

## Electron-energy-loss and x-ray photoelectron spectra of MgF<sub>2</sub>

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The electron-energy-loss spectrum of MgF<sub>2</sub> is compared with the x-ray photoelectron spectra; the presence and the role of the three types of electronic transitions present in the large-band-gap crystals—plasmons, excitons, and interband transitions—are identified. The data are compared with previous experimental literature and with the calculated band structure.

Magnesium fluoride is an anisotropic, large-band-gap crystal, having the rutile structure [space group  $D_{4h}^{14}$  ( $P4_2/mnm$ )] with two fluorine ions associated with each magnesium ion. When forming the solid, the electrons, as in all the strongly ionic crystals, are transferred from the  $s$  state of the metal atom to the  $p$  state of the fluorine.

The valence band is mainly composed of the outermost  $p$  electrons of the fluorine and the lowest conduction band is mainly composed of the excited  $s$  state of the magnesium. In these large-band-gap crystals, three types of electronic transitions are present in the spectra: plasmons, excitons, and interband transitions. The purpose of this work is to identify, through x-ray photoelectron spectra (XPS) and electron-energy-loss (EELS) measurements, the presence and the role of these three types of transitions comparing our spectra both with previous experimental literature and with the energy-band structure calculated by Jouanin *et al.*<sup>1</sup> and Chaney.<sup>2</sup>

### EXPERIMENTAL DETAILS

The experiments were carried out in a very-high-vacuum (VHV) apparatus (VG ESCA-3 MK2) using, for x-ray photoelectron spectra (XPS) and Auger measurements, an Al  $K\alpha_{1,2}$  x-ray source ( $h\nu=1486.6$  eV) and for electron-energy-loss (EELS) measurements a chamber equipped with an electron-gun source. The samples were prepared by evaporating *in situ* a MgF<sub>2</sub> or Mg metal layer on a Cu plate in a ( $1 \times 10^{-8}$ )-Torr vacuum. During the measurements, the vacuum was about  $1 \times 10^{-9}$  Torr and the temperature that of liquid nitrogen. Changes in the chemical composition of the surface during measurements indicate that the electron beam has induced some sample damage.<sup>3,4</sup>

Such damage can occur almost instantaneously upon exposure to the electron beam or irradiation by x rays, and was present in our samples. Consequently, the incident electron beam was kept below 1 kV and the incident-beam position on the sample changed after each measurement. Under our experimental conditions, an excess of Mg metal was observed on the surface of MgF<sub>2</sub>.

Regarding a possible vacuum desorption at low temperature, account should be taken of the possibility of for-

mation and accumulation of bulk vacancies.<sup>5</sup>

In Tables I and II, we report the peak positions in EELS below the elastic peak ( $\Delta\epsilon$ ) and the satellite positions from the main peak ( $\Delta\epsilon$ ) in XPS and Auger spectra, placing the energy zero at the center of the main peaks. In our figures, the EELS spectra are recorded in second derivative because it gave better resolution and greater accuracy in the energy position. All the errors limits are valued at  $\pm 0.5$  eV.

### DISCUSSION

Figures 1 and 2 report the EELS spectra of MgF<sub>2</sub> at the two incident electron-beam energies  $E_p=200$  and 1000 eV to differentiate the surface from the bulk phenomena, utilizing the relationship between the intensity of the loss peaks and the incident-electron penetration. The spectra were recorded using a standard ac modulation technique with a peak-to-peak modulation of 1 eV and with the

TABLE I. MgF<sub>2</sub> EELS peak position ( $\Delta\epsilon$  in eV) below the elastic peak measured at the incident-electron-beam energies of  $E_p=200$  and 1000 eV. The error limit is valued as  $\pm 0.5$  eV.

$E_p=200$ (eV) <sup>a</sup>	$E_p=1000$ (eV) <sup>a</sup>	$E_p=1000$ (eV) <sup>b</sup>
4.2	4.2	
	5.0	
6.4		6.4
8.2	8.0	8.5
11.4		11.2
	12.5	12.4
	13.6	13.5
14.5		
17.8	17.8	17.5
22.4	22.0	22.0
23.5	24.0	24.0
	31.5	
	39.0	
	42.0	
	47.0	
	49.5	
	55.0	

<sup>a</sup>Liquid-nitrogen temperature.

<sup>b</sup>Room temperature.

TABLE II. Experimental  $\text{MgF}_2$  ESCA and Auger peak positions ( $\Delta\epsilon$  in eV) of the satellites relative to the main peaks. The center of the main peaks is set at 0.0 eV. The error limit is valued as  $\pm 0.5$  eV.

Mg 2s	ESCA		Auger
	F 1s		
5.0	5.0		4.5
11.5	11.5		
	14.5		15.0
16.0			
21.5	21.0		21.0
24.5	24.5		25.0
31.0	31.0		31.0
34.0	35.0		35.0
	39.0		
	49.0		
	55.5		

sample at liquid-nitrogen temperature.

In Fig. 1(b) we have overlapped to the liquid-nitrogen-temperature spectrum, the spectrum at room temperature (dotted line) to emphasize the differences present at the different temperatures. Because excess Mg metal is present on the surface of the sample due to radiation damage, Figs. 2(a) and 2(b) also illustrate the spectrum of Mg metal measured at the same incident energies (dotted lines). As demonstrated by Jenkins *et al.*,<sup>6</sup> slight oxidation on the Mg-metal surface does not change the positions of the Mg EELS peaks. At  $E_p = 200$  eV, where the surface transitions dominate, Mg metal on the  $\text{MgF}_2$

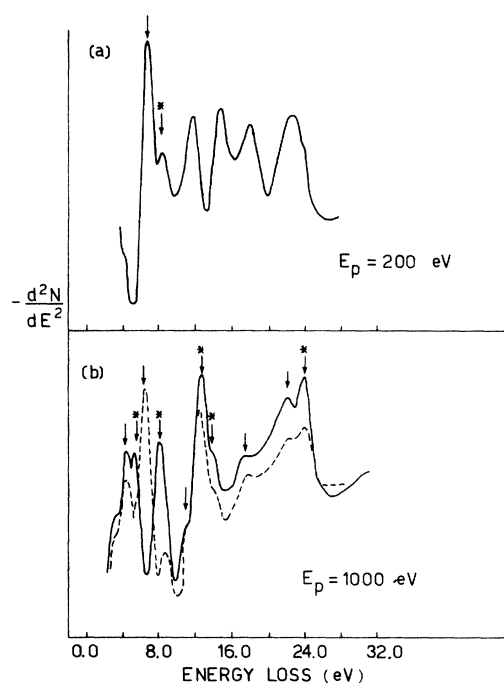


FIG. 1. EELS spectra of  $\text{MgF}_2$ : (a)  $E_p = 200$  eV at liquid-nitrogen temperature; (b)  $E_p = 1000$  eV at liquid nitrogen temperature (—) and room temperature (---).

surface prevails. Indeed, as shown in Fig. 2(a), the spectrum recorded on  $\text{MgF}_2$  and on the Mg metal are very similar. This similarity disappears at  $E_p = 1000$  eV [Fig. 2(b)].

Inspection of Figs. 1 and 2 leads to the following conclusions: (1) The strong peak at 6.4 eV, present at  $E_p = 200$  eV (and present also at  $E_p = 1000$  eV, but only at room temperature), is clearly the same peak as observed in Mg metal. This peak disappears completely when the sample is measured at liquid-nitrogen temperature. This occurrence demonstrated that the induced electron-beam damage is very rapid at the surface, but becomes much slower in the depth, when the sample is kept at liquid-nitrogen temperature. The other peaks present in both  $\text{MgF}_2$  and Mg-metal spectra are marked, in the two figures, by a simple arrow.

(2) Because electron-beam damage is less important under these conditions, we will concentrate our discussion specifically on the  $\text{MgF}_2$  EELS spectrum recorded at  $E_p = 1000$  eV and at liquid-nitrogen temperature. In Fig. 2, the peaks unambiguously associated with the  $\text{MgF}_2$  losses are marked by an arrow with an asterisk.

As shown in Figs. 1 and 2, the overlap of the Mg-metal transitions, on the  $\text{MgF}_2$  spectra, is present especially at

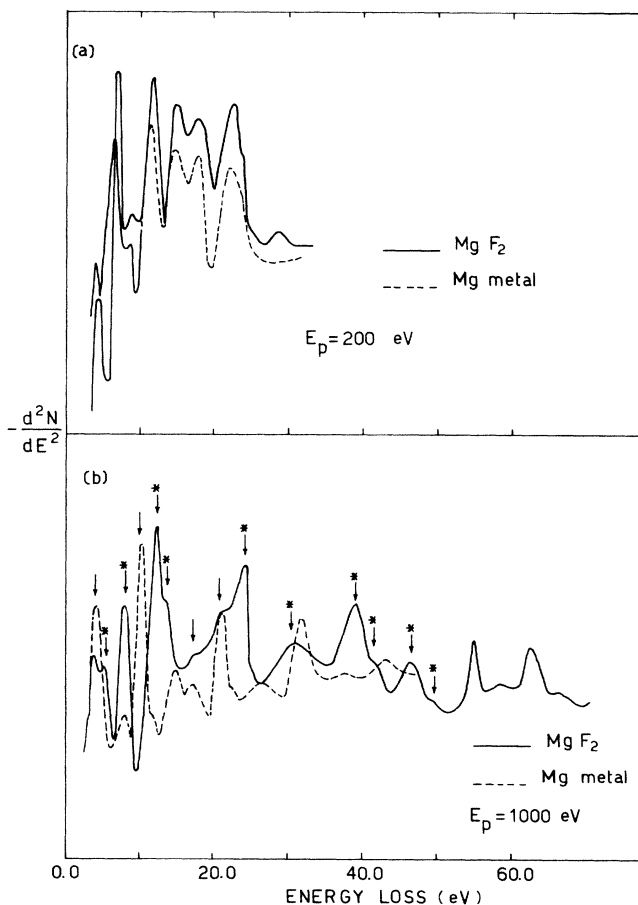


FIG. 2. Overlapped EELS spectra of  $\text{MgF}_2$  (—) and Mg metal (---) at liquid-nitrogen temperature and at (a)  $E_p = 200$  eV and (b)  $E_p = 1000$  eV.

energy losses  $< 25$  eV; consequently, the interpretation of the  $\text{MgF}_2$  peaks in this range is a very delicate problem.

It is known that at about 11.7 eV, an exciton that we observe in XPS is present.<sup>7-10</sup> In EELS, this energy zone is obscured by the strong plasmon peak of Mg metal (Fig. 2). The peak at 5.0 eV, present in our spectra only at  $E_p = 1000$  eV and nitrogen temperature and which disappears at room temperature, may be associated (as in XPS) with the presence of  $F$  centers<sup>11</sup> or attributed to self-trapped excitons.<sup>12,13</sup> Next to this position, we observe a peak at about 4.2 eV, also present in Mg-metal spectrum. Likewise, we observe a peak at 8.0 eV (not reported in the literature) which appears very strong at liquid-nitrogen temperature and weak at room temperature with the character of an exciton. At the same energy, we observe a much weaker peak in Mg metal, so we must conclude that there exists an overlap between the two  $\text{MgF}_2$  and Mg-metal peaks.

Further difficulties are involved in the interpretation of the doublet at 12.5 and 13.5 eV. This doublet is present only in the bulk spectrum ( $E_p = 1000$  eV) and is not temperature dependent [Fig. 1(b)]; we therefore exclude the possibility that it is excitonic in nature. In the literature, this range of energy is highly populated by transitions and assignments vary.<sup>2,7-10</sup>

Making use of polarized light in their reflectance measurements, Thomas *et al.*<sup>7</sup> were able to split the two components (parallel and perpendicular) of the complex dielectric constant. They find three parallel component peaks at 11.6, 12.8, and 18.6 eV and three perpendicular peaks at 12.1, 13.0, and 15.0 eV.

Chaney<sup>2</sup> associates Thomas's results with calculated band structure, assigning the two parallel peaks (11.6 and 12.8 eV) to the single calculated band transition  $\Gamma'_2 \rightarrow \Gamma_1$  and the two perpendicular peaks (12.1 and 13.0 eV) to the  $\Gamma'_3 \rightarrow \Gamma_1$  transition. The theoretical band gap, as calculated by Chaney, is indeed larger (13.8 eV) than both the experimental<sup>7</sup> value (about 12.4 eV) and the value of 12.8 eV, corrected for the polarization effects, as calculated by Jouanin *et al.*<sup>1</sup>

Consistent with these conclusions, we assign the two transitions present in the EELS spectrum at 12.5 and 13.5 eV as interband transitions. The strong peak at 24.0 eV corresponds to the collective oscillation of electrons (volume plasmon): the double plasmon is also visible at 47.0 eV. We will discuss the other peaks present in the  $\text{MgF}_2$  loss spectrum (31.5, 39.0, 42.0, and 49.5 eV) together with the XPS spectra emphasizing the peak at 31.5 eV that in XPS exhibits a strong difference in its relative intensity when measured as a satellite of Mg 2s or of F 1s.

### XPS AND AUGER SPECTRA

Given the importance of the interband transitions in assigning the satellites appearing in XPS and Auger spectra, it is important to look at the  $\text{MgF}_2$  crystal symmetry and, therefore, at the crystal potential. The polarization effects induced by the extra electron are significant for optical transitions in insulators: when the electron jumps from the valence to the conduction band, the charge displace-

ment polarizes the ions. This gap anisotropy is clearly shown in the calculations of Jouanin *et al.*,<sup>1</sup> who in introducing some suitable approximations in their model, obtain for the band gap the value of 12.8 eV, in good agreement with the experimental results of Thomas *et al.*<sup>7</sup>

With a different theoretical approach (self-consistent model), the values of the band gap obtained by Chaney<sup>2</sup> (13.6–13.8 eV) are not as good as those of Jouanin *et al.* Likewise, the width of the valence band resulting from the theoretical calculations (about 5.8 eV for Jouanin and 2.1 eV for Chaney) are both far from our experimental full width at half maximum (FWHM) of  $4.0 \pm 0.2$  eV.

Since there exists the possibility that, in the experimental measurements, the band gap might be masked by the exciton peak, it seemed useful to compare our first satellite in XPS with the EELS spectrum.

We begin our discussion by fixing the transition observed at 11.5 eV as the well-established exciton observed in EELS and the peak observed at 5.0 eV (5.4 eV in EELS) as an  $F$  center, which appears when the sample is electron-beam or x-ray-irradiated<sup>11-14</sup> at low temperature. In both our XPS spectra [Fig. 3(b)] we observe some other peaks also found by Williams *et al.*,<sup>9</sup> Stephan *et al.*,<sup>10</sup> and Gout *et al.*<sup>15</sup> in their reflectance measurements.

In the F 1s region a shoulder is present at 14.5 eV and in the Mg 2s region, a peak at 16.0 eV. These peaks (that we ascribe to interband transitions) are assigned by Jouanin *et al.*<sup>1</sup> to the transitions from  $\Gamma'_3$  or  $\Gamma_3$  valence levels to the  $\Gamma_1$  conduction band. An alternative interpretation is proposed by Chaney<sup>2</sup> which assigns these peaks to the  $X_1 \rightarrow X_1$  and  $X_2 \rightarrow X_1$  transitions, respectively.

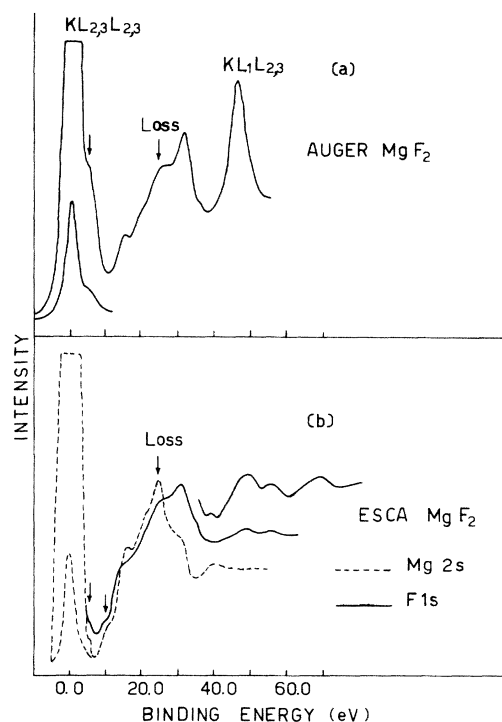


FIG. 3. (a) Auger spectrum; (b) XPS spectra of the Mg 2s (---) and F 1s (—) regions in  $\text{MgF}_2$ .

The peak at 21.0–21.5 eV can be ascribed to the  $\Gamma_5 \rightarrow \Gamma_4$  transition. A strong volume plasmon peak, which was previously discussed in EELS, is present at 24.5 eV.

We emphasize the zone around 31.0 eV because here we observe a strong difference in the relative intensity of this satellite when it is observed in the XPS F 1s or Mg 2s regions [Fig. 3(b)]. We noticed a similar difference in our XPS spectra of the alkali fluorides<sup>16</sup> and in the alkali-earth difluorides,<sup>17</sup> and ascribed it to the copresence of two phenomena at the same energy: an interband transition and an excitonic transition. In this case, the transition concerned is a  $F^- 2s$  excitonic transition present in our EELS spectrum [Fig. 2(b)] at 31.5 eV.

Jouanin *et al.* assign the transition at 39.0 eV to the first transition from the F 2s level to the conduction band [ $\Gamma_5(F^- 2s) \rightarrow \Gamma_1$ ] and that at 55.5 eV to the first interband transition from the deep  $Mg^{2+} 2p$  level to the  $\Gamma_1$  conduction band. Both of these transitions are also present in EELS. In our spectra, we observe other peaks (17.5 and 22.0 eV in EELS; 35.0 eV in XPS; 49.0 eV in XPS and

EELS) that have no counterpart in the theoretical assignment but, that we think may be ascribed to interband transitions. In Fig. 3(a), the Auger spectrum, measured in the XPS system, is also reported to show the evident resemblance between the satellites present in the  $KL_{2,3}L_{2,3}$  zone and those found in the F 1s and Mg 2s x-ray photoemission spectra when the relative main peaks are aligned as in Fig. 3.

In conclusion, the presented comparison of the energy-loss spectra and the x-ray photoelectron spectra, in large-band-gap crystals, allows us to characterize the presence of three types of transitions: plasmons, excitons, and interband.

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