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Electronic structure of the alkaline-earth fluorides studied by photoelectron spectroscopy

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Precise values have been determined for the binding and separation energies of the outer electronic bands of the alkaline-earth fluorides using 40.81-eV ultraviolet and Al $K\alpha$ (1486.6 eV) x-ray photoelectron spectrometry. Excellent agreement is found between the experimental and Born-model theoretical values for the energy separation between the outermost levels of the alkaline-earth and fluorine ions when the experimental values are corrected for relaxation (polarization) effects and when the Madelung energy alone is taken to represent the electron-lattice interaction. Very good agreement also occurs between experimental and theoretical values for the absolute binding energies. These results are accounted for by the fact that the substantial repulsive energy existing in the alkaline-earth fluorides is stored predominantly as interionic elastic potential energy and has little effect on the electronic energy levels on the ions. Comparison of the bandwidths of the alkaline-earth fluorides from the present work and alkali-metal fluorides from previous work shows that the F^- $2p$ valence-band width is a function of the nearest-neighbor distance and independent of the particular compound.

I. INTRODUCTION

The Born model of strongly ionic crystals has been of considerable value in the development of physical chemistry and solid-state physics. This model is based on the assumption that crystals are built up of positive and negative ions, and that for a spherically symmetric charge distribution the electrostatic force between two such ions depends only on their distance apart. The success of this model is illustrated by the excellent agreement, for a wide range of strongly ionic compounds, between the theoretical lattice energy, calculated on the basis of the Born model, and the corresponding experimental values derived from thermodynamic data by means of the Born-Haber cycle.[1-3]

The theoretical lattice energy is given[4,5] by the following expression:

$$E_l = E_M - E_r + E_V - E_z \,, \tag{1}$$

where E_M is the Madelung energy (point-charge electrostatic energy), E_r is the repulsive energy, and E_V and E_z are the van der Waals and zero-point energies, respectively. Generally, E_r is of order $0.1E_M$, and E_V and E_z are much smaller ($\sim 0.01E_M$).

Recently, we reported the results of systematic photoelectron studies of the alkali halides.[6-8] A method was presented which takes account of sample charging associated with the emission of photoelectrons from an insulating material, and which allows the precise determination of binding energies with respect to the vacuum level. Overall, the agreement between the experimentally determined parameters of the outer p bands of the alkali metal and halogen ions, particularly the binding energies, band separation energies, and chemical shifts, are in good agreement with the predictions of the Born model.

The present work extends these investigations to the alkaline-earth fluorides. In this regard two important differences between the alkali halides and the alkaline-earth fluorides are noted. First, MX_2 type crystals share the Madelung energy approximately in the ratio 2 : 1 for the M^{++} and the X^- ions, respectively. The same is true for the repulsive energy. Second, the Madelung and repulsive energies of the alkaline-earth fluorides are large ($E_M \simeq 30$ eV, $E_r \simeq 5$ eV) compared to the corresponding values for the alkali halides. These two characteristics of the alkaline-earth fluorides make it possible to give a definite interpretation of the effects of the Madelung and repulsive energy terms on the energy levels of the outer p bands of the alkaline-earth fluorides.

II. EXPERIMENTAL

In the present work an ultraviolet photoelectron spectrometer (UPS) and an x-ray photoelectron spectrometer (XPS) were used. The experimental details in regard to the UPS spectrometer parameters, energy calibration, sample preparation, and method of determining binding energies have been published.[6] Briefly, uv photons from a helium discharge lamp, operated under conditions which optimize the production of 40.81 eV radiation, strike a freshly evaporated target, and the photoelectrons are energy analyzed by a 90°-sector spherical electrostatic analyzer. The effects of sample charging were accounted for by recording several spectra for each sample within the first 30 s. after evaporation; binding energies at time zero were determined from the spectra by an extrapolation procedure, as discussed previously.[6]

The XPS spectrometer used in the present work has been described in detail elsewhere.[9,10] It consists of a 90°-sector, spherical, electrostatic electron energy analyzer with an Al *Kα* (1486.6 eV) soft-x-ray source of cylindrical symmetry. Samples were prepared by evaporation from a tantalum boat onto a rotating, polished-aluminum, cylindrical substrate. The XPS spectrometer was used to measure the energy separation of the outer bands of the ions for samples where the outer bands were too tightly bound to be accessible to high-resolution UPS.

III. THEORY

In the most general terms the theoretical binding energy E_b^{th} of an outer electronic level of an ion in a crystal can be written

$$E_b^{\text{th}} = E_b^{\text{fi}} \pm E_{e-l} , \qquad (2)$$

where E_b^{fi} represents the binding energy of the level in the free ion and E_{e-l} is the electron-lattice interaction, representing the total effect on the level when the ion assumes a lattice position in the crystal. In determining E_{e-l} we are guided by the success of the expression for the theoretical lattice energy given by Eq. (1). If in the first instance we represent E_{e-l} by E_M then we may write the binding energies $E_{bM}^{\text{th}}(M^{++})$ and $E_{bM}^{\text{th}}(\text{F}^-)$ of the outer levels of the alkaline-earth and fluorine ions as follows:

$$E_{bM}^{\text{th}}(M^{++}) = E_b^{\text{fi}}(M^{++}) - E_M(M^{++}) , \qquad (3)$$

$$E_{bM}^{\text{th}}(\text{F}^-) = E_b^{\text{fi}}(\text{F}^-) + E_M(\text{F}^-) , \qquad (4)$$

where $E_b^{\text{fi}}(M^{++})$ and $E_b^{\text{fi}}(\text{F}^-)$ are the binding energies of the outermost levels of the free alkaline-earth and fluorine ions with respect to the vacuum level E_{vac}, and where $E_M(M^{++})$ and $E_M(\text{F}^-)$ are the Madelung energies associated with the alkaline-earth and fluorine ions, respectively.

From Eqs. (3) and (4), the predicted energy separation between the outermost levels of the alkaline-earth and fluorine ions in the crystal may be written

$$E_{sM}^{\text{th}} \equiv E_b^{\text{fi}}(M^{++}) - E_b^{\text{fi}}(\text{F}^-) - [E_M(M^{++}) + E_M(\text{F}^-)] . \qquad (5)$$

The value of $E_b^{\text{fi}}(\text{F}^-)$ is known[11] and values for

TABLE I. Summary of Born-model theoretical values of binding and separation energies of the outer electronic bands of the alkaline-earth fluorides. Values with and without repulsive energy are listed. Symbols are defined in the text, and all energy values are in eV.

Sample	$E_b^{\text{fi}}(M^{++})$	$E_b^{\text{fi}}(\text{F}^-)$	Nearest-neighbor distance (Å)	$E_M(\text{F}^-)$	$E_M(M^{++})$	E_M	$E_r(\text{F}^-)$	$E_r(M^{++})$	$E_{bM}^{\text{th}}(\text{F}^-)$	$E_{bM}^{\text{th}}(M^{++})$	$E_{bMr}^{\text{th}}(\text{F}^-)$	$E_{bMr}^{\text{th}}(M^{++})$	E_{sM}^{th}	E_{sMr}^{th}
BeF_2	153.85	3.45	(1.67)	...	...	...	...	...	...	...	...	...	...	...
MgF_2	80.12	3.45	1.99	...	...	34.83	...	...	...	...	...	...	41.84	...
CaF_2	51.21	3.45	2.37	10.73	19.94	30.67	2.76	4.61	14.18	31.27	11.42	26.66	17.09	15.24
SrF_2	44.4	3.45	2.51	10.11	18.78	28.89	2.35	4.26	13.56	25.62	11.21	21.36	12.06	10.15
BaF_2	38.1	3.45	2.69	9.45	17.59	27.04	2.02	3.88	12.90	20.51	10.88	16.63	7.61	5.75

$E_b^{\text{fi}}\,(M^{++})$ are given by the third ionization potential.[12, 13] The Madelung energy per molecule can be written

$$E_M = \tfrac{1}{2}[2e\phi(M^{++}) + (-2e)\phi(\mathrm{F}^-)]$$
$$\equiv E_M(M^{++}) - E_M(\mathrm{F}^-), \qquad (6)$$

where $\phi(M^{++})$ is the potential at an alkaline-earth lattice site and $\phi(\mathrm{F}^-)$ is the potential at a fluorine lattice site. Benson and van Zeggeren[14] have shown that a fluorite structure is obtained from the superposition of CsCl and NaCl lattices, and that $\phi(M^{++})$ and $\phi(\mathrm{F}^-)$ are then readily determined to be

$$\phi(M^{++}) = -\alpha(\mathrm{NaCl})e/2\pi\epsilon_0 a_0 - \alpha(\mathrm{CsCl})e/\sqrt{3}\pi\epsilon_0 a_0, \qquad (7)$$

$$\phi(\mathrm{F}^-) = \alpha(\mathrm{CsCl})e/\sqrt{3}\pi\epsilon_0 a_0, \qquad (8)$$

where α(NaCl) and α(CsCl) are the well-known Madelung constants for the NaCl and CsCl crystal lattice structures, respectively, and a_0 is the lattice constant. The fluorite structure pertains to CaF_2, SrF_2, and BaF_2.

If alternatively we include the repulsive-energy term E_r as well as the Madelung energy E_M to represent $E_{e\text{-}l}$ in Eq. (2), then we would obtain the binding energies $E^{\text{th}}_{bMr}(M^{++})$ and $E^{\text{th}}_{bMr}(\mathrm{F}^-)$ of the outer levels of alkaline-earth and fluorine ions as follows:

$$E^{\text{th}}_{bMr}(M^{++}) = E_b^{\text{fi}}\,(M^{++}) - E_M(M^{++}) - E_r(M^{++}), \qquad (9)$$

$$E^{\text{th}}_{bMr}(\mathrm{F}^-) = E_b^{\text{fi}}\,(\mathrm{F}^-) + E_M(\mathrm{F}^-) - E_r(\mathrm{F}^-), \qquad (10)$$

and the energy separation may now be written

$$E^{\text{th}}_{sMr} = E_b^{\text{fi}}\,(M^{++}) - E_b^{\text{fi}}\,(\mathrm{F}^-) - [E_M(M^{++}) + E_M(\mathrm{F}^-)]$$
$$-[E_r(M^{++}) - E_r(\mathrm{F}^-)]. \qquad (11)$$

Values for $E_r(M^{++})$ and $E_r(\mathrm{F}^-)$ may be calculated from the Born-Mayer expression for the repulsive energy[15] (see Appendix).

In Table I we list calculated values of E_M, $E_M(M^{++})$, $E_M(\mathrm{F}^-)$, $E_r(M^{++})$, $E_r(\mathrm{F}^-)$, $E^{\text{th}}_{bM}(M^{++})$, $E^{\text{th}}_{bM}(\mathrm{F}^-)$, $E^{\text{th}}_{bMr}(M^{++})$, $E^{\text{th}}_{bMr}(\mathrm{F}^-)$, E^{th}_{sM}, and E^{th}_{sMr} for the alkaline-earth fluorides with fluorite structure. In addition, values of E_M and E_{sM} for MgF_2 with tetragonal rutile structure are listed. The breakdown of E_M into $E_M(M^{++})$ and $E_M(\mathrm{F}^-)$ is not available for the rutile structure. Similar comments apply to BeF_2, which has a tetragonal pseudocubic structure.

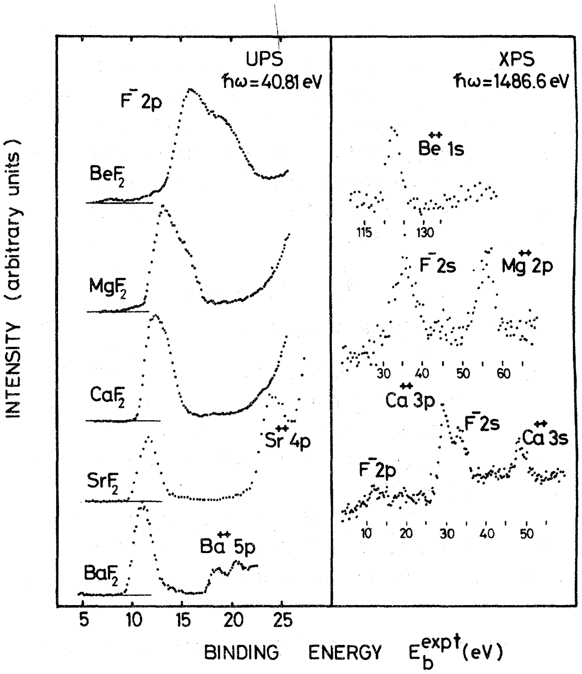

FIG. 1. Present alkaline-earth-fluoride UPS and XPS spectra taken under the conditions described in Sec. II of the text.

IV. RESULTS AND DISCUSSION

In Fig. 1 we show the UPS and XPS photoelectron spectra of the outer bands of the alkaline-earth fluorides taken with instrumental resolutions (full width at half-maximum) of 0.3 and 1.0 eV, respectively. Various features of the spectra of Fig. 1 are summarized in Table II. Before comparing these experimental results with the

TABLE II. Summary of present UPS and XPS experimental values of binding and separation energies of the outer electronic bands of the alkaline-earth fluorides, together with polarization energies and experimental values corrected for polarization. Symbols are defined in the text, and all values are in eV. The experimental uncertainties in binding energies are estimated to be 0.1 eV, and 0.2 eV in all other experimental values.

Sample	E_b^{expt} (F⁻)	E_{hw} (F⁻)	E_{tw} (F⁻)	E_b^{expt} (M^{++})	E_s^{expt}	E_p (F⁻)	E_p (M^{++})	E_b^{corr} (F⁻)	E_b^{corr} (M^{++})	E_s^{corr}
BeF_2	17.2	5.8	8.9	122.5	105.3	···	···	···	···	···
MgF_2	14.5	3.7	6.3	56.1	41.6	···	···	···	···	···
CaF_2	12.3	3.0	4.8	29.9	17.6	2.06	1.73	14.36	31.63	17.27
SrF_2	11.6	2.4	4.4	23.9	12.3	1.56	2.01	13.16	25.91	12.75
BaF_2	11.0	2.0	3.4	18.2	7.2	1.39	2.02	12.39	20.22	7.83
				20.2	9.2				22.22	9.83

predictions of the Born model, as discussed above, it is necessary to consider the effects of the electronic polarization as a result of the emission of a photoelectron from the crystal lattice leaving a positive hole. The experimental values of binding energy corrected for polarization effects, $E_b^{\mathrm{corr}}(M^{++})$ and $E_b^{\mathrm{corr}}(\mathrm{F}^-)$, have been calculated from

$$E_b^{\mathrm{corr}}(M^{++}) = E_b^{\mathrm{expt}}(M^{++}) + E_p(M^{++}) , \tag{12}$$

$$E_b^{\mathrm{corr}}(\mathrm{F}^-) = E_b^{\mathrm{expt}}(\mathrm{F}^-) + E_p(\mathrm{F}^-) , \tag{13}$$

where $E_b^{\mathrm{expt}}(M^{++})$ and $E_b^{\mathrm{expt}}(\mathrm{F}^-)$ are the uncorrected experimental binding energies for the alkaline-earth and fluorine levels, respectively, and $E_p(M^{++})$ and $E_p(\mathrm{F}^-)$ are the corresponding polarization energies.[16, 17]

From Eqs. (12) and (13), the corrected experimental separation E_s^{corr} between the outermost levels of the alkaline-earth and fluorine ions may be written

$$E_s^{\mathrm{corr}} \equiv E_b^{\mathrm{expt}}(M^{++}) - E_b^{\mathrm{expt}}(\mathrm{F}^-) + E_p(M^{++}) - E_p(\mathrm{F}^-) , \tag{14}$$

$$E_s^{\mathrm{corr}} = E_s^{\mathrm{expt}} + E_p(M^{++}) - E_p(\mathrm{F}^-) , \tag{15}$$

where E_s^{expt} is the uncorrected experimental separation. Values of $E_b^{\mathrm{corr}}(M^{++})$, $E_b^{\mathrm{corr}}(\mathrm{F}^-)$, and E_s^{corr} are also listed in Table II and have been calculated using values of $E_p(M^{++})$ and $E_p(\mathrm{F}^-)$ from Starostin and Ganin.[16, 17]

A comparison of the separation of the outermost levels is a more sensitive test of the theory than is a comparison of the experimental and theoretical absolute binding energies, since the inherent experimental uncertainties are much smaller in the former case. We therefore present a comparison, in Fig. 2, of the experimental separation without polarization correction (E_s^{expt}) with both the theoretical values E_{sM}^{th} and E_{sMr}^{th}. The agreement between E_s^{expt} and E_{sM}^{th} is clearly superior. Figure 2 also provides a comparison between the polarization-corrected separation E_s^{corr} and the same two theoretical values. The agreement between E_s^{corr} and E_{sM}^{th} is again good. It would appear that the systematic difference of approximately 2 eV evident in the comparisons involving E_{sMr}^{th} is therefore directly attributable to the term $[E_r(M^{++}) - E_r(\mathrm{F}^-)]$ in Eq. (11).

Because the polarization correction term in Eq. (15) is small (~0.5 eV), it is not immediately clear from Fig. 2 that its inclusion improves agreement between theory and experiment, but this can be demonstrated by a consideration of absolute binding energies. In Fig. 3 we show a comparison of $E_b^{\mathrm{expt}}(M^{++})$ with $E_{bM}^{\mathrm{th}}(M^{++})$ and of $E_b^{\mathrm{corr}}(M^{++})$ with $E_{bM}^{\mathrm{th}}(M^{++})$. It is apparent that values of $E_b^{\mathrm{expt}}(M^{++})$

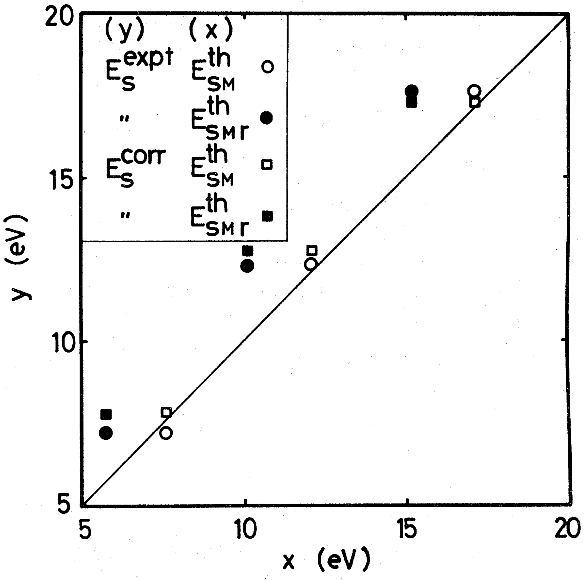

FIG. 2. Comparisons between experimental and theoretical values of the energy separations between the F^- $2p$ level and the outermost alkaline-earth level of $\mathrm{CaF_2}$, $\mathrm{SrF_2}$, and $\mathrm{BaF_2}$. Raw experimental values and polarization-corrected values are each compared to theoretical values with and without repulsive energy. Symbols are defined in the text.

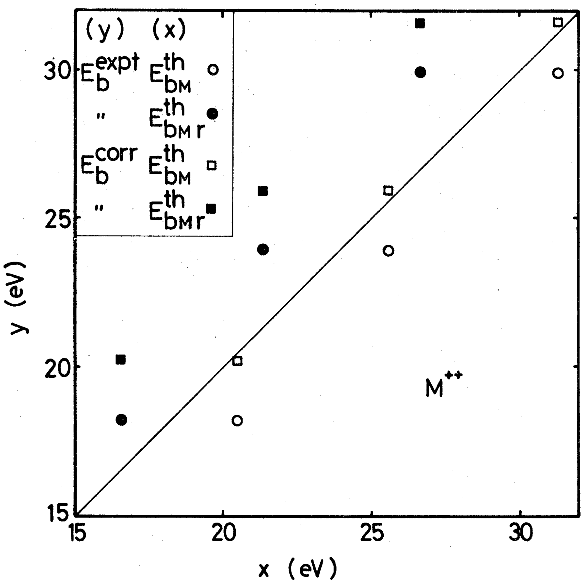

FIG. 3. Comparisons between experimental and theoretical values of the absolute binding energies of the outermost alkaline-earth levels of $\mathrm{CaF_2}$, $\mathrm{SrF_2}$, and $\mathrm{BaF_2}$. Raw experimental values and polarization-corrected values are each compared to theoretical values with and without repulsive energy. Symbols are defined in the text.

are systematically in error and that the application of the polarization correction giving $E_b^{\rm corr}(M^{++})$ produces excellent agreement between theory (not including repulsion terms) and experiment. Values of $E_{bMr}^{\rm th}(M^{++})$ are also plotted in Fig. 3 for comparison. It is clear that these values are also systematically in error.

In Fig. 4 we show the electronic energy-level diagram for the alkaline-earth fluorides with fluorite structure. The over-all agreement between the theoretical values given by Eqs. (3) and (4) (i.e., by taking the Madelung energies *alone* to represent the electron-lattice interaction), and the experimental values corrected for polarization [Eqs. (12) and (3)] is very good. This is a striking result in that it indicates that the electrons in the outermost levels of the ions do not "see" the repulsive forces between the various ions to any significant degree. This suggests a hard-sphere ionic model for the alkaline-earth fluorides in which the repulsive energy due to the interpenetration of the electron wave function of the ions is stored predominantly as interionic elastic potential energy and has negligible perturbational effect on the electronic energy levels of the individual ions. Thus, the individual electron energy levels of strongly ionic solids are apparently insensitive to small electron wave-function overlap whereas, by contrast, the energy-band widths (discussed briefly below) are very sensitive to this overlap. This model is consistent with other models used in quantum-mechanical calculations of binding energies of strongly ionic molecules.[18]

As mentioned above, the breakdown of E_M for $\mathrm{MgF_2}$ into $E_M(M^{++})$ and $E_M(\mathrm{F}^-)$ is not available, and neither are polarization corrections $E_p(M^{++})$ and $E_p(\mathrm{F}^-)$. An approximate comparison of the theoretical and experimental values for the energy separation of the outermost levels of $\mathrm{MgF_2}$ may be made since $E_{sM}^{\rm th}$ is calculable, and since the uncertainty in using $E_s^{\rm expt}$ rather than $E_s^{\rm corr}$ is small (~0.5 eV) for reasons discussed above. Reference to Tables I and II shows values of 41.8 eV for $E_{sM}^{\rm th}$ and 41.6 eV for $E_s^{\rm expt}$ for $\mathrm{MgF_2}$, which represents good agreement.

In the present study of the electronic structure of the alkaline-earth fluorides one further observation may be made concerning the total width $E_{\rm tw}(\mathrm{F}^-)$ and the full width at half-maximum $E_{\rm hw}(\mathrm{F}^-)$ of the F^- $2p$ valence bands. In Fig. 5 we show $E_{\rm tw}(\mathrm{F}^-)$ and $E_{\rm hw}(\mathrm{F}^-)$ as a function of the nearest-neighbor distance for the alkaline-earth fluorides. Also included in Fig. 5 for comparison are the corresponding values for the alkali-metal fluorides.[7] It is apparent from Fig. 5 that the bandwidths show strong dependence on the nearest-neighbor distance irrespective of whether the compounds are monovalent or divalent. The systematic broadening of the valence band with decreasing nearest-neighbor distance is most probably due to a progressive increase in electron wave-function overlap.

V. CONCLUSIONS

Excellent agreement has been found between the polarization (relaxation) corrected experimental values for the energy separation and absolute binding energies of the outermost levels of the alkaline-earth fluorides and the corresponding theoretical values obtained by using the Madelung energy alone to represent the electron-lattice interaction. This implies that the positions of the electron energy levels in the ions are negligibly affected by the repulsive forces between the ions. Comparison of the bandwidths of the F^- $2p$ valence bands in both alkaline-earth and alkali-metal fluorides has shown that bandwidth is a function of nearest-neighbor separation and is independent of the cation valence in these fluorides.

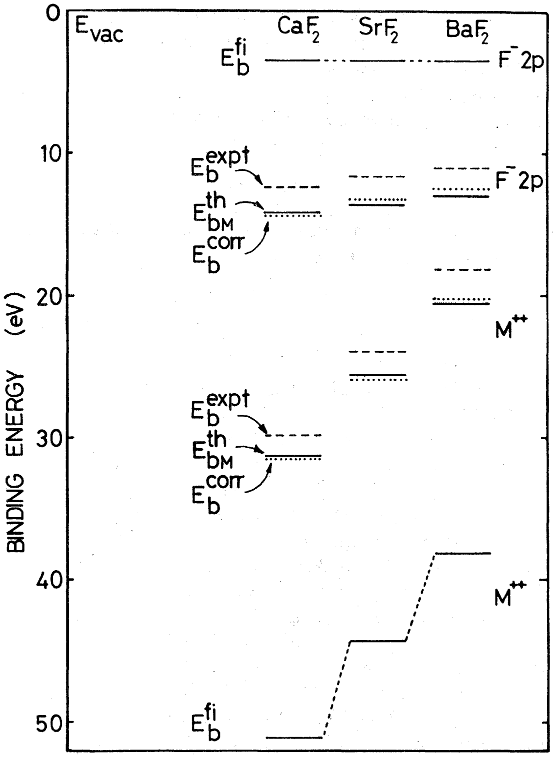

FIG. 4. Electronic-energy-level diagrams for $\mathrm{CaF_2}$, $\mathrm{SrF_2}$, and $\mathrm{BaF_2}$. The free ion $E_b^{\rm fi}$ and Born-model theoretical $E_{bm}^{\rm th}$ (no repulsive energy) values are shown together with the raw experimental values $E_b^{\rm expt}$ and the experimental values which have been corrected for polarization effects $E_b^{\rm corr}$.

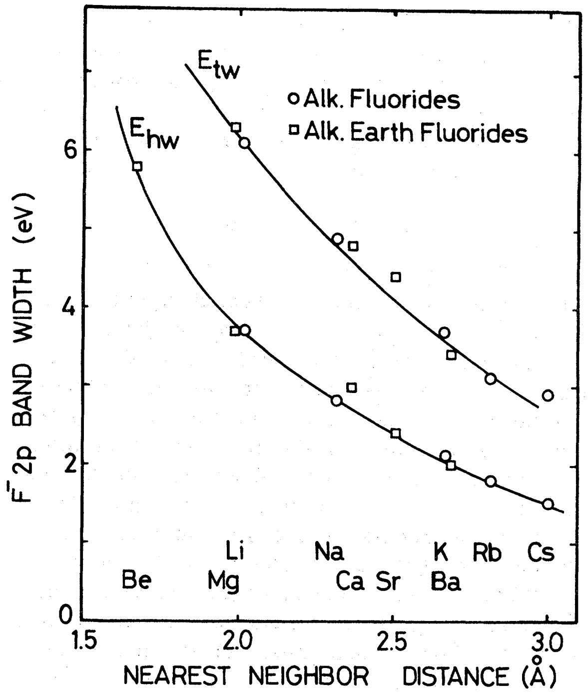

FIG. 5. Comparisons between experimental values of the F$^-$ $2p$ valence-band widths and nearest-neighbor distances for the alkaline-earth fluorides and the alkali-metal fluorides; total widths $E_{\rm tw}$ and full widths at half-maximum $E_{\rm hw}$ are shown. Lines are drawn to indicate the general trend of the results only.

APPENDIX

Estimates for the repulsive-energy parameters used in this work have been made using the model of Born and Mayer.[15] Their formulation for E_r is as follows:

$$E_r = b\{nc_{+-}\exp[(r_+ + r_- - r_0)/p] + \tfrac{1}{2}n'c_{++}\exp[(2r_+ - k_1 r_0)/p] + n''c_{--}\exp[(2r_- - k_2 r_0)/p]\}, \tag{A1}$$

where r_0 is the equilibrium distance between anion and cation; b is a known repulsion constant; n is the number of nearest unlike neighbors of a cation; n' and n'' are the number of nearest like neighbors of a cation and anion, respectively; r_+ and r_- are basic radii of cation and anion, respectively; c_{+-}, c_{++}, c_{--} are Pauling factors for the dependence of the repulsion of two ions on their charges and number of electrons in their outermost shells; p is a constant obtainable from compressibility data; k_1 is the ratio of shortest cation-cation distance to r_0; and k_2 is the ratio of the shortest anion-anion distance to r_0.

The total repulsive energy may be decomposed into the individual contributions of the anions and cations as follows:

$$E_r = \tfrac{1}{2}[E_r(M^{++}) + 2E_r(\mathrm{F}^-)], \tag{A2}$$

and hence

$$E_r(M^{++}) = b\{nc_{+-}\exp[(r_+ + r_- - r_0)/p] + n'c_{++}\exp[(2r_+ - k_1 r_0)/p]\}, \tag{A3}$$

$$E_r(\mathrm{F}^-) = b\{\tfrac{1}{2}nc_{+-}\exp[(r_+ + r_- - r_0)/p] + n''c_{--}\exp[(2r_- - k_2 r_0)/p]\}. \tag{A4}$$

Values for the above parameters for the various compounds were taken from Harries and Morris.[19]

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