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Ultraviolet photoemission studies of BaF_2 and $BaCl_2$

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Photoemission measurements on evaporated films of BaF_2 and $BaCl_2$ were made at photon energies of 8–27 eV. Spectral quantum yields and energy distributions of photoemitted electrons were measured. The photoelectron spectra show high-density-of-states structures at 2.5 ± 0.2, 5.2 ± 0.2, and 7.5 ± 0.2 eV above the vacuum level for BaF_2 and 3.5 ± 0.2 eV above the vacuum level for $BaCl_2$. The spectra also provide information on the valence-band widths, band thresholds, and the spin-orbit splitting of the Ba^{++} $5p$ core band of $BaCl_2$. The energy differences between the regions of initial and final high densities of states are compared with the transition energies of certain structures found in the optical and energy-loss spectra of BaF_2.

INTRODUCTION

The electronic structure of alkaline-earth halides has been investigated recently. Reflectance measurements using synchrotron radiation provided spectra which show prominent features in the spectral region above 10 eV.[1] While these features can be associated with excitonic and interband transitions, a more detailed interpretation of the spectra is not possible because the band structure is not known. More recently, x-ray emission measurements have been made to obtain information on the band structure.[2,3] The emission bands of BaF_2 and $BaCl_2$ were found to be asymmetric with subbands on the high-energy side. The presence of these satellites is ambiguous, but they are believed to be due to double ionization of the halogen ion.[2] Because of double-ionization effects, it is difficult to interpret the emission spectra. In view of this difficulty, it is desirable to perform different measurements to provide energy-band data.

In this paper we report the results of ultraviolet photoelectron spectroscopy which show regions of high density of states in the valence and conduction bands, valence-band widths, and band thresholds of BaF_2 and $BaCl_2$. Moreover, the measured quantum yields of these materials are presented.

MEASUREMENTS AND RESULTS

The photoemission measurements were made with dispersed radiation in the photon energy range 8–27 eV. A normal-incidence vacuum uv monochromator[4] and a grazing incidence monochromator[5] were used to disperse the radiation

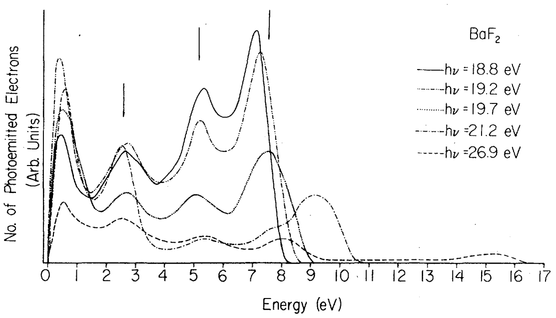

FIG. 1. Normalized energy distributions of photoelectrons from BaF_2. The energy distribution curves are plotted as a function of final-state kinetic energy above the vacuum level (zero energy). Arrows indicate positions of conduction-band structures above the vacuum level. The structures indicated here are not Auger peaks. Any Auger peak that may appear in this case as a result of Auger decay of the Ba^{+2} holes would be located near the vacuum level. Such a peak would be obscured by the scattered electron peak due to the emission cutoff.

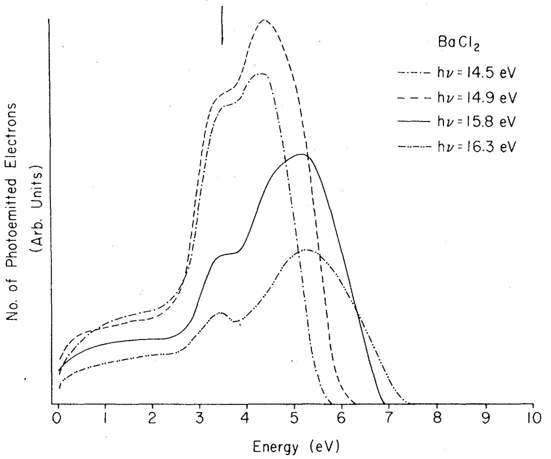

FIG. 2. Normalized energy distributions of photoelectrons from $BaCl_2$. The energy distribution curves are plotted as a function of final-state kinetic energy above the vacuum level (zero energy). Arrow indicates the position of a conduction-band structure above the vacuum level.

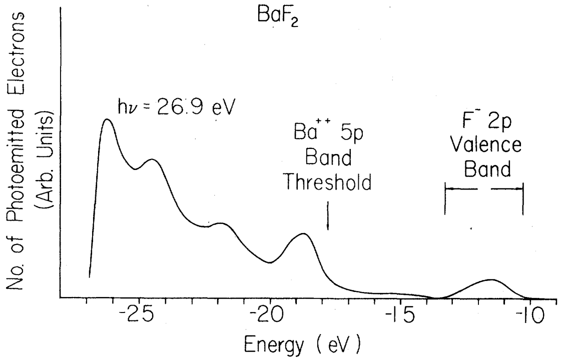

FIG. 3. Photoelectron spectrum of BaF_2 at photon energy of 26.9 eV. The energy distribution curve is plotted as a function of initial state energy below the vacuum level (zero energy). The band thresholds are found at −10.7 and −18.0 eV relative to the vacuum level.

from gas discharge sources. Photoemission from thin films of BaF_2 and $BaCl_2$ were measured *in situ* immediately after evaporation at 10^{-8}–10^{-7} Torr using the technique described previously.[4,6]

In Figs. 1 and 2, the photoelectron spectra show stationary structures above the vacuum level (zero energy) for different photon energies. These features arise as a result of inelastic scattering of the primary photoelectrons to regions of high density of states above the vacuum level. These high-density-of-states regions are probably associated with the 5*d* states of the Ba^{+2} ions.

In Figs. 3 and 4, the photoelectron spectra exhibit the valence- and core-band thresholds as well as the valence-band widths of BaF_2 and $BaCl_2$. The 26.9 eV spectrum of BaF_2 shows the band thresholds, but the spin-orbit splitting of the Ba^{+2} core band is obscured by the conduction-band structure. The splitting of the Ba^{+2} core band of $BaCl_2$, however, can be seen clearly for photon energy of 26.9 eV.

The bandwidths, band thresholds, splitting of the Ba^{+2} core, and the locations of conduction-band structures of BaF_2 and $BaCl_2$ are summarized in Table I. The band thresholds are given relative to the vacuum level.

The spectral quantum yields of BaF_2 and $BaCl_2$ are shown in Fig. 5. There is a pronounced dip in the spectral yield of $BaCl_2$ at 18.5 eV.

DISCUSSION

It is interesting to note that the conduction-band structure of BaF_2 is different from that of $BaCl_2$. This is somewhat surprising from the standpoint that the lower part of the conduction band depends mainly on the excited states of the Ba^{+2} ions. On the other hand, the crystal structures of these materials are different, BaF_2 being CaF_2 type[1] and $BaCl_2$ being $PbCl_2$ type.[7] Moreover, the nearest-neighbor distance of $BaCl_2$ is larger than that of BaF_2. A calculated density of states for the conduction bands is needed to explain the observed features. The conduction bands of the fluorite structure have been calculated,[8] but no calculation for $BaCl_2$ seems to be available.

The valence-band spectrum of BaF_2 is in good agreement with the photoelectron spectra reported by Lapeyre and Anderson[9] and Poole *et al.*[10] The valence-band spectra of BaF_2 and $BaCl_2$ show that

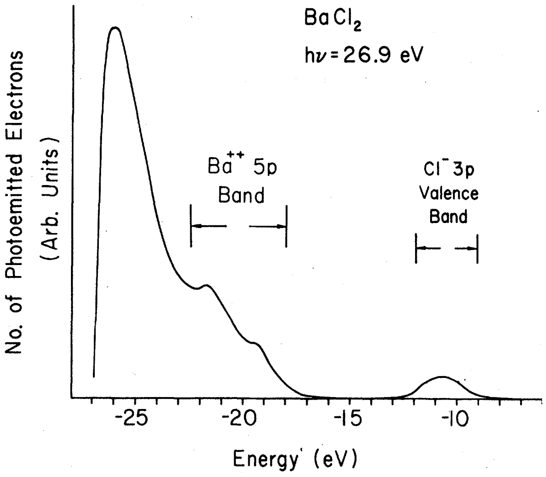

FIG. 4. Photoelectron spectrum of $BaCl_2$ at photon energy of 26.9 eV. The energy distribution curve is plotted as a function of initial-state energy below the vacuum level (zero energy). The band thresholds are found at −9.0 and −18.0 eV relative to the vacuum level.

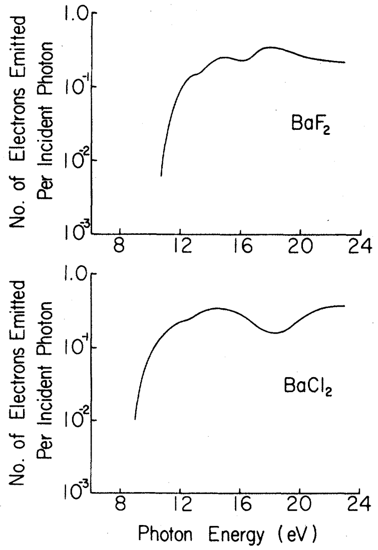

FIG. 5. Spectral quantum yields of BaF_2 and $BaCl_2$.

TABLE I. Values of energy-band parameters determined from photoelectron spectra of BaF_2 and $BaCl_2$. The values are in eV. Conduction-band structures and band thresholds are located relative to the vacuum level.

	BaF_2	$BaCl_2$
Conduction-band structures	2.5 ± 0.2	3.5 ± 0.2
	5.2 ± 0.2	
	7.5 ± 0.2	
Valence-band threshold	10.7 ± 0.2	9.0 ± 0.2
Valence-band width	2.9 ± 0.2	2.6 ± 0.2
Ba^{+2}-5*p* core threshold	18.0 ± 0.2	18.0 ± 0.2
Total width of Ba^{+2}-5*p* core		4.2 ± 0.2
Core splitting		2.2 ± 0.1

the F^- 2*p* band of BaF_2 is wider than the Cl^- 3*p* band of $BaCl_2$. Furthermore, the valence-band threshold of BaF_2 is greater than that of $BaCl_2$. These differences are consistent with the fact that the nearest-neighbor separation is smaller in BaF_2 than in $BaCl_2$. The larger bandwidth for smaller interionic separation suggests that there is a significant overlap of wave functions for the valence bands of these materials. The higher threshold for the valence band of BaF_2 indicates that the Madelung energy is larger in BaF_2, inasmuch as the ionization energies of the free F^- and Cl^- ions are about the same.[11,12]

The Ba^{+2} core-band spectrum of $BaCl_2$ shows a spin-orbit splitting of 2.2 ± 0.1 eV, which is in good agreement with the splittings observed for BaF_2 and $BaBr_2$.[13] The highest occupied states of the Ba^{+2} 5*p* bands of BaF_2 and $BaCl_2$ are found to be approximately 18 eV below the vacuum level. However, the binding energy of these core states relative to the top of the valence band is about 1 eV greater in $BaCl_2$.

Since we have located the regions of high density of states above the vacuum level, we can determine the energy difference between regions of high density of states of the valence and conduction bands. It is of interest to compare tnese values with the transition energies of maxima as seen in the characteristic energy-loss spectra.[14] In Table II, we list the values of the energy difference between the valence-band peak and the conduction-band structures above the vacuum level along with the energy values of maxima of $-\mathrm{Im}\epsilon^{-1}$ and ϵ_2 functions for BaF_2. The close agreement shown in the comparison of these values suggests that the maxima of the ϵ_2 functions at 14.4, 17.2, and 19.5 eV for BaF_2 could be due to transitions from the valence band to high density of final states. It should be mentioned, however, that the 17.2 and 19.5 eV transitions can also be associated with core excitons.[14]

The interesting point to note in the photoemission data of $BaCl_2$ is the spectral yield which displays a broad peak at photon energy of approximately 14 eV. Since the energy difference between the peak of the valence-band spectrum and the observed conduction-band structure is about 13.8 eV, the peak of the yield curve is probably due to electronic transitions from the valence band to the high density of states at 3.5 eV above the vacuum level of $BaCl_2$. The rise in yield above 18 eV can be associated with transitions from the Ba^{+2} core.

The comparison of energy difference between the regions of initial and final high densities of states with the transition energies shown in Table II provides a method of checking our interpretation of the photoelectron spectra. If the nondirect-transition model for photoemission is applied, the en-

TABLE II. Values of energy differences between initial and final high densities of states, and transition energies of maxima of $-\mathrm{Im}\epsilon^{-1}$ and ϵ_2 functions (Ref. 14) for BaF_2.

Energy difference (eV)	Transition energy (eV) of maximum of $-\mathrm{Im}\epsilon^{-1}$	Transition energy (eV) of maximum of ϵ_2
	11.0	10.2
	13.8	12.6
14.7	15.0	14.4
	16.3	16.0
17.4	17.8	17.2
19.7	20.2	19.5
	22.7	21.8

ergy distribution of unscattered photoelectrons should be proportional to the product of the initial and final densities of states.[15] Since the dielectric function ϵ_2 is proportional to the integral of the distribution over all final states, a maximum of ϵ_2 should appear as a result of photoexcitation from initial states of high density to final states of high density. The agreement of the energy difference with the transition energy of a distinct maximum in the absorption spectrum indicates that the nondirect-transition model is applicable to photoemission from BaF_2 and $BaCl_2$.

ACKNOWLEDGMENT

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