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Valence band photoelectron spectra of CrBr₃ insulators*

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Abstract. The valence band structure of CrBr₃ has been obtained by ultraviolet and x-ray photoelectron spectroscopy. The comparison of the x-ray photoemission valence band spectrum with published band calculations for the ground state within a one-electron formalism shows satisfactory agreement between observed and calculated structures. The contribution of the Cr 3d electrons relative to that of the Br 4p electrons in the photoemission energy distribution has been evaluated and compared with the ratio of photoionization cross sections for Kr 4p⁶ (calculated) and Cu 3d¹⁰ (experimental) at 40.8 eV. The degree of the p/d hybridization has then been estimated to be around 10–15%.

1. Introduction

The electronic properties of insulating transition metal halides (TMHs) (Kakizaki *et al* 1983, 1985, Fujimori and Minami 1984, Starnberg *et al* 1986, Hüfner 1985) and oxides (Eastman and Freouf 1975, Hüfner *et al* 1984, Wertheim *et al* 1973) have been the subject of x-ray photoemission spectroscopy (XPS), ultraviolet photoemission spectroscopy (UPS) and optical studies (Pollini *et al* 1984, Carricaburu *et al* 1986, Pollini *et al* 1989, Thomas *et al* 1990), because of their fundamental importance and the current interest in surface adsorption and oxidation studies.

These materials are more complicated than ordinary semiconductors or insulators (i.e. alkali halides) in that they contain both band-like and 'localized' d states. It is well known that the correlation of the d electrons is an essential concept for the actual band structure of these narrow d-band materials and that the p–d gap in both oxides and TMHs originates from the d-electron localization as explained by the Mott–Hubbard model (Mott 1949, Hubbard 1963) where the correlation energy U is larger than the band width W of d-like symmetry. Anyway, as pointed out by White and Mott (1971), in the Mott–Hubbard model, hybridization plays a central role. For Ni halides (Kakizaki *et al* 1983, 1985, Hüfner 1985) both the resonant photoemission results and the main d-band photoemission have been interpreted within the Mott–Hubbard model; more specifically it is shown that the main d emission comes from a d hole ($d^8\bar{L}$) screened by a ligand (L)–metal charge transfer and that the satellite is the d^7 final state produced from the initial state. Thus for NiO (and Ni halides) an energy band diagram in the sense of Mott can

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be constructed where the d_{8L} state is a *true* band, although the electrical conduction is still not possible owing to the large experimental value of $U \approx 13$ eV versus $W = 2-3$ eV (Hüfner 1985). Since no satellite emission was observed in our case, 'we were not able to draw such an energy band diagram from experiment. The only theoretical information about the ground-state electronic structure of CrBr_3 is due to the spin-restricted one-electron band calculation by Antoci and Mihich (1978).

One important point to know is the band width of the 3d electrons and the degree of p-d hybridization in the valence band. The photoemission technique is very useful for this type of information; in NiI_2 , for instance, angle-resolved photoemission data have shown that the main 3d structures observed in the spectra involve a $p(\text{I}) \rightarrow d(\text{Ni})$ charge transfer in the photoemission process, making hybridization an essential part of the electronic structure. Strong hybridization with ligand orbitals can delocalize the 3d states, thereby making them describable within a band structure (which is, however, different from the results of ground-state calculations) (Starnberg *et al* 1986).

Recently, we have measured the optical properties of CrBr_3 (Pollini *et al* 1989) in the visible to ultraviolet ranges; the results indicate that the charge-transfer transitions from the outermost p shell of the halogen to the 3d and 4s states of the metal ion give rise to the onset of strong allowed features (charge transfer and interband transitions). The optical absorption below the fundamental edge is well described by the ligand-field theory, according to which the optical transitions occur between crystal-field split levels of the $3d^n$ ion.

In the following we present the valence band photoemission measurements on CrBr_3 and evaluate the order of magnitude of the p-d hybridization factor.

2. Experimental details

Single crystals (about $10 \text{ mm} \times 5 \text{ mm}$) of CrBr_3 were used and cleaved *in situ* at pressures of 10^{-10} mm Hg. UPS measurements were performed in an ultra-high-vacuum system (10^{-10} mm Hg), in which there were a sample manipulator and a hemispherical energy analyser, by using a He discharge lamp (He II; 40.8 eV). The photoelectrons were analysed along the normal to the sample with an energy resolution of about 0.2 eV. XPS measurements were performed with another classical apparatus (ESCALAB MKII vacuum generator) provided with Al $K\alpha$ radiation (1486.6 eV). The instrumental resolution of the apparatus due to the excitation source and hemispherical electron energy analyser was about 1.2 eV.

Photoelectron spectroscopy is an efficient method of investigating the energy states of valence electrons as well as core electrons. Observed valence-state spectra reflect the density of states or, more rigorously, the partial density of states modified by the transition moment. It is worthwhile recalling that, in the XPS regime ($\hbar\omega > 200$ eV), one may assume a near constancy of the electric dipole matrix element between the initial and final state $P_{nm}(\mathbf{K})$; in this approximation describing the photoemission process an XPS spectrum represents the density of states in the valence band. This is the reason why XPS has been applied to so many investigations of the valence states of solids. In UPS spectroscopy, where exciting radiation has an energy of less than 40 eV, valence-state spectra are modified more by the conservation of the electron wavevector. However, the modification due to the energy or wavevector dependence of the transition moment is not very important in the narrow spectral regions to be observed.

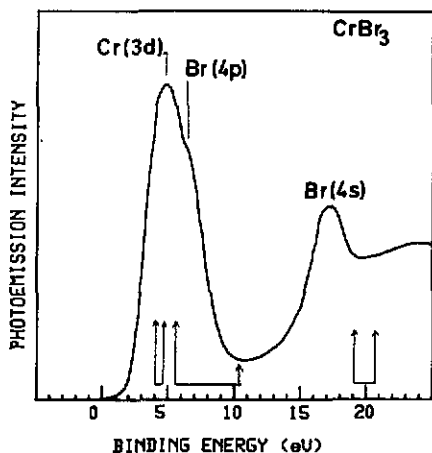


Figure 1. X-ray photoemission valence band spectrum of CrBr_3 at room temperature. The peak assignments are reported. The arrows mark, from left to right, the upper and lower limits of the Cr 3d, Br 4p and Br 4s bands, respectively, resulting from the Antoci-Mihich calculations. The band structure has been shifted rigidly to make the highest occupied d band coincident with the onset of the photoemission spectrum.

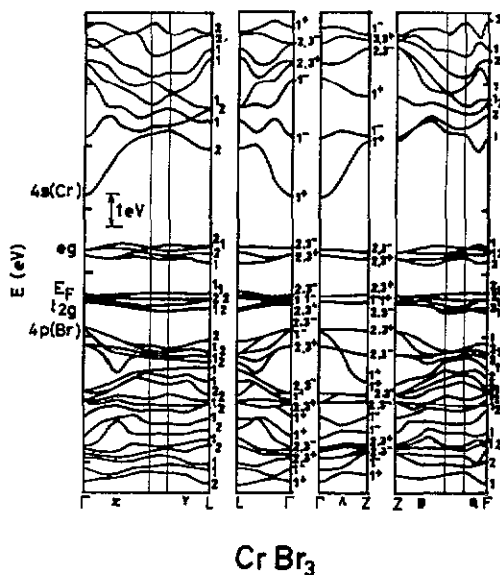


Figure 2. Self-consistent band structure of CrBr_3 according to the intersecting-sphere model. The forbidden gap is rigidly shifted in order to give agreement between the observed optical gap (Pollini *et al* 1989) and that calculated at the zone centre Γ (Antoci and Mihich 1973). The Fermi level E_F is also reported together with crystal-field notation (t_2g and e_g) for the partly filled split 3d band.

CrBr_3 crystals have a hexagonal unit cell with $a = 6.26 \text{ \AA}$ and $c = 18.20 \text{ \AA}$. The low-temperature ($T < 450 \text{ K}$) structure of CrBr_3 is a layer-type structure BI_3 (space group, C_{2h}^2). The three-dimensional lattice consists of a stack of sandwiches formed by a hexagonal network of Cr ions between two layers of Br ions, which form cubic close-packed layers on each side of the transition-metal layer. The adjacent sandwiches are bound by weak van der Waals forces, while the bonding is prevalently ionic within the sandwiches. The crystals are not hygroscopic and are very stable.

Recently, we have evaluated the fractional ionic character f_i^{DT} of CrBr_3 in the framework of the Phillips dielectric theory (Pollini *et al* 1989); f_i^{DT} has shown values varying from 0.79 to 0.86 according to the chosen average energy gap of the compound, i.e. $\langle E_g \rangle$ or E_g^{Penn} , respectively.

3. Experimental results and discussion

In figure 1, the xps spectrum of the valence band region of CrBr_3 is shown. The Br 4s peak and the Br 4p band with the Cr 3d band can easily be observed. Since the origin of the zero binding energy is difficult to determine because of sample charging effects, we have taken this origin at the top of the valence bands. The band at about 17 eV is assigned to the 4s level of Br, while the mixed 4p-3d valence band has a maximum at around

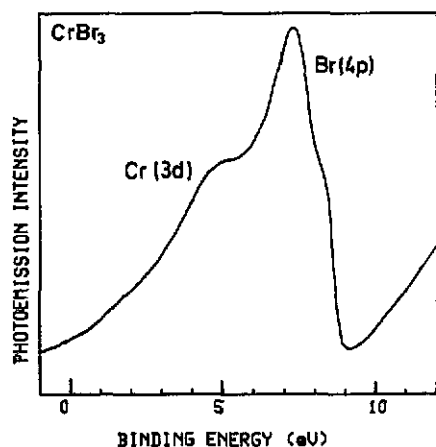


Figure 3. Valence state UPS spectrum of CrBr_3 excited with radiation from the He II line (40.8 eV). The positions of the 3d and 4p bands are indicated.

5 eV. If the valence band structure (Antoci and Mihich 1978) is directly utilized to predict the photoemission spectrum, we should expect at high energies a single structure associated with Cr 3d bands. Measuring the binding energies from the middle levels of the half-filled 3d band (t_{2g}^3) we should expect structures associated with the Br 4p bands ranging from -1 to -5.9 eV. We should then find a rather sharp structure associated with the narrow Br 4s bands occurring between -16.5 and -15 eV (figure 2). Notwithstanding the fact that many-body effects influencing the photoemission spectra are neglected in the band calculation (self-restricted calculation for the ground state within a one-electron formalism), it is, however, surprising to note that the theoretical results are able to predict the experimental spectrum rather well, if we except a rather strong contribution of the d states to the valence band and a somewhat large gap between the d band and the lower-lying 4s band.

Figure 3 shows the valence state UPS spectrum of CrBr_3 , excited by radiation from the He II line (40.8 eV). The binding energy of the d band (about 5 eV) like that of the p band (about 7.2 eV) does not change with photon energy, whereas we observe a strong decrease in the 3d-state emission relative to 4p-band emission. The variation with the excitation energy of the bands located around 5 and 7 eV suggests that the band at 5 eV partially originates from the d levels of the Cr ion and the band around 7 eV from the 4p band of the halogen ion. In the UPS valence band spectrum, the 3d (Cr) band shows a tail at low binding energies caused by charging effects.

The peak synthesis of the xps valence band (figure 4) which shows the relative position of the p-d bands gives evidence that the d and p components have the same width, i.e. 2.40 eV. The binding energies for the 3d and 4p bands are located at around 5 eV and 7.8 eV, respectively. This also indicates that the d states of the valence band of CrBr_3 are delocalized and that the electronic structure of the valence band does not arise from localized d states and delocalized p states, but is more probably due to a p-d band mixture.

This is an important point since we could in this case exclude for CrBr_3 the old description of the partial d-state density in terms of the ligand-field theory, i.e. in terms of the $3d^{n-1}$ final-state ionization potentials (Eastman and Freouf 1975). In this picture, for CrBr_3 (as for Cr_2O_3), photoionization would result in a d^2 configuration with a 3T_1 state (Eastman and Freouf 1975, Wertheim *et al* 1973).

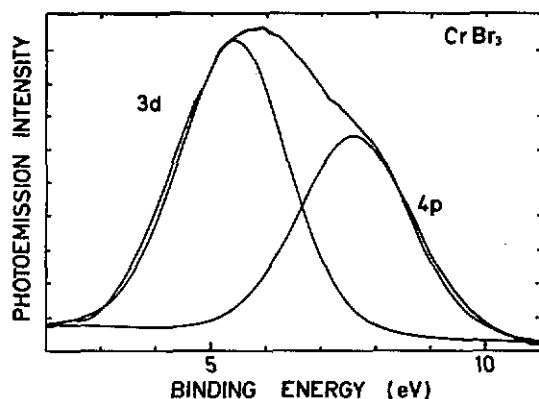


Figure 4. Valence state XPS spectrum of CrBr_3 ; the peak synthesis shows the components of the 3d–4d band structure, due to the 3d state of chromium and 4p band of bromine ($\Delta p-d = 2.24$ eV).

This state is seen in the XPS spectra of Cr_2O_3 and shows itself in the valence band region of the O 2p band towards lower binding energies. The separation between O 2p and Cr 3d peaks is about 4 eV and the width of the 3d band is around 2 eV. CrBr_3 is like Cr_2O_3 ; the average separation between p and d peaks is 2.24 eV with a 3d band width of about 2.40 eV. We see that in this 'localized' picture of the d levels the state 3T_1 of the d^2 configuration would be observed in the valence band region of the Br 4p band and would be broadened by the effect of the crystal field and exchange energy. It seems rather difficult to explain the broadening of the valence band on this basis; instead, because of the decrease in the p–d gap in Cr compounds, there may be a stronger hybridization of the p and d states.

Now, we estimate the degree of hybridization in CrBr_3 by following the same method as used for silver iodide (Eastman 1974) and transition-metal chlorides (Kakizaki and Ishii 1986). From the calculated photoionization cross sections σ_{ns} , σ_{np} , σ_{nd} , etc, for subshell electrons in the noble gases (Kennedy and Manson 1972) we can determine, for instance, the relative contributions of 4p and 3d electrons to the photoemission energy distributions. Furthermore, we can find the trends of such cross sections σ which are seen in photoemission and optical experiments from the photon dependence of σ of s, p, d and f electrons.

In the case of CrBr_3 , after subtracting the low-energy part of the UPS spectrum (from 0 to 3 eV), eliminated because of the strong charging effects, we have taken the ratio of the integrated intensity of the Br 4p band to that of the Cr 3d states.

In order to compare our results with similar cases (Eastman 1974) and to calculate the effective atomic cross sections (Kennedy and Manson 1972) we have calculated the p-to-d intensity ratio for the $4p^6$ and $3d^{10}$ configurations, which means multiplying the ratio of the experimental areas by 0.1 and obtaining a value of about 0.34. Now, by using the calculated cross sections of Kr for the intensity ratio

$$\sigma_{4p^6}(\text{Kr})/\sigma_{3d^{10}}(\text{Kr})$$

we get a value of 0.95. Better agreement with the experiment can be obtained if we use the experimental photoionization cross section $\sigma_{3d^{10}}(\text{Cu})$ (Kuntz 1976) instead of

Table 1. Experimental and calculated photoionizations cross sections for outer-shell electrons in the noble gases. (After Kennedy and Manson using Hartree-Fock wavefunctions.)

	Experimental p-to-d ratio	Calculated (Kennedy-Manson) ratio	Kennedy-Manson correction
CrBr ₃	0.34	$\sigma_{4p^6}(\text{Kr})/\sigma_{3d^{10}}(\text{Kr}) = 0.95$	$\sigma_{4p^6}(\text{Kr})/\sigma_{3d^{10}}(\text{Cu}) = 0.27$
Cr ₂ O ₃	0.56	$\sigma_{2p^6}(\text{O})/\sigma_{3d^{10}}(\text{Kr}) = 2.4$	$\sigma_{2p^6}(\text{Ne})/\sigma_{3d^{10}}(\text{Cu}) = 0.70$

$\sigma_{3d^{10}}(\text{Kr})$, as done for NiO (Eastman 1974) and transition-metal chlorides (Kakizaki and Ishii 1986). In this case the ratio

$$\sigma_{4p^6}(\text{Kr})/\sigma_{3d^{10}}(\text{Cu}) \approx 0.27.$$

We now propose to explain the small discrepancy between the experimental and the corrected cross sections by considering the presence of p-d hybridization. In this case, σ_{4p^6} can be replaced by $(1 - 1.67f)\sigma_{4p^6} + f\sigma_{3d^{10}}$ and $\sigma_{3d^{10}}$ by $(1 - f)\sigma_{3d^{10}} + 1.67f\sigma_{4p^6}$ where f is the percentage of d electrons mixed with the upper p band (hybridization factor), and 1.67 is the ratio 10/6 of the electron occupancy in the 3d and 4p states; f is then found to be approximately equal to 0.1.

The value of the hybridization factor (varying from 0.10 to 0.16) is slightly affected by the way that we subtract the low-energy part of the observed spectrum and is reduced when we eliminate the spectral range where charging effects are present.

For Cr₂O₃ at $h\nu = 40.8$ eV (Eastman 1974) the experimental value of the p-to-d integrated intensity ratio is equal to 0.56 (with six p electrons and ten d electrons). The calculations of Manson and Kennedy give for $\sigma_{2p^6}(\text{Ne})/\sigma_{3d^{10}}(\text{Kr})$ a value of 2.4, which is much too high, or, if the experimental cross section $3d^{10}$ of Cu is considered, one gets $\sigma_{2p^6}(\text{Ne})/\sigma_{3d^{10}}(\text{Cu}) \approx 0.70$. In this case, the agreement with experiment is better (table 1).

4. Conclusions

The photoemission spectra of CrBr₃ insulators show that both 3d electrons of Cr and 4p electrons of Br contribute to the valence band structure, which is composed of two rather broad p and d bands and whose binding energy is determined quite accurately.

The description of the valence band photoelectron spectra in terms of multiplet and crystal-field splitting analogous to the case of Cr₂O₃ may be attempted, although it does not explain the origin of the large d-state broadening well. This band broadening can, however, be explained more naturally by considering the decrease in the p-d gap in Cr halides and the hybridization occurring in these compounds (TMHs). In NiI₂, for instance, the hybridization is found to be so strong as to cause a delocalization of the d electrons, observed by angular resolved photoemission.

To compare the calculation of Manson and Kennedy with the differential UPS cross sections, we have used the $3d^{10}$ cross sections of Cu, which show good agreement with experiment. In this way the degree of hybridization of the p-d valence band can be evaluated. In CrBr₃, we have found that f has the same order of magnitude as in TMH (about 10%).

The degrees of the 3p–3d hybridization in transition-metal chlorides have values smaller than 0.3 (Kakizaki and Ishii 1986).

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