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Ultraviolet photoelectron spectra of ZnF_2 and $ZnCl_2$

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Energy distributions of photoelectrons from ZnF_2 and $ZnCl_2$ films were measured in the photon energy range 10–27 eV. The photoelectron spectra show features that can be identified as the effect of crystal-field splitting in the Zn 3*d* levels in the final state. While the splitting in ZnF_2 appears to be obscured by the F^- 2*p*-band peak, the doublet structure due to the crystal-field effect in $ZnCl_2$ can be seen below the Cl^- 3*p*-band spectrum. The crystal-field strength 10*Dq* in $ZnCl_2$ as indicated by the splitting is found to be 3.1 ± 0.2 eV.

I. INTRODUCTION

The x-ray photoelectron spectrum of ZnF_2 was reported recently by Kowalczyk *et al.*[1] They found a peculiar peak shape in the Zn 3*d* and F 2*p* region. The spectrum shows a shoulder on the lower binding energy side of the 3*d* peak. Because of the broad-pedestal shape, the spectrum could not be fitted into two simple peaks, i.e., a Zn 3*d* peak plus F 2*p* peak. They attribute the peak shape to crystal-field splitting in the single-hole $3d^9$ final states. Since the satellite structure is not well resolved, the exact nature of the splitting is not completely understood.[2]

An obvious difficulty in the analysis of the ZnF_2 spectrum is that the crystal-field splitting in the 3*d* levels is obscured by the F^- 2*p*-band peak. It may be worthwhile to investigate the splitting in a similar compound in which the halide *p* band has a lower binding energy. For example, if the binding energy of the Cl^- 3*p* band relative to the vacuum level is lower than that of the F^- 2*p* band, the splitting should appear more clearly in $ZnCl_2$ than in ZnF_2.

To check this experimentally, we measured the ultraviolet photoemission from ZnF_2 and $ZnCl_2$. The spectra show evidence of the splitting. From the observed separation of the peaks, we estimate the strength of the crystal-field splitting in the 3*d* levels of $ZnCl_2$ to be 3.1 eV.

II. PHOTOELECTRON SPECTRA

The ultraviolet photoemission measurements were made with dispersed radiation in the photon energy range 10–27 eV. The radiation from gas-discharge sources was dispersed with a normal incidence monochromator and a grazing incidence monochromator.[3,4] Energy distributions of photoelectrons from evaporated films of ZnF_2 and $ZnCl_2$ were measured *in situ* using the technique described previously.[5,6]

The photoelectron spectra shown in Fig. 1(a) display a conduction-band structure above the vacuum level of ZnF_2. A stationary peak can be seen at 3.5 ± 0.2 eV above the vacuum level with increasing photon energy. This feature reflects a region of high density of states in the conduction band.[5,6]

In Fig. 1(b), the spectra show two prominent peaks due to electrons excited from the Zn^{++} 3*d* and F^- 2*p* bands. These two peaks can also be seen in the photoelectron spectrum at 40.8 eV.[7] The highest occupied states are found at -12.3 ± 0.3 eV below the vacuum level (zero energy). The narrow peak located at -18.3 eV below the vacuum level can be associated with the Zn 3*d* states. The other peak at lower binding energy is broader, but it is not symmetrical. This is particularly noticeable in the spectrum at 21.2 eV. If we associate this peak with the F^- 2*p* band of ZnF_2, the asymmetric feature could just be a band-structure effect. On the other hand, the structure could be the effect of crystal-field splitting in the 3*d* levels as suggested by Kowalczyk *et al.*[1]

The uv photoelectron spectra of $ZnCl_2$ are shown in Figs. 2(a) and 2(b). The highest occupied states are located at -10.2 ± 0.2 eV below the vacuum level. The observed threshold is in agreement with the expectation that the Cl^- 3*p* band has lower binding energy than the F^- 2*p* band in zinc halides. As shown in Fig. 2(b), the peak associated with the Cl^- 3*p* band has a shoulder on the side of higher binding energy. We interpret this feature as a band-structure effect. The next two peaks at higher binding energies can be related to the Zn 3*d* states of $ZnCl_2$. The separation of these two peaks is 3.1 ± 0.2 eV.

III. DISCUSSION

It is interesting to note that the ultraviolet photoelectron spectra of ZnF_2 show two resolved peaks, whereas the x-ray photoelectron spectrum exhibits a high $3d$ peak with a shoulder. A possible explanation for the difference is that the probability of photoexcitation from the F^- $2p$ band is higher in the uv region than in the x-ray region. A similar change in relative intensity of the peaks has also been noted in the comparisons of x-ray and ultraviolet photoemission spectra of other transition-metal fluorides and chlorides.[8,9]

In comparison with the spectra of other transition-metal compounds, we find a difference in the level ordering of the d and p states. Whereas the major components due to the $3d$ electrons of Mn, Fe, Co, and Ni ions have lower binding energy than the F^- $2p$ or Cl^- $3p$ bands,[8,9] most of the electrons from the $3d$ states of the zinc compounds are found to have higher binding energy than the corresponding halide bands.

The structure of the Cl^- $3p$ band of $ZnCl_2$ can be seen in the uv photoemission spectra. The spectra shown in Fig. 2(a) indicate a bandwidth of approximately 3 eV with a higher density of states in the upper part of the band. Unfortunately

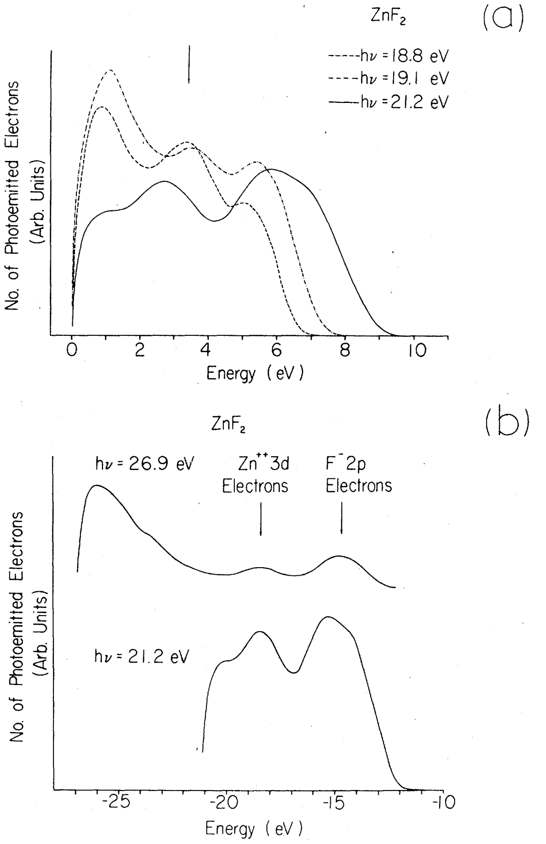

FIG. 1. (a) Normalized energy distributions of photoemitted electrons from ZnF_2. The energy distribution curves are plotted as a function of final-state energy above the vacuum level (zero energy). Arrow indicates a region of high density of states at 3.5 ± 0.2 eV above the vacuum level. (b) Photoelectron spectra of ZnF_2 at photon energies 21.2 and 26.9 eV. The energy distribution curves are plotted as a function of energy below the vacuum level (zero energy). Arrows indicate peaks that are associated with electrons excited from the Zn^{+2} $3d$ and F^- $2p$ bands. For photon energy of 21.2 eV, the F^- $2p$-band peak shows a noticeable shoulder on the low-binding-energy side.

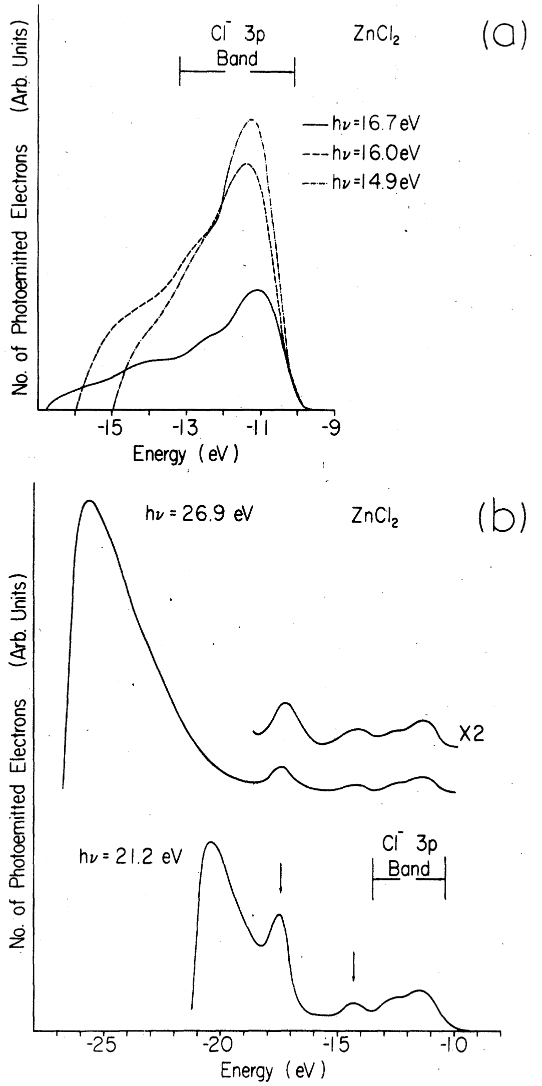

FIG. 2. (a) Valence-band spectrum of $ZnCl_2$. The energy distribution curves are plotted as a function of initial-state energy below the vacuum level (zero energy). The spectrum is associated with the Cl^- $3p$ band of $ZnCl_2$. The width of the Cl^- $3p$ band is approximately 3 eV. (b) Photoelectron spectra of $ZnCl_2$ at photon energies 21.2 and 26.9 eV. The energy distribution curves are plotted as a function of energy below the vacuum level (zero energy). Vertical arrows indicate peaks due to crystal-field splitting in the Zn $3d$ levels in the final state.

we have no calculated density of states for comparison with this result. Since the structure due to the 3*d* electrons has higher binding energy than the Cl^- 3*p* band of $ZnCl_2$, it seems likely that the Cl^- 3*p* band does not overlap appreciably the 3*d* levels in $ZnCl_2$. This observation is in agreement with the interpretation of the spectral absorption of $ZnCl_2$, which suggests that only a small fraction of the *d* states mixes into the valence band.[10]

The peaks located at −17.4 and −14.3 eV in Fig. 2(b) are associated with electrons excited from the Zn 3*d* states of $ZnCl_2$. The separation of the peaks is much larger than the spin-orbit splitting in the 3*d* states of the free Zn ions. We interpret the peaks as crystal-field splitting in the 3*d* levels in the final state. This splitting occurs when a hole is created in an otherwise completely filled *d* shell of the Zn^{2+} ion. The crystal-field strength is 3.1 ± 0.2 eV as indicated by the separation of the peaks. This is somewhat larger than the splitting for similar ions. For most trivalent metal ions, the observed optical values of the crystal-field strength are about 2.5 eV.[11]

Since a theoretical description of the crystal-field splitting in $ZnCl_2$ is not available, it may be useful to estimate the splitting from a simple model involving a cubic field. To the first approximation Zn ions could be considered to be in a cubic field in $ZnCl_2$, although the metal ion is actually situated in a tetrahedral complex.[11,12] In crystal-field theory, the strength $10Dq$ is the splitting of the 3*d* level in a cubic field. For a hydrogenlike atom situated in a cubic field of six point charges, each of charge $-e$, the quantities D and q are given by

$$D = 35e^2/4a^5 ,$$

and

$$q = \frac{2}{105}\int_0^\infty |R(r)|^2 r^6\, dr ,$$

where a is the distance between the atom and each point charge, and $R(r)$ is the radial wave function of the 3*d* state. An approximate value of $10Dq$ for $ZnCl_2$ may be calculated by assuming that the Zn^{3+} ion is located in a cubic field with interionic separation a. We assume a is 2.3 Å inasmuch as the Zn-Cl separation in the crystalline state of $ZnCl_2$ is 2.3 Å.[12] To find q we must first choose a suitable function $R(r)$ for the 3*d* electron of the ion.

Since the Zn ion is tripositive in the final state, it seems reasonable to approximate the function $R(r)$ of the ion by a 3*d* radial wave function of a hydrogenlike atom in which the nuclear charge is 4*e*. The hydrogenlike radial function[13] for a nuclear charge of 4*e* is

$$R_{nl}(r) = A_{nl}\, e^{-\alpha r/2}(\alpha r)^l L_{n+l}^{2l+1}(\alpha r) ,$$

where $\alpha = 8/na_0$ and

$$A_{nl} = \{\alpha^3(n-l-1)!/2n[(n+l)!]^3\}^{1/2} .$$

For $n=3$, $l=2$, and $a_0 = 0.53 \times 10^{-10}$ m, the value of $10Dq$ is found to be 2.94 eV. This is only slightly less than the observed splitting of 3.1 ± 0.2 eV. The close agreement is surprising, in view of the simplifying approximations we have made.

If we interpret the noticeable shoulder on the low-binding-energy side of the F^- 2*p*-band peak as a component of the 3*d* structure in ZnF_2, the splitting due to the crystal field would be approximately 4 eV, which is in agreement with the estimate reported by Kowalczyk *et al.*[1] The larger splitting in ZnF_2 is expected because the interionic distance of ZnF_2 is smaller than that of $ZnCl_2$. Using the value of 2.04 Å for the Zn-F separation in ZnF_2,[14] we calculated a splitting of 5.4 eV from our simple model of the crystal-field splitting in ZnF_2.

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