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Experimental study of the electronic structure of $KMgF_3$

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Two kinds of photoemission experiments were performed to study the electronic structure of $KMgF_3$ and correlate it with theoretical and optical data. Photoelectron energy distribution curves were used to explore the valence-band density of states and the shallow K and Mg core levels. Partial-yield spectroscopy was used to measure the optical-absorption coefficient near the Mg $L_{2,3}$ edge. We detected three absorption peaks, two of which correspond to one-electron transitions, while the third has an excitonic final state. The corresponding core-excitonic binding energy, 4.8 eV, is of magnitude comparable to that of the K $M_{2,3}$ core exciton.

In a recent article Heaton and Lin[1] reported the first self-consistent-field (SCF) first-principles band-structure calculation of a perovskite-structure crystal and used the results to interpret the reflectivity spectra. The calculation was performed for the cubic-structure material $KMgF_3$. Its high ionicity, nonmagnetic character, and simple cubic structure make $KMgF_3$ an ideal prototype for electronic-state investigations in this important class of crystals. To test the results of the band-structure calculations and to further correlate the theoretical band structure with optical properties we performed two different kinds of photoemission spectroscopy experiments. Photoelectron energy distribution curves (EDC's) were taken with a synchrotron radiation source to explore the valence-band states and the shallow p core levels of K and Mg. The soft-x-ray optical-absorption spectrum was measured in the region of the Mg $L_{2,3}$ edge by partial-yield spectroscopy.[2,3] Our EDC's show that the band-structure calculations give the correct valence bandwidth when the Kohn-Sham exchange model is used. The optical-absorption coefficient in the Mg $L_{2,3}$ edge region exhibits three peaks. Two of these peaks are due to one-electron transitions from the Mg $2p$ level to conduction-band states. The third peak has an excitonic final state involving s-like states at the bottom of the conduction band.

The experiments were performed on single-crystal $KMgF_3$ cleaned *in situ* by grinding with a diamond wheel. Details of the experimental systems are described in Ref. 4. In particular, the pressure was in the low 10^{-10}-torr range throughout the experiment to prevent sample contamination. The photons necessary for the photoemission experiments were provided by the "Grasshopper" beam line of the University of Wisconsin Synchrotron Radiation Center. Due to the extremely wide forbidden gap the crystals became positively charged when exposed to the photon beam. Charging effects were partially compensated by a low-energy electron flux from an incandescent filament. The residual charging effects were corrected by using the Mg $2p$ and K $3p$ core levels to align the EDC's in energy.

Figure 1 shows a series of EDC's taken at different photon energies. The zero of the energy scale is set to coincide with the position of the Mg $2p$ level. The F $2p$ states give rise to the valence-band states in peak A. From a linear extrapolation of the leading edge of the EDC's we estimate the top of the valence band, E_v, to be 46.6 eV above the Mg $2p$ level. The K $3p$ level is 12.7 eV below E_v. The origin of the fourth peak B in the EDC's is not clear although it could be related to the K $3s$ states. We see in Fig. 1 that the total width of the peak A is ~ 6.5 eV. From the experimental width of the core levels we estimate the total instrumental broadening—including charging effects—not to exceed 2.5 eV. The combined broadening contributions from monochromator and electron analyzer are ~ 0.6 eV and the remaining broadening is due to charging effects. Therefore, after correcting for the above broadening, we conclude that the valence bandwidth is not less than

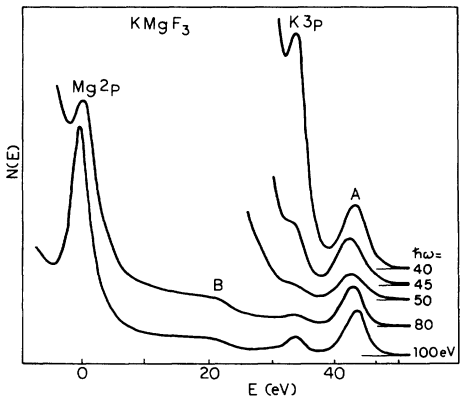

FIG. 1. Photoelectron energy distribution curves taken on $KMgF_3$ at different photon energies. The zero of the energy scale is set to coincide with the Mg $2p$ peak.

4–4.5 eV in agreement with the x-ray photoemission data by Beaumont *et al.*[5] The theoretical valence bandwidth has been calculated by using five different versions of the local exchange approximation.[1] Its value ranges between 4.1 and 2.5 eV for exchange α parameters ranging between $\frac{2}{3}$ and 1.33 and β parameters between 0 and $\frac{1}{6}$. It is interesting to note that a valence bandwidth of 4.1 eV, in agreement with the experimental results, is obtained for the Kohn-Sham exchange model ($\alpha=\frac{2}{3}$ and $\beta=0$) as the Kohn-Sham model is more appropriate for the ground state than is the choice $\alpha=1$ which leads to a 3.3-eV width. The use of the Wigner interpolation formula as an approximate potential also gives a valence bandwidth (4.0 eV) in close agreement with the experimental value. However, both the Kohn-Sham model and the Wigner interpolation formula give a 7-eV band gap which is much smaller than the experimental value of 12.4 eV. A larger calculated band gap is obtained with $\alpha=1$ or higher, but the valence bandwidth becomes too small. The underestimate of the band gap by the Kohn-Sham model is because of the following reason. In the Hartree-Fock one-electron Hamiltonian, the Coulomb potential includes the interaction energy of the electron with itself which is canceled by an identical term in the exchange potential, but the cancellation is not exact when an approximate local exchange such as the Kohn-Sham model is used. The incomplete removal of the self-interaction energy reduces the binding energies of the valence states and consequently the band gap. Recently, a correction for the self-interaction term has been made in the energy-band calculation of the LiCl crystal.[6] This increases the band gap from the uncorrected value of 6.3 eV (Kohn-Sham exchange with correlation) to 9.9 eV in good agreement with 9.4 eV from experiment. The valence bandwidth, however, increases only slightly (from 2.9 to 3.1 eV). In the case of $KMgF_3$ since the Kohn-Sham exchange gives good agreement with experiment for the valence bandwidth, we expect that addition of the self-interaction correction would significantly improve the band gap and provide a band structure in good overall agreement with experiment.

Figure 2 shows two different partial-yield spectra in the photon energy region of the Mg $L_{2,3}$ absorption edge. These curves are plots of the total yield of photoelectrons in a given kinetic energy window versus photon energy. It was demonstrated by Gudat and Kunz[2] and confirmed by many other authors[3] that peaks in the optical-absorption coefficient correspond to peaks in the partial-yield curves. Some of the partial-yield features, however, are spurious rather than related to optical absorption. Optical-absorption peaks can be easily identified since they appear at the same photon energy in partial-yield curves taken with different kinetic energy windows.

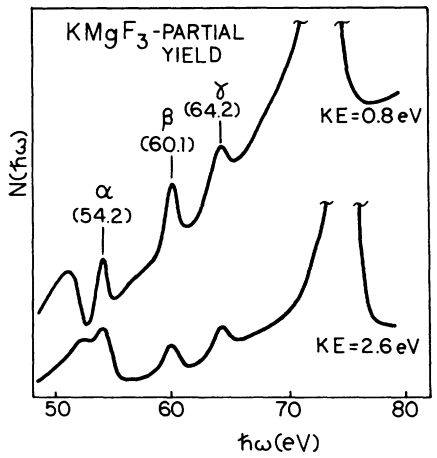

FIG. 2. Partial-yield spectra (Refs. 2 and 3) in the energy region of the Mg $L_{2,3}$ optical-absorption edge. The center of the kinetic energy window is indicated for each curve. Three different optical-absorption features, peaks α, β, and γ, appear at the same photon energy in both curves.

Other peaks not related to the absorption coefficient, e.g., those due to primary electrons, appear instead at different photon energies. We see in Fig. 2 three optical-absorption features, peaks α, β, and γ, and two spurious features. In particular, the spurious peak at photon energies above 70 eV is due to primary photoelectrons excited from the Mg $2p$ level, the energy of which is affected by photon-energy-dependent charging effects. The spurious peak at 50–53 eV is probably related in a similar way to peak B in the EDC's. We emphasize that the position of the optical-absorption peaks is *not* affected by charging effects. In a one-electron picture the position of peak β corresponds to transitions between the Mg $2p$ level and states $60.1-46.6=13.5$ eV above E_v. We compare this with the two structures in the reflectivity spectra of Takahashi and Onaka[7] at 13–15 eV which were interpreted in Ref. 1 as transitions to the K $3d$ conduction band from the upper part of the valence band where the density of states exhibits two peaks. Since these two peaks are slightly below the top of the valence band, the K $3d$ conduction band should be placed approximately 12.5–14.5 eV above E_v. We identify these states as the final states associated with peak β.

Peak γ corresponds to transitions whose final states are $64.2-60.1=4.1$ eV above the final states associated with peak β. The theoretical conduction-band density of states presented in Fig. 4 of Ref. 1 shows a small peak at 2 eV above the K $3d$ manifold. However, the band calculation was not carried out much above the K $3d$ bands because a very large basis set is needed to determine accurately the high-conduction states. Nevertheless one may expect some structures

in the density of states at energies above the K $3d$ bands because of the higher bands associated with the K $4p$ and Mg $3p$ states. Indeed we see in the reflectivity spectra[7] three structures at energies 1–5 eV above the K $3d$ peaks.

If we take the forbidden gap as 12.4 eV,[1,7] the one-electron final states for peak α would be 4.8 eV below E_c, the bottom of the conduction band. Therefore this peak must correspond to an excitonic final state. Beaumont *et al.*[5] estimated from their experiments a core excitonic binding energy of 3.4 eV for the K $M_{2,3}$ edge. However, these authors may have overestimated the forbidden gap[7] and underestimated the distance between the K $3p$ level and E_v. Using the 12.4-eV gap and deriving E_v by linear extrapolation of the leading edge, we estimate from the results of Beaumont *et al.*[5] a K $M_{2,3}$ core excitonic binding energy of 4.1 eV. The magnitude of this binding energy suggests that the peak-α core exciton involves Γ-point, s-like electrons near E_c. Indeed this hypothesis gives for peak α a core-exciton binding energy of 4.8 eV of magnitude comparable to the binding energy of the K $M_{2,3}$ exciton. The higher-excited-state absorption peaks of this Γ-point exciton cannot be distinguished from the noise.

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