

Self-consistent band structure of CuCl

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A self-consistent calculation is given for the band structure of copper chloride, which shows the absence of a small, indirect gap in the electron spectrum of this dielectric.

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The unique characteristics of the band structure of copper chloride, in which the valence-band ceiling is formed by *d*-similar states, makes this dielectric extremely interesting from the point of view of electron-hole pairing and possible formation of biexcitons, i.e., exciton molecules. According to an experimental estimate,⁽¹⁾ $m_e = 0.415 m_0$, $m_h = 20 m_0$. A report on the anomalously high diamagnetic susceptibility of copper chloride⁽²⁾ is also now the subject of extensive discussion.⁽³⁾ An important but unresolved problem is the presence or absence of a small (~ 0.4 eV) indirect gap in the electron spectrum of CuCl, whose existence is necessary for possible explanation of this anomalous diamagnetism.

Band-structure calculations (see, e.g., Ref. 4) given earlier were not self-consistent relative to the crystal potential. The purpose of our paper is to obtain a self-consistent

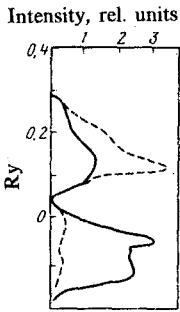


FIG. 2. Curves for the photoelectron energy distribution of CuCl at excitation energies $\hbar\omega = 21.2$ eV and $\hbar\omega = 40.8$ eV (dashed line), taken from Goldman *et al.*⁽⁷⁾

physical reason for this behavior is the strong localization of the wave functions, the narrowness of the valence bands, and a large charge exchange between the copper and the chlorine in the formation of the compound.

We shall now consider several important aspects of the band structure. Because of lattice symmetry in the valence band, a strong hybridization takes place between the chlorine 3p states and the copper 3d states, so that at the point Γ the upper and lower states Γ_{15} are hybrid p - d states. Thus, about 70% of Γ_{15}^U is comprised of d orbitals, and Γ_{15}^L has a more defined p nature.

The measurement of photoelectron absorption spectra with different excitation energies makes it possible to study the partial density states of electrons in the valence band. Figure 2 shows photoelectron spectra with $\hbar\omega = 21.2$ eV and $\hbar\omega = 40.8$ eV obtained in Ref. 7. The first characterizes the density of electron states with p symmetry, and the second that with d symmetry. A strong hybridization of p and d states can be seen. The location of the fundamental peaks, in particular the high peak of the d similar states, which belong to the narrow nonhybridized Γ_{12} band, are in reasonable agreement with the theoretical calculation in Fig. 1. We note that our calculation gives better agreement between theory and experiment than a recent Hartree-Fock calculation⁽⁸⁾ with a nonlocal exchange potential. In addition, it can be seen that the upper Γ_{15} band is broader than the experimental band, and the lower Γ_{15} band is much narrower.

The location of the low-lying, atom-like, 3s-valence chlorine band can be determined from x-ray emission spectra,⁽⁷⁾ not shown in Fig. 1. For CuCl, the experimental value of the separation between the absorption edge and this band is 15.8 eV. In our calculation this separation turned out to be 14.7 eV. We note that in Ref. 8 the location of this band is much deeper (~ 25 eV).

However, the calculation with the local exchange potential evidently always gives strongly reduced values of the energy gap between the valence states and the conduction band states. In our calculation a direct gap is obtained at the point Γ , whose magnitude is only 0.7 eV. The experimental value of this gap is 3.4 eV. In the calculation with a nonlocal exchange potential and with correlation corrections in the eigenenergy region,⁽⁸⁾ a value, which is closer to the experimental value of 4 eV, was ob-

tained. This situation is not unique or characteristic only for CuCl, but reflects a general tendency. We cite, for example, the calculations for LiH.^{9,10} However, the general structure of the valence and conduction bands in both calculations turns out to be completely identical, and in particular shows an absence of any indirect gap smaller than the direct one.

Thus, the self-consistent band calculations do not support the CuCl band structure model, in which there is a small indirect gap. On the other hand, the values obtained in our calculation of the effective masses of the electrons and holes near the point Γ give a ratio $m_h/m_l = 15$, which is close to the experimental value, and does not contradict the model for the biexciton generation in this material.

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