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Satellites in x-ray photoelectron spectroscopy of insulators. I. Multielectron excitations in CaF_2,SrF_2, and BaF_2

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The satellites appearing in the core region of the x-ray photoelectron spectra of alkaline-earth difluorides have been investigated in order to obtain information about the density-of-states distribution through interband transitions. The photoemission results are compared with recent theoretical band-structure models. There are differences in the relative intensities of the satellites appearing in different core regions.

I. INTRODUCTION

Little theoretical work has been done on the band structure of CaF_2, SrF_2, and BaF_2 crystals. Previous interpretations of optical measurements are very uncertain because the theorists have either started with the erroneous assumption that the valence bands of alkaline-earth and alkali-halide crystals were identical or have attempted to attribute all the features of the spectra to transitions in free ions. These assumptions make the ordering of the energy levels doubtful: the occurrence of the minimum in the conduction band, e.g., has been assumed to lie both at the X point[1,2] and/or at the Γ point[3] in the Brillouin zone.

The latest calculated electronic band structures[4,5] definitely agree in assigning the lowest conduction band at the Γ point and the top of the valence band at the X point (different than that found for the rocksalt structure). We return to this point in the discussion of the results.

Given that these recent band-structure calculations are now available, it seems useful to reexamine the x-ray photoelectron spectra (XPS) of these alkaline-earth difluorides, especially regarding the satellites appearing in both the metals and fluorine core zones.

II. EXPERIMENTAL

X-ray photoelectron spectra of alkaline-earth difluorides were measured on an Esca-3 MKII photoelectron spectrometer (Vacuum Generators Ltd.) using an Al $K\alpha_{1,2}$ x-ray source ($h\nu = 1486.6$ eV) and a base pressure of $\sim 1.0 \times 10^{-9}$ Torr. Optical grade powders were used in the measurements. For convenience, in the figures the zero has been placed at the center of the main peak. The distances of the satellites from the main peaks ($\Delta\epsilon$) are reported in Tables I—III with the proposed assignments.

III. DISCUSSION

The common important feature of the electronic structure in the ionic crystals is that, on forming solids, the electrons are transferred from the s state of the metal to the p states of the halide atom. These fully occupied anion p states dominate the valence band (VB), while the cation-excited s and d states form the basis for the first and second set of conduction bands (CB).

In Fig. 1 we report the XPS valence bands of the three difluorides. The measured full widths at half maximum are, for BaF_2, 2.5 eV, for SrF_2, 2.8 eV, and for CaF_2, 3.2 eV; the error is evaluated to be ± 0.3 eV. The valence band of CaF_2 and SrF_2 shows a weak structure identified in Fig. 1 by the arrows P_1,P_2,P_3. If we estimate the distance $P_1 \rightarrow P_3$ as the maximum splitting of the valence band ($X_1 - X_2'$), we find a value of ~ 2.7 eV in the case of CaF_2. This value is not overly far from the value of 2.0 eV, recently calculated by Heaton and Lin,[5] but higher than 1.5 eV calculated by Albert *et al.*[4] In general, the self-consistent-field calculation using the LCAO method appears to be in better agreement with the experimental results. The older calculations of Ganin *et al.*[6] and

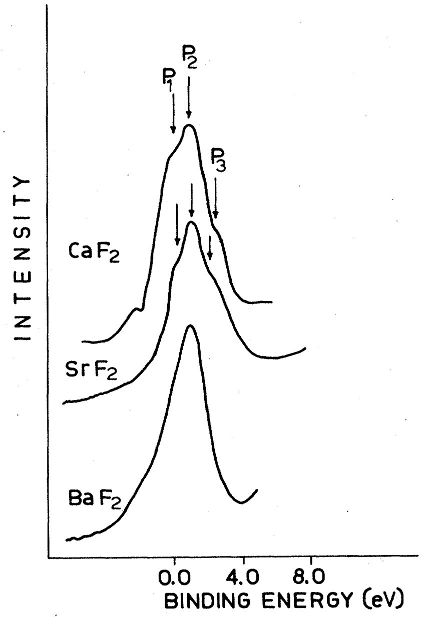

FIG. 1. XPS spectra of the valence region in CaF_2, SrF_2, and BaF_2.

Starostin and Ganin[7] give considerably higher values for the total width of the F_{2p} valence zone: for BaF_2, 5.8 eV; for SrF_2, 7.0 eV; and for CaF_2, 9.97 eV.

A. CaF_2

CaF_2 is the alkaline-earth fluoride which has been studied the most, both theoretically and experimentally. From the Heaton and Lin[5] model, it is possible to deduce the following:

(i) The presence of two F atoms in a unit cell give rise to two distinct VB levels at the Γ point (Γ'_{25} and Γ_{15}). At the Γ point, around each nonequivalent F^- site, the p orbitals can be mixed to form two types of combination: (a) a bonding symmetric combination (Γ'_{25}); (b) an antisymmetric antibonding combination (Γ_{15}). Γ_{15} lies higher than Γ'_{25}, while at the point X, a phase reversal occurs: the X_1 state lies below Γ'_{25} and X'_2 above Γ_{15}. The VB edges are at X. The participation of Ca^{2+} in VB states is small.

(ii) The lowest CB state is at Γ. The Ca contribution to Γ_1 is mainly of s type whereas the Γ_{12} and Γ'_{25} states result directly from the Ca $3d$ states with a possible mixing (in Γ'_{25}) with F_p orbitals. These authors place Γ_{12} below Γ'_{25}. The Γ_{15} state in CB is composed of p-type orbitals of both Ca and F. In these calculations, the direct band gap at Γ ($\Gamma^v_{15} \rightarrow \Gamma^c_1$) is ~ 10 eV, but, because the top of the valence band is in X, the minimal gap (9.8 eV) is an "indirect" transition ($X'^{v}_2 \rightarrow \Gamma^c_1$).

Experimentally the value of the band gap, reported by Rubloff[3] from reflectance spectra is 12.1 eV. As mentioned above, there is disagreement between theorists[4,5] and experimentalists[3,8] in interpreting the observed transitions, because, given the sparsity of theoretical work, the experimentalists assumed an analogy between alkaline-earth fluorides and KCl and CaO. However, CaF_2 differs from KCl and CaO in that the cation coordination in these latest crystals is of cubic geometry (eight nearest neighbors). This leads to a reversal of the $\Gamma'_{25} \rightarrow \Gamma_{12}$ ordering.

Our XPS spectra are reported in Figs. 2 and 3(a). Figure 2 reports the core zones where the satellites are observed more clearly. In Fig. 3(a) we have overlapped these zones to have an immediate insight of the coincidence in the energy positions of the peaks and of the differences in their relative intensities. Both these aspects are important in the following discussion.

We compare our results with the experimental works of Rubloff,[3] Ganin *et al.*,[6] and Frandon *et al.*[8] The reflectance spectra reported by Rubloff, who used synchrotron radiation, is richer in detail than are our XPS spectra; i.e., in the region $\Delta\epsilon = 10-17$ eV, Rubloff observes eight peaks against our two satellites. The satellites observed in XPS can originate from: (a) collective electron oscillations (plasmons) or (b) interband transitions.

Our principal interest resides in the interband transitions, so we will first identify the plasma oscillations to put out this problem from our discussion. Useful references for this identification are the works of Ganin *et al.*[6] and of Frandon *et al.*[8] who assign the transition at 17.0 eV as a valence-electron plasmon and that at ~ 36.0 eV as

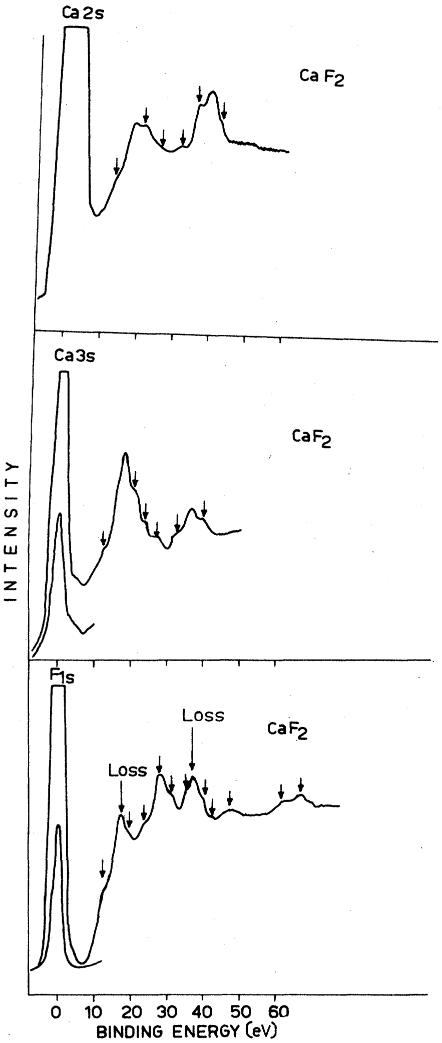

FIG. 2. XPS spectra of the F_{1s}, Ca_{3s}, and Ca_{2s} regions in CaF_2.

TABLE I. Experimental values of the separation energy $\Delta\epsilon$ (eV) of the satellites relative to the main peaks F_{1s}, Ca_{3s}, and Ca_{2s} in CaF_2. (The center of the main peaks is set at 0.0 eV.) The error limit is evaluated as ±0.5 eV.

	$\Delta\epsilon$		
F_{1s}	Ca_{3s}	Ca_{2s}	Assignment
13.0	12.5	12.5	$\Gamma'^{v}_{25} \rightarrow \Gamma^c_{12}$ or $\Gamma^v_{15} \rightarrow \Gamma'^{c}_{25}$
17.0	17.0	17.0	Loss
19.5	20.0	20.0	$X'^{v}_5 \rightarrow X^c_1$
24.0	24.0	24.0	$\Gamma'^{v}_{25} \rightarrow \Gamma^c_{15}$
27.5	27.0		$\Gamma^v_{15}(p+) \rightarrow \Gamma^c_1$
31.0	32.5	30.5	$X^v_5(p+) \rightarrow X^c_3(d+)$
35.0		35.0	$\Gamma^v_{15}(p+) \rightarrow \Gamma^c_{25}(d+)$
37.0	37.0	37.5	Loss
39.5	39.5	40.5	
47.5			
62.0			
66.5			

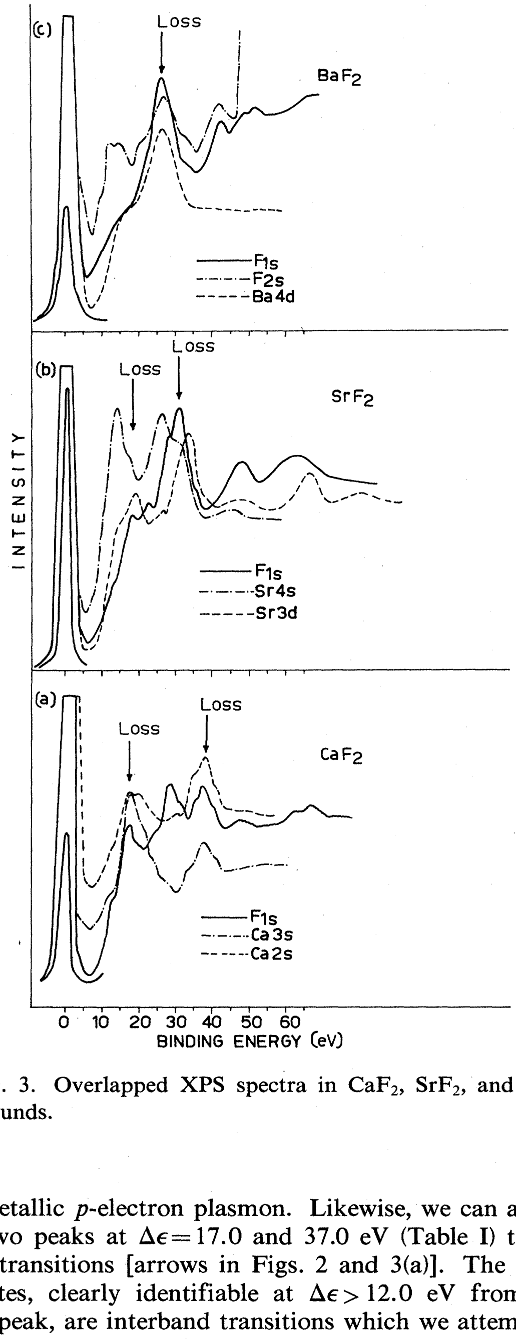

FIG. 3. Overlapped XPS spectra in CaF_2, SrF_2, and BaF_2 compounds.

the metallic p-electron plasmon. Likewise, we can assign our two peaks at $\Delta\epsilon=17.0$ and 37.0 eV (Table I) to the same transitions [arrows in Figs. 2 and 3(a)]. The other satellites, clearly identifiable at $\Delta\epsilon>12.0$ eV from the main peak, are interband transitions which we attempt to assign with the help of the recent theoretical calculations. The Heaton and Lin[5] band structure helps us only for transitions in the range 11—22 eV. For transitions of higher energy we must utilize some indications proposed in the works of Albert *et al.*,[4] Ganin *et al.*,[6] and Amaral *et al.*[9]

The first transition that we observe is at $\Delta\epsilon=12.5$—13.0 eV and, from Heaton and Lin,[5] it can be assigned to a $\Gamma_{25}'^{v}\rightarrow\Gamma_{12}^{c}$ (or $\Gamma_{15}^{v}\rightarrow\Gamma_{25}'^{c}$). The $\Delta\epsilon=17.0$ eV peak is in the valence electron plasmon position; at $\Delta\epsilon=20.0$ eV we find a peak attributable to the $X_5'^{v}\rightarrow X_1^{c}$ transition.

Transitions higher than these are from the next valence band formed by Ca_{3p} levels. The peak at $\Delta\epsilon=24.0$ eV is assigned by Albert *et al.*[4] to the $\Gamma_{25}'^{v}\rightarrow\Gamma_{15}$ transition and the peak that we find at $\Delta\epsilon=27.0$ eV is assigned by these authors to a $\Gamma_{15}^{v}\rightarrow\Gamma_{1}^{c}$ exciton.

There is disagreement between Albert *et al.*[4] and Ganin *et al.*[6] regarding the assignment of the doublet in the range 31—35 eV. This doublet, present in the calcium compounds, is characteristic of the Ca^{2+} ion. Albert assigns the lower peak (31—32 eV in our spectra) to $X_5^{v}\rightarrow X_3^{c}$ and the higher peak (35.0 eV) to $\Gamma_{15}^{v}\rightarrow\Gamma_{25}^{c}$. Conversely, Ganin assigns the 32.0 eV peak to $\Gamma_{15}^{v}\rightarrow\Gamma_{1}^{c}$ and the 35.0-eV peak to the $L_2'^{v}\rightarrow L_1^{c}$ transition.

The phototransitions from the F_{2s} valence band appear as weak structures in the energy range 35.0—41.0 eV (Ganin), so the transition that we observe at $\Delta\epsilon=39.5$ eV is from the F_{2s} band. In the spectrum of F_{1s} we observe also three very weak satellites at $\Delta\epsilon=47.6$, 62.0, and 66.5 eV that are assignable to transitions to higher levels in the conduction band.

The second point to emphasize is the remarkable differences in the relative intensities of the satellites belonging to different regions of the spectrum. Because this difference is a peculiarity of all the difluorides examined in this paper, we will return to this subject later.

B. SrF_2 and BaF_2

We will discuss our experimental results in the light of the theoretical works of Ganin and co-workers,[6,7] Amaral *et al.*,[9] and Timofeenko and Bazhenov,[10] and the experimental reflectance spectra reported by Rubloff,[3] Frandon *et al.*,[8] and Raisin *et al.*[11] For SrF_2 and BaF_2 our spectra are less rich in satellites (Figs. 4 and 5) than the reflectance spectra. We separate the plasmon transitions from interband transitions.

In SrF_2 we know[6,8] that the position of the valence electron plasmon is at 17.5 eV and that of the p-cation plasmon at $\sim$30.0—31.0 eV [marked with arrows in Figs. 4 and 3(b)]. The interband transitions can be separated into transitions with the initial state at F_{2p}^{-} and that with the initial state at Sr_{4p}^{2+} or deeper. Peaks found at $\Delta\epsilon=11.0$ and 13.5 eV (Table II) belong to the first set, those at $\Delta\epsilon=22.0$, 26.0, and 28.0 eV to the second set. In our spectrum, the peak at $\Delta\epsilon=11.0$ eV shows a very different intensity in the different core regions. It appears as a very strong peak in the Sr_{4s} region and becomes a shoulder in the Sr_{3d} and F_{1s} zones. In this position, Rubloff and Frandon observe a doublet (10.6 and 11.8 eV); they assign the first peak to an exciton and the second to the edge transition $\Gamma_{15}^{v}\rightarrow\Gamma_{1}^{c}$ (Rubloff). The 13.5 eV peak is assigned by Timofeenko and Bazhenov[10] to $\Gamma_{15}^{v}\rightarrow\Gamma_{12}^{c}$. Transitions at higher energy are from Sr_{4p}^{2+}: The weak peak at $\Delta\epsilon=22.0$ eV (that we observe only in the F_{1s} region) can be identified as the core exciton $Sr_{4p}^{2+}\rightarrow\Gamma_{1}^{c}$.[3,9]

The next peaks are (i) a strong peak at $\Delta\epsilon=26.0$ eV in Sr_{4s}, which becomes a shoulder in the Sr_{3d} region and disappears in F_{1s} overlapped by other strong transitions and (ii) a peak at $\Delta\epsilon=28.0$ eV present only in F_{1s}. Ganin *et al.*[6] have assigned these two peaks to the $X_4'^{v}\rightarrow X_1^{c}$ and $X_4'^{v}\rightarrow X_3^{c}$ transitions, respectively. Other bands in the regions at 30.0—65.0 eV from the main peak are from the deeper initial states F_{2s}^{-} and Sr_{4s}^{+2} up to higher conduction

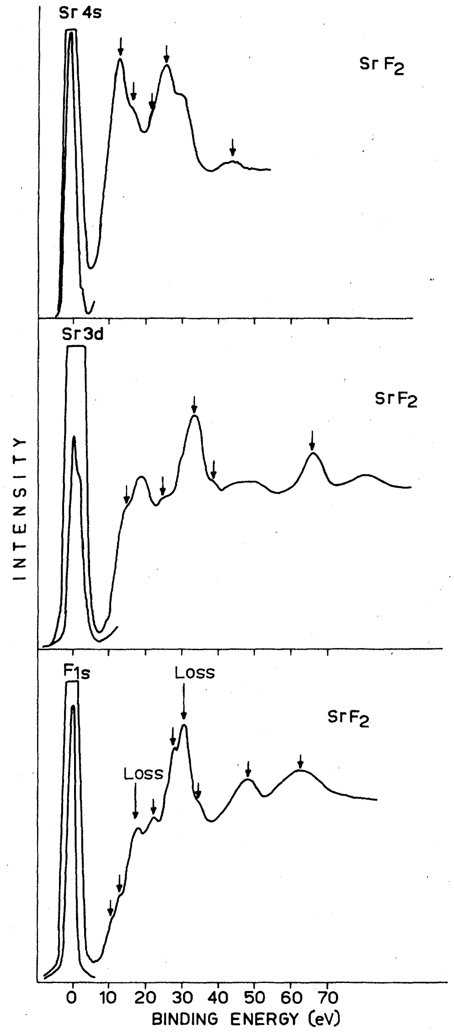

FIG. 4. XPS spectra of the F_{1s}, Sr_{3d}, and Sr_{4s} regions in SrF_2.

TABLE II. Experimental values of the separation energy $\Delta\epsilon$ (eV) of the satellites relative to the main peaks F_{1s}, Sr_{4s}, and Sr_{3d} in SrF_2. (The center of the main peak is set at 0.0 eV.) The error limit is evaluated to be ±0.5 eV.

	$\Delta\epsilon$		
F_{1s}	Sr_{4s}	Sr_{3d}	Assignment[a]
11.0	11.0		$\Gamma_{15}^{v}\rightarrow\Gamma_{1}^{c}$
13.5	13.5	14.0	$\Gamma_{15}^{v}\rightarrow\Gamma_{12}^{c}$
17.5	18.0	17.5	Loss
22.0			$Sr_{4p}^{2+}\rightarrow\Gamma_{1}^{c}$
	26.0	26.0	$X_4^{\prime v}\rightarrow X_1^{c}$
28.0	28.0		$X_4^{\prime v}\rightarrow X_3^{c}$
30.0	30.0	30.0	Loss
		33.0	
35.0			
		37.5	
	44.0		
48.5		(48.0)	
64.5		66.0	

[a]See text.

bands, but no calculations exist for these high binding-energy levels. In particular, we observe in the Sr_{3d} region a strong peak at $\Delta\epsilon=33.0$ eV and a shoulder at $\Delta\epsilon=37.5$ eV and, in the F_{1s} region, a shoulder at $\Delta\epsilon=35.0$ eV. Other peaks, between 44.0 and 66.0 eV, are present in these regions, belonging to higher transitions.

In all the regions of BaF_2 (Fig. 5) we observe a strong peak at $\Delta\epsilon=26.0$ eV that we assign to the *p*-cation plasmon. Among the crystals examined in this study, only BaF_2 allows measurements in the F_{2s} region, very rich in satellites. Here we observe a shoulder at 9.5 eV (possibly due to the Ba_{5s} transition or to an exciton) a doublet at $\Delta\epsilon=12.0$ and 14.5 eV and another doublet (present also in the F_{1s} region) at $\Delta\epsilon=32.5$ and 41.5 eV. In the F_{1s} and Ba_{4d} regions a peak at $\Delta\epsilon=17.5$ is also present (Table III).

Ganin and co-workers assign the $\Delta\epsilon=12.0$ eV peak to the $\Gamma_{15}^{v}\rightarrow\Gamma_{25}^{c}$ transition; that at $\Delta\epsilon=14.5$ eV to the

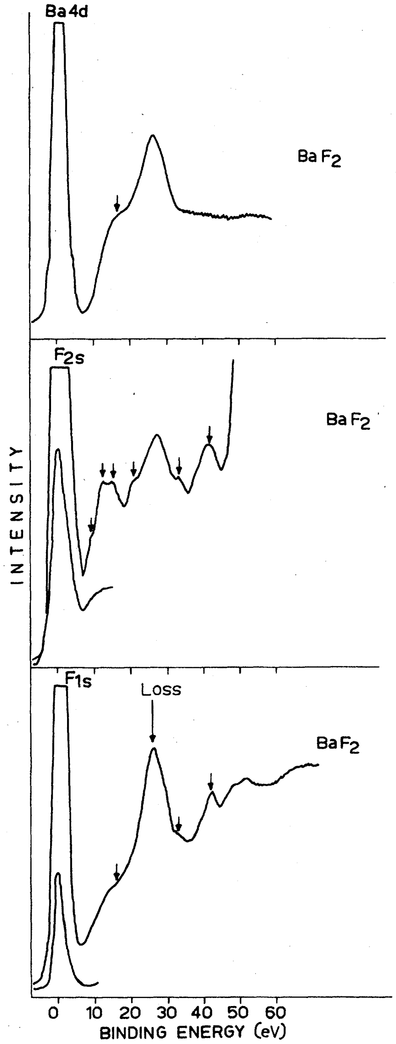

FIG. 5. XPS spectra of the F_{1s}, F_{2s}, and Ba_{4d} regions in BaF_2.

TABLE III. Experimental values of the separation energy $\Delta\epsilon$ (eV) of the satellites relative to the main peaks F_{1s}, F_{2s}, and Ba_{4d} in BaF_2. (The center of the main peaks is set at 0.0 eV.) The error limit is evaluated to be ±0.5 eV.

	$\Delta\epsilon$		
F_{1s}	F_{2s}	Ba_{4d}	Assignment
	9.5		
	12.0		$\Gamma_{15}^{v} \rightarrow \Gamma_{25}^{\prime c}$
	14.5		$X_2^{\prime v} \rightarrow X_3^c$
17.5		17.5	$X_5^{\prime v} \rightarrow X_1^c$
	21.0		exciton $\Gamma_6^{-v} \rightarrow \Gamma_1^c$
26.0	26.5	26.0	Loss
32.5	32.5		
42.0	41.5		

$X_2^{\prime v} \rightarrow X_3^c$ and that at $\Delta\epsilon = 17.5$ eV to the $X_5^{\prime v} \rightarrow X_1^c$. Transitions around the value of 21.0 eV are assigned by Frandon *et al.* to excitons. The other transitions that we observe at $\Delta\epsilon = 32.5$ and 41.5 eV are not reported by the other experimentalists. These are, presumably, from the initial state Ba_{5p}^{2+} to higher conduction bands.

In Fig. 3 we have overlapped the spectra of the different core regions in the same compound to show the remarkable differences in the relative intensities of the satellites assigned to interband transitions. Because the positions of the plasmon are unambiguous and the position of the interband transitions must be the same in all regions, these differences in the intensity appear significant and theoretical studies would be useful to elucidate this point.

The Wannier model predicts that strong excitons should be present in ionic crystals. We return to this subject in the following paper,[12] but we recall here two suggestions of Pantelides:[13] (i) The presence of excitons both below and within the conduction-band continuum and modification of the matrix elements due to electron-hole scattering may alter the density of states dramatically; (ii) in such systems (ionic crystals) there exist markedly different behavior depending upon whether the "anion" or the "cation" is excited.

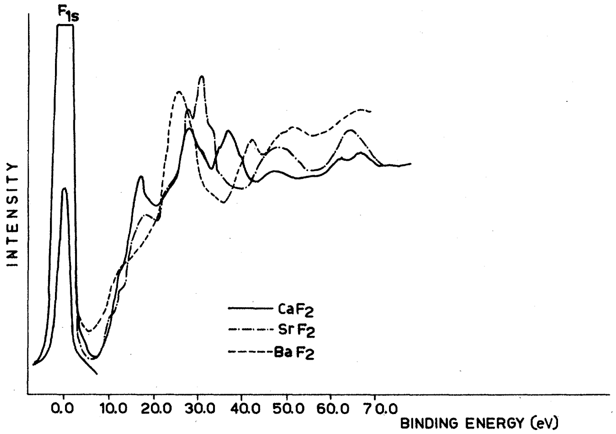

FIG. 6. Overlapped XPS spectrum of F_{1s} region in the CaF_2, SrF_2, and BaF_2 compounds.

In Fig. 6 we have overlapped the F_{1s} regions of the three different difluorides. In this case, the different positions of the plasmons in the different crystals became predominant, overshadowing the other phenomena.

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