simulate broadening effects for comparison with experimental data.

In practice, the sum was carried out over 44 basis functions \( i \), 9 eigenstates \( m \), and 60 special \( k \) points that have been defined for efficient calculation of averages over the BZ of periodic functions of the wave vector\(^{13}\).

### III. Results and Discussion

The semiempirical band structure and TDOS of CuCl calculated by the MBBSIS are shown in Fig. 1. The zero of the binding-energy scale was referenced to the valence-band maximum at the \( \Gamma \) point in Fig. 1. The valence bands of the MBBSIS were fitted to the energies at the \( \Gamma \), \( X \), and \( L \) high-symmetry points determined from the ARPES data of Westphal and Goldmann (solid circles in Fig. 1).\(^4,5\) Since they greatly increased the average deviation in the valence bands, conduction bands above the second band of \( \Gamma \) symmetry were not used in the fit in order to optimize the agreement of the MBBSIS valence bands with the CuCl ARPES data.\(^4,5\) The average deviation from the experimental ARPES data was \(-0.35\) eV for CuCl, which was \(-2\) times larger than that for fits of the fluorite or rocksalt-structure compounds.\(^2,3\) The largest contribution to the average deviations from the ARPES data occurred at the first and second bands of \( \Gamma \) symmetry (the \( \text{Cl} 3s \) band and the conduction-band minimum). Even when the two parameters \( V_{111}(B) \) and \( V_{311}(B) \) for the complex Hamiltonians were included, the fit was not improved.

Westphal and Goldmann\(^4\) compared the critical points in the valence band of CuCl obtained from the ARPES data with those from various band-structure calculations. Most of the existing band structures significantly disagreed with the ARPES data.\(^4,5\) The semirelativistic band structure obtained by Ves \textit{et al.},\(^{14}\) using a self-consistent local-density potential with a linear combination of muffin-tin-orbital atomic-sphere approximation method, appears to be the best of the first-principles calculations, but the MBBSIS band structure showed a better agreement with the ARPES data. The valence bands of CuCl calculated by the MBBSIS also agreed well with a strictly empirical band-structure model,\(^5\) which had been

\[
\text{FIG. 1. Semiempirical energy bands and TDOS of CuCl. The energy scale is referenced to the valence-band maximum and the TDOS scale is in electrons of one spin per eV per primitive unit-cell volume.}
\]
proposed on the basis of the critical-point energies along $\Gamma_L$ and $\Gamma_X$ determined from angle-resolved photoemission, secondary-electron emission results, and optical data. As discussed in the review of Goldmann, the top of the MBBSIS valence band of CuCl (the second band of $\Gamma_{15}$ and the first band of $\Gamma_{12}$ symmetry) is derived primarily from Cu 3$d$ states with a 25% contribution from Cl 3$p$ orbitals. The second band of $\Gamma_1$ symmetry is predominantly Cu 4$s$ in character. The lowest-energy bands with $\Gamma_{15}$ symmetry have largely Cl 3$p$ character with some Cu 3$d$ admixture, and the lowest $\Gamma_1$ band is entirely Cl 3$s$. In Fig. 1, the energy bands originating from the second band of $\Gamma_{15}$ symmetry at 0 eV and the first band of $\Gamma_{15}$ symmetry at $-2$ eV are essentially Cu 3$d$ $t_{2g}$ and $e_g$ bands. The bandwidth of the 3$d$ bands is $\approx2$ eV, and the $e_g$ bands are nearly flat along the high-symmetry line of the BZ. An almost flat band-gap region exists between the Cu 3$d$ and Cl 3$p$ bands. The total DOS with 0.3-eV Gaussian broadening in Fig. 1 showed a sharp peak at $-2$ eV, which arises from the flat portion of the Cu $e_g$ band. For the Cl 3$p$ bands, two separate peaks are resolved. The consensus of experimental results is that CuCl has a direct band gap of 3.4 eV between the valence-band maximum $\Gamma_{15}$ and the conduction-band minimum $\Gamma_1$. The energy gap between the second band of $\Gamma_{15}$ symmetry and the second band of $\Gamma_1$ symmetry calculated with the MBBSIS is 1.7 eV larger than the experimental results, since the second band of $\Gamma_1$ symmetry was not used in the fitting procedure.

Figure 2 shows the total and the $d$-, $p$-, and $s$-orbital projected DOS calculated with the MBBSIS (solid lines) and those deduced from x-ray photoemission spectroscopy (XPS) (circles in a) (Ref. 16), UPS (circles in b,c) (Ref. 15), and SXS ($\times$'s) (Refs. 18 and 19) spectra. All the DOS were calculated at 60 special $k$ points with 1.0 eV full width at half maximum broadening to simulate the experimental resolution and intrinsic broadening effects. In Fig. 2(a) the calculated TDOS is compared with the XPS spectrum. The XPS spectrum basically represents the experimental TDOS, since, in the $x$-ray photoemission process, the entire BZ is sampled. The agreement between this calculation and the XPS spectrum is good, except for the intensity of the lower-binding-energy peak (around $-5$ eV) from the Cl 3$p$ orbital. The calculation showed a higher DOS than for the XPS spectrum at that energy, but the width of the feature was well represented. The difference in intensity of this feature is likely to be the result of the photoionization cross sections for the different components of the bands. Scofield has reported that the photoionization cross section at 1254 eV photon energy for Cu 3$d$ is about 4.5 times larger than for Cl 3$p$.

In the past, SXS was the primary experimental technique to determine a partial DOS for the valence bands of solids. In the soft x-ray emission process, the dipole selection rule ($\Delta l=\pm1$) is obeyed for the transitions from the initial valence states to the final core states with well-defined orbital symmetry, and thus by choosing a suitable final core state, the partial DOS can be extracted. UPS spectra may also be useful in determining the partial DOS, because of the strong dependence on photon energy of the photoionization cross section of the orbitals with different angular momenta. The photoionization cross section of Cu 3$d$ orbitals is nearly constant over 10–40 eV photon energy, but that of Cl 3$p$ orbitals decreases rapidly, because of a Cooper minimum in the Cl 3$p$ photoionization cross section at 43 eV photon energy. Therefore, UPS spectra taken at $h\nu=40.8$ eV mostly represent the $d$ DOS, and those taken at $h\nu=21.2$ eV the $p$ DOS.

The SXS spectrum labeled by $\times$'s in Fig. 2(b) for the $L_{2,3}$ transitions from the valence band to the Cl 2$p$ core level represents mainly the $d$ DOS in the valence bands, since the $l\rightarrow l+1$ channel dominates the $l\rightarrow l-1$ channel. Because of the spin-orbit splitting of the Cl 2$p$ final states, additional broadening is apparent in the SXS spectra. The peaks at $-1.2$ and $-1.9$ eV, corresponding to $L_3$ transitions from the valence band (VB) to Cl(2$p_{3,2}$), agree very well with the peak positions in the UPS spectra and the calculated $d$ DOS.

The circles in Fig. 2(b) represent the UPS spectrum taken at $h\nu=40.8$ eV, which reflect the experimental $d$ DOS. This spectrum agrees even better with the calculated $d$ DOS. The deconvolution of the $d$ DOS into $t_{2g}$ and $e_g$ contributions indicated that the peak around $-5$ eV contained both $t_{2g}$ and $e_g$ components, whereas the peak around $-6$ eV was derived mainly from the $t_{2g}$ states. The calculated $s$ DOS in Fig. 2(d) shows a peak around $-6$ eV, and thus also might contribute to the corresponding experimental peak in Fig. 2(b).

In Fig. 2(c) the SXS spectrum ($\times$'s) for transitions from the VB to the Cl 1$s$ level, and the UPS spectrum (circles) taken at $h\nu=21.2$ eV, represent the experimental $p$ DOS. Both agree well with the calculated $p$ DOS.
extra SXS peak around $-3.5$ eV was attributed to a satellite feature. The UPS spectrum showed two nearly resolved peaks around $-5$ eV, whereas the SXS spectrum has one peak because of the large natural lifetime broadening. The calculated $p$-DOS curves with $0.3$-eV Gaussian broadening resulted in two separate peaks, as in Fig. 1. A decomposition of the MBBSIS eigenvectors shows that 23% of the $p$ DOS for the Cl $3p$ orbitals contributes to the top valence band, which reflects the degree of hybridization of Cl $3p$ with Cu $3d$ orbitals. This agrees with the experimental observations\cite{kim15,kim16} that the top valence band consisted of a 23–25% contribution from the Cl $3p$ orbitals.

The MBBSIS parameters that were used in obtaining the semi-empirical band structure and DOS for CuCl are listed in Table I, along with the standard deviations. The values of the $A_4$ and $A_5$ parameters that are responsible for the dispersion of the $e_g$ bands are nearly zero. The value of the hybridization parameter $B_1$ is also negligible compared to its standard deviation, which means that the $e_g$ bands show little hybridization with the other bands. The small amount of hybridization of the Cu $e_g$ bands with Cl $3p$ bands can be explained by the fact that the $e_g$ orbitals point away from the Cl ions in the zinc-blende structure.

IV. CONCLUSIONS

The MBBSIS was used to generate the valence-band structure of the zinc-blende compound CuCl, and to project $l$-specific partial DOS, which can be very useful in studying the hybridization of atomic states in compounds and in verifying the quality of the MBBSIS bands. The semi-empirical band structure for CuCl was obtained by fitting the energy bands to the ARPES data of Goldmann and Westphal\cite{westphal4,westphal5} and agreed very well with the strictly empirical band-structure model. Partial DOS's for CuCl were obtained by projecting $s$, $p$, and $d$-like components out of the mixed basis. The calculated $p$ and $d$ DOS agreed very well with the experimental $p$ and $d$ DOS obtained by SXS and UPS. The UPS spectra provided a much clearer representation of the partial DOS than that from the SXS spectra, and thus demonstrate a further advantage of variable-photon-energy UPS for the study of the electronic structures of materials.

ACKNOWLEDGMENTS

Support for this project was provided by the U.S. Office of Naval Research. R.S.W. acknowledges the partial support of the Camille and Henry Dreyfus Foundation and the Alfred P. Sloan Foundation, and the helpful suggestions of D. S. Pan.

\begin{table}[ht]
\centering
\caption{MBBSIS parameters for CuCl. All values in electron volts except $R$ in units of $4a/\pi$ and the lattice constant in angstroms. The ± signs indicate the standard deviation of each parameter. The parameters are intentionally reported with more significant figures than justified by the standard deviations in order to produce band structures that are essentially identical to those shown in Fig. 1 with MBBSIS.}
\begin{tabular}{lcc}
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\textsuperscript{1}R. L. Benbow and N. V. Smith, Phys. Rev. B 27, 3144 (1983), and references therein.
\textsuperscript{21}J. H. Scofield, J. Electron Spectrosc. 8, 129 (1976).