Resonant Electron Transfer in Ionic Fluorine Compounds Following 1*s* 2*p* Ionization

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The fluorine $K\alpha$ x-ray spectra produced by 5.5-MeV He^+ bombardment of a series of alkali and alkaline-earth fluorides were measured with a curved-crystal spectrometer. An anomalously low intensity of the KL^1 peak arising from $1s^{-1}(2s2p)^{-1}$ initial states was observed for KF and SrF_2. Evidence is presented for a resonant electron-transfer mechanism associated with the formation of a molecule-ion between adjacent cation and anion sites.

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Previous investigations of the effect of chemical environment on the relative intensities of $K\alpha$ x-ray satellites produced by heavy-ion bombardment have revealed that L-vacancy filling processes can effectively compete with $K\alpha$ x-ray emission on a time scale of the order of 10^{-14} sec.[1-4] This conclusion is based upon the observation that the relative intensities of $K\alpha$ x-ray transitions from initial states having vacancy configurations $1s^{-1}(2s2p)^{-n}$ decrease for high n and increase for low n in going from compounds having low valence-electron densities to compounds having high valence-electron densities. Moreover, comparisons of the spectra of a variety of gaseous and solid compounds have indicated that interatomic transitions from the valence levels of neighboring atoms can play a dominant role in the L-vacancy filling process.[2-4]

Recently, Uda *et al.*[5] examined the $K\alpha$ satellite intensity distributions of a number of fluorine compounds having covalencies ranging from 0.09 (NaF) to 0.57 ($[CF_2]_n$). They found that the fluorine L-vacancy filling rate increases linearly with covalency for these particular compounds. However, spectra for the additional compounds KF, SrF_2, and BaF_2, measured by Deconninck and Van den Brock,[6] show large KL^1 satellite [initial state $1s^{-1}(2s2p)^{-1}$] intensity variations which cannot be understood in terms of simple covalency or electron-density arguments since all of the alkali and alkaline-earth fluorides have about the same values of these parameters. In this Letter, we report the results of a systematic investigation of the KL^0, KL^1, and KL^2 x-ray groups of fluorine in eight of the alkali and alkaline-earth fluorides. We shall show that the anomalous behavior of the KL^1 satellite intensity in these highly ionic compounds is consistent with the resonant transfer of an electron between the np level of the metal ion and the $2p$ level of the fluorine ion.

A beam of 5.5-MeV He^+ ions from the Texas A&M variable-energy cyclotron was used to excite $K\alpha$ x-ray emission in thick targets of NaF, KF, RbF, CsF, MgF_2, CaF_2, SrF_2, and BaF_2. This particular beam was chosen because of its relatively high efficiency for exciting $1s^{-1}(2s2p)^{-n}$ states having $n < 3$. The spectral measurements were performed using a 12.7-cm curved-crystal spectrometer mounted with the focal-circle plane normal to the beam direction so that x rays were viewed at an observation angle of 90°. The spectrometer employed a flow proportional counter (P-10 gas at 1 atm) having a 65-$\mu g/cm^2$ stretched polypropylene window and a rubidium acid phthalate crystal.

Spectra obtained for the alkali (group I) and alkaline-earth (group II) fluorides are compared in Fig. 1. The effects of He-ion energy loss on these spectra are expected to be negligible since the mean thicknesses for the absorption of the F K x rays in the various targets are small (100–800 $\mu g/cm^2$). The three peaks discernible in each spectrum, in order of increasing energy, arise from the KL^0, KL^1, and KL^2 x-ray groups. The main point of interest here is the peculiar behavior of the relative intensity of the KL^1 peak. It is apparent that the intensity of this peak undergoes a drastic reduction in going from NaF to KF, and then steadily rises again from KF to RbF to CsF. The group-II fluorides exhibit a similar trend, with the KL^1 intensity minimum displaced down one row in the periodic table to SrF_2. The relative intensity of the KL^2 peak, however, does not appear to vary appreciably in either series.

We propose a resonant electron transfer mechanism to explain the observed behavior of the KL^1 peak relative intensity. Consider the following process involving a group-I fluoride:

$$M^+(\text{g.s.}) + F^+(1s^{-1}2p^{-1}) \rightleftarrows M^{2+}(np^{-1}) + F(1s^{-1}).$$

Here, $F^+(1s^{-1}2p^{-1})$ represents a collision-excited

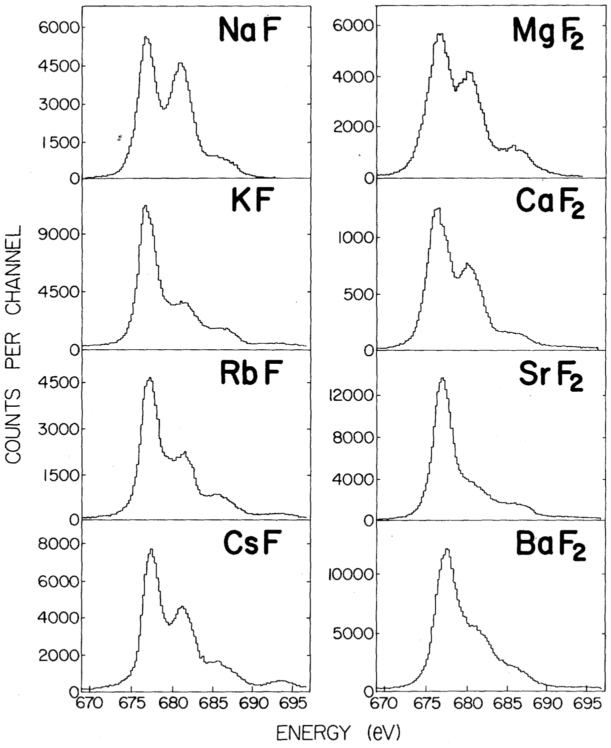

FIG. 1. Spectra of fluorine $K\alpha$ x rays excited by 5.5-MeV He^+ incident on group-I and group-II fluorides.

fluorine ion having an electron configuration $1s^1 2s^2 2p^5$ (the precollision configuration is F^-; $1s^2 2s^2 2p^6$), M^+(g.s.) represents a neighboring alkali-metal ion in its electronic ground state (outer-shell configuration $ns^2 np^6$), $M^{2+}(np^{-1})$ represents the metal ion with an np electron removed, and $F(1s^{-1})$ represents a fluorine atom with a 1s vacancy. Presumably when the energy change ΔE associated with this process is zero, an electron is free to transfer back and forth between the two ions if the barrier penetration probability is high (i.e., if the Coulomb barrier between the two ions is small). The effect of this resonance on the observed $K\alpha$ x-ray spectrum would be to transfer intensity from the KL^1 peak to the KL^0 peak.

In order to show the plausibility of the above mechanism, it is necessary to devise a method for calculating ΔE. The problem of relating free-ion binding energies to ionic-solid binding energies has been discussed in terms of a point-charge model by Citrin and Thomas,[7] and by Poole *et al.*[8] The point-charge model is also applicable to the present problem in which we wish to calculate the energy required to transfer an electron from the np level of the metal ion (in an ionic lattice) to the 2p level of a fluorine ion (in an ionic lattice) when the initial electron configuration of the fluorine ion (F^+) is $1s^1 2s^2 2p^5$. This energy change can be expressed as the sum of (a) the energy expended to remove an electron (to infinity) from the np level of a metal ion located next to an F^+ ion, and (b) the energy released when an electron is inserted into the 2p level of an F^+ ion located next to an M^{2+} (group I) or M^{3+} (group II) ion. The first energy is given by the equation

$$E_1 = E_M^{FI}(np) + E_M^{\alpha} + 2e^2/R - E_M^{P}(np), \qquad (1)$$

where $E_M^{FI}(np)$ is the np binding energy of the free metal ion, E_M^{α} is the Madelung energy of the metal ion, $2e^2/R$ is the additional Coulomb energy required due to the neighboring F^+ ion (R is the nearest-neighbor distance), and $E_M^{P}(np)$ is a polarization energy which accounts for the decrease in the np binding energy caused by the polarization of electrons from neighboring ions. In a similar fashion, the second energy is given by

$$E_2 = -E_F^{FI}(2p;1s^{-1}) + E_F^{\alpha} - e^2/R + E_F^{P}(2p;1s^{-1}), \qquad (2)$$

where $E_F^{FI}(2p;1s^{-1})$ is the 2p binding energy of a free F atom having a 1s vacancy ($1s^1 2s^2 p^6$), E_F^{α} is the Madelung energy of the F^- ion, e^2/R is the additional Coulomb energy gained due to the neighboring M^{2+} or M^{3+} ion, and $E_F^{P}(2p;1s^{-1})$ is a polarization energy which accounts for the decrease in the 2p binding energy caused by the polarization of electrons from neighboring ions. Adding Eqs. (1) and (2) gives (neglecting the polarization energies)

$$\Delta E = [E_M^{FI}(np) - E_F^{FI}(2p;1s^{-1})] + E^{\alpha} + e^2/R, \quad (3)$$

where $E^{\alpha} = E_M^{\alpha} + E_F^{\alpha}$. Equation (3) may be rewritten in terms of normal solid-state binding energies for the ions in their ground states by noting that the energy required to remove an np electron from a metal ion in a normal (unexcited) lattice is given by the first two terms of Eq. (1) (neglecting polarization). An equivalent relationship applies to the 2p binding energy of an F^- ion. The result of this transformation is

$$\Delta E = [E_M^{S}(np) - E_F^{S}(2p)] - [E_F^{FI}(2p;1s^{-1}) - E_F^{FI}(2p)] + e^2/R, \qquad (4)$$

where the first set of brackets contains the difference between the normal solid-state binding energies (a quantity available from photoelectron

TABLE I. Values of ΔE and of parameters used in the calculations (units are eV).

Compound	$E_M{}^S(np) - E_F{}^S(2p)$ [a]	$E_M{}^{FI}(np)$ [b]	$-E^{\alpha}$ [c]	e^2/R	ΔE_{I} [d]	ΔE_{II} [e]	ΔE_{ave}
NaF	23.5	47.3	21.7	6.2	11.3	12.7	12.0
KF	10.6	31.8	18.8	5.4	−2.1	−1.0	−1.6
RbF	7.7	27.5	17.9	5.1	−5.8	−4.2	−5.0
CsF	5.3	25.1	14.9	4.2	−5.5	−6.9	−6.2
MgF_2	41.6	80.1	34.8	7.2	32.0	31.8	31.9
CaF_2	17.6	51.2	30.7	6.1	6.1	6.7	6.4
SrF_2	12.3	44.4	28.9	5.7	0.7	1.0	0.9
BaF_2	8.2	38.1	27.0	5.4	−4.0	−3.4	−3.7

[a] All values for group I except that for NaF are from Poole *et al.* (Ref. 10). All values for group II are from Ref. 8. The value for NaF is from Pollak (Ref. 11).

[b] All values except those for SrF_2 and BaF_2 are from Ref. 9. The values for SrF_2 and BaF_2 are from Ref. 8.

[c] Calculated for group I (see text) and taken from Ref. 8 for group II.

[d] Calculated using Eq. (3).

[e] Calculated using Eq. (4).

measurements) and $E_F{}^{FI}(2p)$ is the electron affinity of fluorine [3.5 eV (Ref. 9)].

The calculation of ΔE was carried out using both Eqs. (3) and (4). The results are listed in Table I along with the values of the various terms in these equations. The energy $E_F{}^{FI}(2p; 1s^{-1})$ was calculated with the Hartree-Fock program of Fischer[12] by taking the difference of total energies between the appropriate initial and final states, and found to be 20.5 eV. Calculations performed in the same way for atomic fluorine yielded agreement with experimental values to within 0.3 eV for the $2p$ binding energy and to within 0.9 eV for the $1s$ binding energy. The Madelung energies for group I were calculated using the Madelung constants given by Tosi[13] and the internuclear separations (R) were obtained from Ref. 13 (group I) and Ref. 8 (group II). It is evident that the ΔE values obtained with Eqs. (3) and (4) are in very good agreement. Polarization energies have been neglected in these calculations; however, the results of Citrin and Thomas[7] and of Poole *et al.*[8] indicate that these energies are of the order of 1 to 2 eV. Nevertheless, as may be seen from Eqs. (1) and (2), the polarization energies, for the most part, cancel in the calculation of ΔE.

Referring to the last column of Table I where the average values of ΔE are listed, it is evident that the KL^1 intensity minima coincide with ΔE minima. This is shown graphically in Fig. 2 where the ratio of the KL^1 intensity to total intensity and the ratio of the KL^2 intensity to total intensity are plotted versus ΔE. The x-ray peak intensities were extracted from the spectra by performing least-squares fits using Voigt functions. In the spectra for KF and SrF_2, the KL^0 and KL^1 peaks were each represented by two Voigtian components, for reasons which will be explained below. The expanded energy scale used in Fig. 2 did not allow inclusion of the data for MgF_2. The intensity ratios obtained for this compound were 0.35 ± 0.05 ($n = 1$) and 0.14 ± 0.02 ($n = 2$). The behavior of the KL^2 intensity ratio, as shown in Fig. 2, is quite different from that displayed by the KL^1 intensity ratio. This observation provides additional support for the proposed mechanism.

The present evidence for resonant electron transfer suggests that a molecular model similar to the one used to describe the V_k center should be applicable. A V_k center is a self-trapped hole

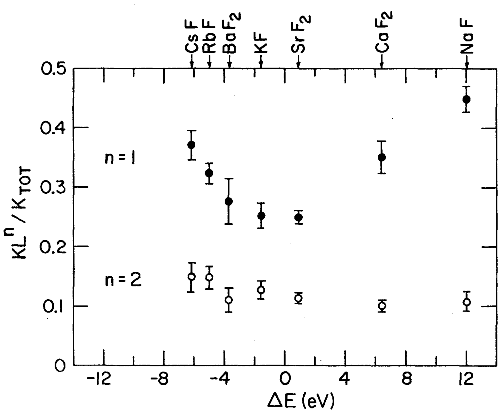

FIG. 2. The relative intensities of the KL^1 ($n = 1$) group as a function of ΔE. The relative intensities of the KL^2 ($n = 2$) x-ray group are plotted at the same ΔE positions for comparison.

in the valence band of an ionic crystal and it may be treated as if an X_2^- molecule-ion is formed between two anion sites.[14] In the present case, the molecular configuration would be $[M^+F(1s^{-1})]^+$ (group I) or $[M^{2+}F(1s^{-1})]^+$ (group II). Thus, in the molecular model, the np orbitals of the metal ion would interact with the $2p$ orbitals of the fluorine ion to form (in order of increasing energy) σ, π, π^*, and σ^* molecular orbitals. The energy difference between the σ_g and $\sigma_u{}^*$ orbitals for a V_k center in NaF is 3.4 eV.[14] The effect of this energy level "splitting" on the experimental spectrum would be to cause an apparent broadening due to the overlap of the transitions from the various possible initial state molecular orbital configurations. Evidence of appreciable broadening of the KL^1 peak in the KF and SrF_2 spectra is provided by the results of a least-squares analysis in which each peak was represented by a single Gaussian. The Gaussian width (full width at half maximum in eV) of the KL^1 peak for each of the compounds was 2.8 (NaF), 4.5 (KF), 3.2 (RbF), 2.9 (CsF), 2.7 (MgF_2), 3.0 (CaF_2), 3.8 (SrF_2), and 3.2 (BaF_2). The two-component representation of the KL^0 and KL^1 peaks in the final analysis of the spectra for KF and SrF_2 (as mentioned above) was for the purpose of approximating the energy-level splitting.

In conclusion, the observed minimization of the fluorine KL^1 x-ray intensity for the compounds KF and SrF_2 is consistent with a resonant electron transfer between the metal-ion np level and the fluorine-ion $2p$ level. This mechanism is highly selective of the state produced in the collision because it requires a close match between the total energies of the pre- and post-transfer (MF) electron configurations. The experimental observations indicate that the two ions involved may be described as a positively charged molecule-ion, analogous to the negatively charged molecule-ion attributed to a V_k center. Theoretical calculations of the resulting molecular orbital structure will be necessary before a detailed understanding of the experimental peak shapes and transition rates can be achieved.

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