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Photoemission determination of the occupied *d*-band position for $CdCr_2Se_4$ and $CdCr_2S_4$

W. J. Miniscalco and B. C. McCollum
GTE Laboratories, Inc., Waltham, Massachusetts 02254

N. G. Stoffel and G. Margaritondo
Department of Physics, University of Wisconsin, Madison, Wisconsin 53706

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Photoemission spectroscopy has been used to investigate the valence band of $CdCr_2Se_4$ and $CdCr_2S_4$. The occupied *d* bands for both materials have been found to lie below the top of the valence band. Comparison is made to recent band-structure calculations, and the implications of this electronic structure for the unusual behavior of the transport properties and absorption edge are discussed.

Chromium chalcogenide spinel magnetic semiconductors have attracted considerable interest because of the interaction between their magnetic and electronic systems. It is now believed that the dominant role in these processes is played by excitations in the narrow *d* bands rather than in the wide *s* and *p* bands. However, the location in energy of these intrinsic *d* bands contributed by the Cr has remained controversial. Here we distinguish between states of *d* character and the occupied, primarily *p*-like states (valence band) and the unoccupied, primarily *s*-like states (conduction band). Using synchrotron radiation photoemission, we have examined the valence-band density of states for $CdCr_2Se_4$ and $CdCr_2S_4$, the two most extensively studied Cr spinels. The dependence on photon energy of the valence-band spectral features was used to distinguish the *d* states from the *s* and *p* states. We find that the filled *d* bands lie below the top of the valence band for both materials. These results lead to new insight into the unusual behavior of their absorption edge and transport properties.

$CdCr_2Se_4$ and $CdCr_2S_4$ are ferromagnetic semiconductors which order at 130 and 84 K, respectively. These materials are distinguished by strong interaction between carriers and spins, typified for $CdCr_2Se_4$ by an absorption edge which shifts to the red with decreasing temperature[1] and unusual transport properties. The latter include strong negative magnetoresistance[2,3] as well as resistivity and Seebeck coefficient anomalies[2,4] in the vicinity of the Curie temperature T_C. Perhaps even more interesting is the converse effect in which steady-state and transient variations in carrier concentration produce changes in the ordering temperature.[5]

Attempts to explain these phenomena have been hindered by a poor understanding of the electronic structure of Cr spinels. This situation has recently improved somewhat with the publication of band-structure calculations for $CdCr_2Se_4$ and $CdCr_2S_4$ performed by using the extended Hückel[6] and the discrete variational $X\alpha$ (DV-$X\alpha$)[7] methods. The octahedral symmetry of the Cr site splits the free-ion *d* levels into a threefold orbitally degenerate t_{2g} lower state and a twofold orbitally degenerate e_g upper state. Intra-Cr exchange introduces a large splitting between the spin components of these states and pushes the levels with antiparallel spin into the conduction band.[6,7] Although significant mixing with anion valence states may occur,[7] for simplicity we retain the t_{2g} and e_g labels for the *d* bands.

Additional clarification of the electronic structure has been provided by the photoluminescence investigation of Yao *et al.*[8] which explained the large discrepancy in energy between the absorption edge and the emission by identifying the fundamental gap for $CdCr_2Se_4$. For these materials the fundamental gap is usually defined as the energy difference between the top of the *p*-like valence band and the bottom of the *s*-like conduction band. These authors found that the luminescence results from transitions at the fundamental gap while *d* bands in this gap are probably responsible for the absorption edge at lower energy.[11] Until now, however, there has been no experimental determination of which *d* bands occupy the fundamental gap and control both the transport properties and the energy of the absorption edge.

The experiments were performed with use of synchrotron radiation from the 240-MeV storage ring at the Synchrotron Radiation Center of the University of Wisconsin, Madison. Details of the apparatus and techniques used can be found in Ref. 9. The $CdCr_2Se_4$ crystals were grown by the flux method[10] and the $CdCr_2S_4$ samples were grown by vapor transport.[11] The lattice parameters were verified by x-ray powder patterns and spectrochemical analysis revealed only trace impurities. As an additional test, samples were subjected to scanning electron microprobe analysis and no variations in composition were found across the faces. Atomically clean surfaces were obtained by grinding *in situ* under ultrahigh vacuum ($< 4 \times 10^{-10}$ Torr) with a diamond grinder. All measurements were made at room temperature.

Figures 1 and 2 show the photoelectron energy distribution curves for $CdCr_2Se_4$ and $CdCr_2S_4$ at a resolution of 300 meV. The spectra remained unchanged at higher resolution. The positions of the two shallowest-in-energy peaks are independent of photon energy, $\hbar\omega$, for both compounds. The remaining features have $\hbar\omega$-dependent positions below 30–35 eV, but this dependence disappears at higher photon energies. This indicates that for $\hbar\omega \geqslant 35$ eV the peak positions correspond to peaks in the density of states. The large peak 10–12 eV below the top of the valence band, E_v, is the Cd $4d$ core level which has been observed at roughly the same position in the related nonmagnetic semiconductors $CdIn_2Se_4$ (Ref. 12) and $CdIn_2S_4$.[13]

From Fig. 1 it is apparent that the different spectral features exhibit a different intensity dependence on $\hbar\omega$. We used this difference to distinguish between d-like features and s- and p-like features. In particular, we see that the shallowest-in-energy peak in Fig. 1 (−1.45 eV) monotonically increases its intensity relative to all other features up to $\hbar\omega = 30-35$ eV. This behavior has been used to identify d- and f-like valence-band features for a large number of magnetic semiconductors, including rare earth and uranium sulfides,[14] FeS_2 and NiS_2,[15] and transition-metal oxides.[16] Accordingly, we identify the t_{2g} states expected in this energy region with the shallowest peak in our spectra. The increase in intensity of this d peak is due to the centrifugal barrier effect.[17] In the upper part of our photon energy range, the d peak is affected by the onset of a Cr $3p$-$3d$ resonance which gives a nonmonotonic intensity vs $\hbar\omega$ behavior.[18] The latter effect is quite pronounced in the high-$\hbar\omega$ spectra shown for $CdCr_2S_4$ in Fig. 2 where the shallowest peak is also d like. We emphasize that throughout our photon energy range, the intensity dependence of the shallowest peak in both Figs. 1 and 2 is different from that of all other features. This and the necessity that the parallel spin t_{2g} states lie somewhere in the valence-band region is strong evidence for the above identification. Indeed, for the nonmagnetic spinels $CdIn_2Se_4$ and $CdIn_2S_4$ which contain no d bands, the upper valence-band states exhibit just the

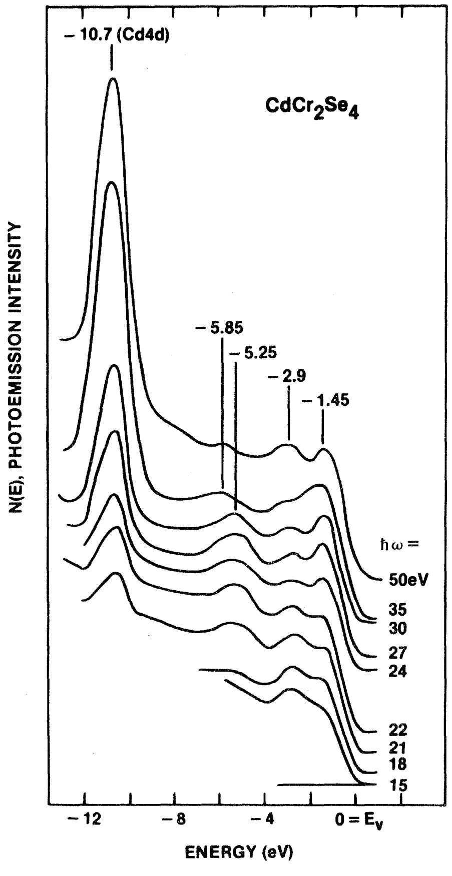

FIG. 1. $CdCr_2Se_4$ energy distribution curves shown for photon energies ranging from 15 to 50 eV. The zero of energy has been assigned to the top of the valence band, E_v. The peak at −1.45 eV corresponds to the parallel spin t_{2g} d band.

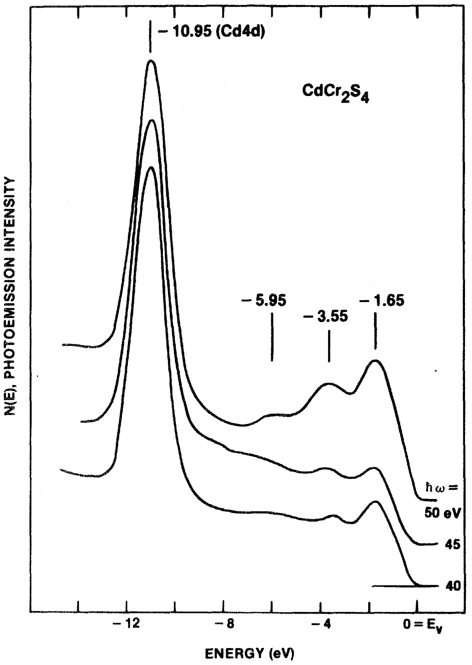

FIG. 2. $CdCr_2S_4$ energy distribution curves shown for photon energies ranging from 40 to 50 eV. The zero of energy has been assigned to the top of the valence band, E_v. The peak at −1.65 eV corresponds to the parallel spin t_{2g} d band.

opposite dependence on photon energy.[12,13] Therefore, we conclude that the correct electronic structure for these two materials is that illustrated in Fig. 3.

The extended Hückel calculation[6] places both the parallel spin t_{2g} and e_g bands in the fundamental gap in contradiction with the photoemission results. For $CdCr_2Se_4$ the *ab initio* DV-$X\alpha$ calculation[7] places the occupied t_{2g} band just below the top of the valence band in agreement with our measurements. For $CdCr_2S_4$, however, this calculation disagrees with our photoemission data and shows the filled d band extending above the top of the valence band. These comparisons are valid even though the measurements were done for the paramagnetic state while the DV-$X\alpha$ calculations are for the ferromagnetic state. This is because the spin splittings for the valence band ($\simeq 0.1$ eV)[7] are negligible on the energy scale of interest. Moreover, intra-Cr exchange ($\simeq 3$ eV)[7] largely determines the spin splittings of the d bands so the positions of these differ little between the paramagnetic and ferromagnetic state.

Our results and the DV-$X\alpha$ calculation for $CdCr_2Se_4$ are consistent with the available transport measurements. Lehmann and Harbeke[19] reported electron mobilities two orders of magnitude smaller than hole mobilities for $CdCr_2Se_4$. This has been interpreted to indicate that hole conductivity takes place in wide bands while electron conductivity occurs in narrow bands as is required by the electronic structure of Fig. 3. We are unaware of mobility measurements for $CdCr_2S_4$, but expect identical behavior due to the similiarity in electronic structure.

The location of the filled d bands has important implications for the carrier-spin coupling as well. It is now possible to conclude that transitions from the top of the valence band to the empty e_g band ($E_e' - E_v$ in Fig. 3) are responsible for the absorption edge. Since the fundamental gap for $CdCr_2Se_4$ increases with decreasing temperature as is typical for nonmagnetic semiconductors,[8] the red-shifting absorption edge results from lowering of the e_g band extremum E_e' with decreasing temperature. The existence of anomalies in the transport properties near T_C only for n-type material indicates that these effects are also associated with the e_g band. Although the mechanisms responsible have yet to be unambiguously identified, the electronic structure in Fig. 3 illustrates why similar effects of magnetic ordering are not observed for hole conduction which is restricted to the valence band.

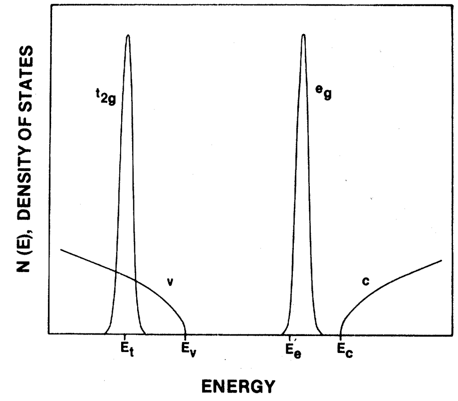

FIG. 3. Schematic electronic structure of $CrCr_2Se_4$ and $CdCr_2S_4$ based upon photoemission and optical measurements. Only the parallel-spin d bands are shown. The fundamental gap is $E_c - E_v$. For $CdCr_2Se_4$ $E_v - E_t$ is 1.45 eV and for $CdCr_2S_4$ it is 1.65 eV. The absorption edge is given by $E_e' - E_v$.

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