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Influence of the chemical bond on the intensities of F $K\alpha$ x-ray satellites produced by electron and photon impacts

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The $K\alpha$ satellite spectra of F emitted from several fluorides irradiated with photons and electrons were examined in some detail. A relative intensity of the first satellite to the diagram line revealed a systematic change depending upon the Pauling bond ionicity or the covalency of fluorides used. Such a change can well be explained by substantial F L-shell vacancy relaxation prior to the K-hole filling for an x-ray emission. The probability for the L-vacancy rearrangement, and the L-shell width are discussed quantitatively.

I. INTRODUCTION

For fluorine compounds the lines labelled as α', α_3, α_4, α_5, and α_6 have been observed on the high-energy side of F $K\alpha_{1,2}$ when they are excited with photons and electrons.[1-5] According to energy calculations the initial states for α', α_3 and α_4 satellites are single-K and single-L hole states denoted as K^1L^1 and those for α_5 and α_6 are K^1L^2 triple-hole states.[6-9] The production of multiply ionized states in the F L shell during K-shell ionization process has been attributed to electron shake-off.[5,8,10,11] The results for F $K\alpha$ x-ray satellites measured, up to now, for several fluorides with photon and electron impacts are summarized as follows:

(1) The relative intensities of the K^1L^1 satellites to the diagram lines are strongly correlative to the electronegativity of the F atom in fluorides.

(2) The transition energies of the multiply ionized states are insensitive to the change in the chemical environments of F atoms, though the spectral profile of the diagram line (K^1L^0) is influenced by chemical compositions, crystal structures, and valence and coordination states.

The change in intensity distributions of the satellites has been considered to be caused by difference in the structure of the hybrid molecular orbitals of the fluorides. However, no attempt has been made to interpret the dramatically large chemical effect reflected in the relative intensity of the K^1L^1 satellite.[12,13] A recent examination of the structures of the $K\alpha$ x-ray satellites for a series of fluorides, produced by the 6-MeV/amu nitrogen impact has revealed the dependence of the intensity distributions on chemical environment.[14] This was explained by an alteration of the primary vacancy distributions (generated at the time of collision), prior to a $K\alpha$ emission, by interatomic electronic transitions. We report here an extensive investigation of the effect of L-shell vacancy rearrangement on the F $K\alpha$ x-ray satellites induced by photon and electron impacts. Measurements of $K\alpha$ x-ray spectra have been performed on a number of solid compounds of F with different bonding characters using 9-keV electrons, and x rays emitted from a rhodium anode. To make clear the K^1L^n multiple ionization mechanism in electron impact, an excitation function has also been measured for the intensity of the K^1L^n satellite relative to the K^1L^0 diagram line in the incident energy range from 3 to 9 keV.

II. EXPERIMENTAL PROCEDURES AND RESULTS

The measurements were carried out using two types of flat-crystal spectrometers for photon and electron excitations. In each spectrometer the positions of the analyzing crystal and detector were controlled electronically. In the case of the electron excitation, the measurements were made with the potassium acid phthalate (KAP, $2d = 26.63$ Å) crystal in the incident energies from 2.8 to 8.7 keV. The fluorescence radiation from the rhodium anode operated at 50 KV and 40 mA was used for the photon ionization measurements. Here the analyzing crystal was rubidium acid phthalate (RAP, $2d = 26.12$ Å). Detection of the reflected x rays was accomplished by means of a gas flow proportional counter (10% methane, 90% argon) with an aluminum-coated polypropylene (1 μm) window. Targets listed in Table I (except for teflon, which was in the form of a sheet) were prepared by pressing finely ground pure powders in the form of pellets. The resulting pellets were then coated with thin carbon films to make them conductive.

No change in the satellite intensity distributions due to anomalous dispersion of the analyzing crystals, RAP and KAP, was observed. This was checked by measuring the scattered radiation from a nonfluorine target in the energy range of

TABLE I. Pauling bond ionicity, intensity ratio of F $K\alpha$ x-ray satellite to the diagram line y_n^X/y_0^X, L-shell refilling probability f, and L-shell width Γ_L for fluorides.

		Photon impact				Electron impact			
Compound	Ionicity	y_1^X/y_0^X	y_2^X/y_0^X	f	Γ_L (a.u.)	y_1^X/y_0^X	y_2^X/y_0^X	f	Γ_L (a.u.)
NaF	0.909	0.493	0.075	0	0	0.523	0.084	0	0
LiF	0.895	0.424	0.085	0.100	0.000 82	0.453	0.116	0.094	0.000 76
CaF_2	0.895	0.392	0.062	0.150	0.001 30				
Na_3AlF_6	0.859	0.414	0.092	0.115	0.000 96	0.423	0.081	0.136	0.001 17
MgF_2	0.859	0.375	0.095	0.177	0.001 58				
AlF_3	0.790	0.332	0.066	0.248	0.002 44	0.357	0.083	0.237	0.002 29
NiF_2	0.702	0.326	0.086	0.259	0.002 58	0.313	0.091	0.310	0.003 31
PbF_2	0.702	0.294	0.080	0.316	0.003 40				
CuF_2	0.668	0.293	0.072	0.318	0.003 43	0.293	0.079	0.344	0.003 87
teflon	0.430	0.194	0.046	0.512	0.007 75	0.216	0.044	0.487	0.007 01

the $K\alpha$ spectra studied. The highest energy of the spectra observed under such experimental conditions was the F K-absorption edge. Corrections for crystal reflectivity, detector efficiency, and absorption were not necessary over the small range of energies spanned by the F K^1L^0 to K^1L^2 x rays.

Figure 1 shows the F $K\alpha$-satellite spectra of the several fluorides induced by (a) photon impact and (b) electron bombardment. The intensity ratios of the K^1L^1 and K^1L^2 satellites to K^1L^0 are tabulated in Table I (denoted by y_1^X/y_0^X and y_2^X/y_0^X, respectively). Here the peak intensities of K^1L^n were determined by means of a least-squares-peak-fitting procedures employing Gaussian functions. Since the background in all the cases is relatively low, errors in the relative intensities are due mainly to the peak deconvolutions. From repeated data runs, the errors in the intensity ratios are estimated to be ~3%. For both the excitation modes, the relative intensities of the K^1L^1 satellites to the diagram lines decrease markedly with increasing covalency C of the fluorides [$C = 1.0 - I$ where I is the Pauling bond ionicity, $I = 1.0 - \exp[-0.25(X_A - X_B)^2]$ with X_N the electro-negativity of element N (Ref. 15)].

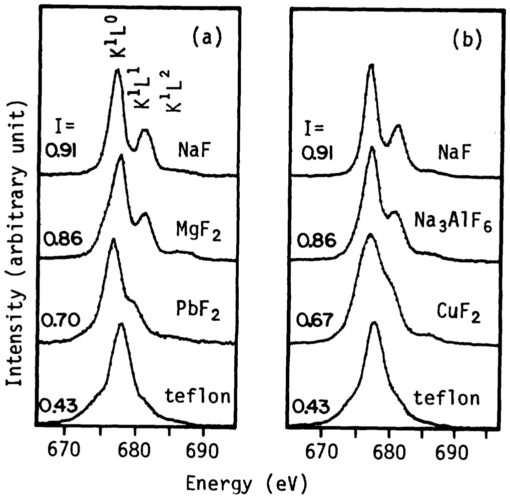

FIG. 1. F $K\alpha$ spectra of several fluorides induced by (a) photon and (b) electron impacts.

III. DISCUSSION

Our main interest is in the magnitude of the K^1L^1 satellite intensity relative to the diagram line, y_1^X/y_0^X, and so no detailed consideration was given to the satellite energies except to note that the observed energies are in good agreement with the calculated ones.

In the case of photon and electron impacts on light elements, the multiple K^1L^n ionization process can be described by the sudden approximation and is termed electron shake-off. The shake-off probability of an outer-shell electron can be calculated from the initial- and final-state wave functions alone, and is independent of the mechanism which produces the initial inner-shell vacancy.[16] This probability should be independent both of the excitation mode and the excitation energy, to the extent that the sudden approximation is valid. In Fig. 2, the intensity ratio y_1^X/y_0^X for NaF is plotted as a function of the electron impact energy. There is no change in the intensity ratio in the range from 3 to 9 KeV. In addition no significant change could be seen in the y_1^X/y_0^X ratio obtained with photon and electron impacts for these fluorides, as shown in Table I. These facts indicate that the electron shake-off process is the principal mechanism for producing primary F K^1L^n vacancy states in fluorides under our ex-

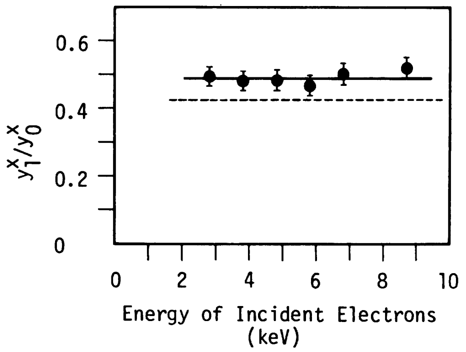

FIG. 2. Observed x-ray intensity ratio y_1^X/y_0^X for NaF as a function of the electron impact energy.

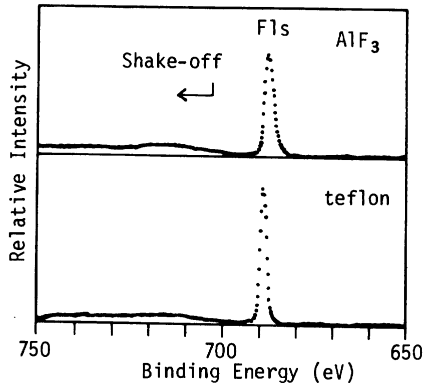

FIG. 3. Photoelectron spectra of AlF$_3$ and teflon in F $1s_{1/2}$, and its shake-up and shake-off regions. Evaporated thin (~50-Å thick) films of the compounds were excited with monochromatized Al $K\alpha$.

perimental conditions.

The experimental values of y_1^X/y_0^X for NaF and LiF are 0.493 and 0.424 respectively, and are comparable to the theoretical value of 0.425 (Ref. 5) calculated for F$^-$, based on the sudden approximation. As can be seen from Table I, however, the y_1^X/y_0^X ratio decreased as the covalent component of F$^-$ in bonding states increased and this behavior cannot be accounted for by the sudden approximation theory of shake-off.

In seeking to understand the intensity variations in the observed F $K\alpha$ x-ray satellites, two possibilities must be considered. The variations are associated either with the vacancy-production process at the time of ionization or with the deexcitation process which follows. Since the shake-off probability of the F L-shell is described in terms of the spatial overlap between initial- and final-states of wave functions of the valence band, the primary vacancy distribution created at the time of impact might be affected by differences in the bonding structures of the fluorides. If in the electron shake-off process the bonding effect is the primary cause of the intensity variations in the observed F $K\alpha$ x-ray satellites, the chemical effect should also be reflected in the photoelectron spectrum which is one of the direct measures of the shake-off electrons. Figure 3 shows x-ray photoelectron spectra (XPS) of $(CF_2)_n$ and AlF$_3$ in the (binding) energy region from 650 to 750 eV, where shake-off and shake-up satellites associated with F 1s photoionization are expected to be seen. Although the structures of the F $K\alpha$ x-ray satellites for these compounds are extremely different, the profiles of the XPS spectra showed no significant change. Thus it is conceivable that the chemical effect reflected in the F $K\alpha$ x-ray satellites is caused by the deexcitation process of the F L-shell vacancies rather than the excitation process.

The valence shell of the fluorides comprises the F L shell so that electrons localized on neighboring atoms are readily available to fill the F L-shell holes produced by photon and electron impacts. The plasmon lifetime in a solid composed of light elements (which is a measure of the response time of valence electrons) is the order of 10^{-17} sec (Ref. 17) and is much shorter than the F K-vacancy radiative lifetime[18] (2.4×10^{-13} sec). Therefore the refilling of L vacancies by valence electrons can occur prior to F $K\alpha$ x-ray emission. This may cause the distortion of the intensity distributions of the K^1L^n satellites to depend upon the difference in the bonding structure. By means of photon and electron impacts, one or two L vacancies are generated at the time of one-electron ejection from the K shell. In this case, the probability of filling these vacancies simultaneously by multiple electrons should be negligibly small. In the case that the L vacancies are filled one at a time by the ligand valence electrons, the probability for L vacancy rearrangement ($K^1L^n \rightarrow K^1L^{n-1}$), $f_{n,n-1}$ is expressed as[19]

$$f_{n,n-1}=\Gamma_L(K^1L^n)/[\Gamma_K(K^1L^n)+\Gamma_L(K^1L^n)]\,, \qquad (1)$$

where $\Gamma_K(K^1L^n)$ and $\Gamma_L(K^1L^n)$ denote the K- and L-shell level widths of the multiply ionized states. For a free F atom, Γ_L should be zero since a vacancy in the L shell, once formed, cannot be refilled by electrons from neighboring atoms. However, Γ_L for the F atom in chemical compounds is not zero because the linewidth Γ_L now involves the decay probability of a state which is associated with molecular orbital wave functions. This results in interatomic electron transitions filling vacancies in the F L-shell. The L-shell widths for the fluorine compounds should therefore depend upon the structure of hybrid molecular orbitals. Using the cascade approximation (Eq. 1) the relative intensity y_n^X for nth satellite of the F $K\alpha$ x-ray is expressed by the primary L-vacancy distribution y_n generated at the time of ionization and by $f_{n,n-1}$ for $n \geq 1$ as

$$y_n^X = (\omega_n/\bar{\omega})(1 - f_{n,n-1})(y_n + f_{n+1,n} y_{n+1} + \cdots)\,. \qquad (2)$$

In the case of $n = 0, f_{n,n-1} = 0$. Here ω_n is a fluorescence yield for a K^1L^n vacancy configuration state and $\bar{\omega}$ is an average fluorescence yield defined as

$$\bar{\omega}^{-1} = \sum_n (y_n^X/\omega_n)\,. \qquad (3)$$

As can be seen from Eq. (2), a higher-order vacancy state is transferred to a lower one with the probability $f_{n,n-1}$, and thus the initial vacancy distribution y_n relaxes into the distribution y_n^X when x rays are emitted. The primary cause of the chemical effects reflected by the structures of the F $K\alpha$ x-ray satellite distributions is then attributed to the decay of F L-vacancy states, whose transition amplitudes are defined by the total F L-shell width. We assume here that the initial vacancy distributions, y_n's, are the same for all the fluorides.

In photon and electron impacts, under our experimental conditions, the highest-order satellite produced was K^1L^2, the intensity of which was at most 0.12 y_0^X and typically much smaller. Therefore the data was analyzed using only the ratios y_1^X/y_0^X's. In this case the L-shell vacancy rearrangement probability $f_{n,n-1}$ is reduced to $f_{1,0}(\equiv f)$, and Eq. (2) is simplified to the form of

$$f = \frac{1 - (y_1^X/y_0^X)(y_0/y_1)(\omega_0/\omega_1)}{1 + (y_1^X/y_0^X)(\omega_0/\omega_1)}\,. \qquad (4)$$

If the ratios ω_0/ω_1 and y_0/y_1 are known for each fluoride, the L-vacancy rearrangement probability f can directly be determined by Eq. (4)

The fact that the fluorescence yield changes with increasing numbers of vacancies has been well recognized.[20] However, the ω_1/ω_0 ratio for various elements has been estimated to be almost unity, even when deduced from Hartree-Fock calculations.[21] Hence we assume that for all the fluorides ω_0/ω_1 is equal to 1/1.055 (Ref. 22), the value obtained experimentally for the Ne atom, although no data or no calculations of the chemical effects reflected in the fluorescence yield currently exist.

The electron shake-off theory based on the sudden approximation gave the ratio $y_1^X/y_0^X = 0.425$ for F^- ion. The experimental values of y_1^X/y_0^X's for highly ionic fluorine compounds such as NaF and LiF are practically the same as the theoretical one.[5] The good agreement between the theory and the experiments for y_1^X/y_0^X indicates that F atoms with large ionicity behave as if they were free ions. Therefore we assume $f = 0$ for NaF, which is the most ionic of the fluorides examined. Based on this assumption, the relative production cross section of the primary L-shell vacancy, y_1/y_0, which is assumed previously to be the same for all the fluorides, can be deduced from the relation

$$y_1/y_0 = \omega_0 y_1^X(\mathrm{NaF})/\omega_1 y_0^X(\mathrm{NaF})\,. \qquad (5)$$

The L-vacancy rearrangement probability f for various fluorides with different ionicities can now be determined by putting the values of ω_1/ω_0 and y_1/y_0 into Eq. (4). The results are shown in Fig. 4(a) as a function of the covalency C of the compounds used. As the total F K-shell width Γ_K is less sensitive than the total F L-shell width Γ_L to the change in the chemical environment, it is reasonable to assume that Γ_K is the same for all the fluorides. Γ_L is now estimated from Eq. (1) by using the theoretical value of $\Gamma_K(K^1L^0)$. The values of Γ_L obtained for the F compounds are shown in Fig. 4(b). They vary almost linearly with C. The values of f and Γ_L are approximately the same as those obtained for 84-MeV N^{4+} impact,[14] the latter being indicated by solid lines in Figs. 4(a) and 4(b).

In the case of heavy ion bombardment with ion velocities much larger than that of the F K-shell electrons, multiple-Coulomb ionization is the principal mechanism[23,24] for the primary production of vacancies, and the higher-order K^1L^n states with $n \geq 2$, which are negligible in the photon and electron excitations, are generated. In such a case, the effect of chemical environment on the fluorescence yields for the higher-order multiply ionized states should be reflected in the

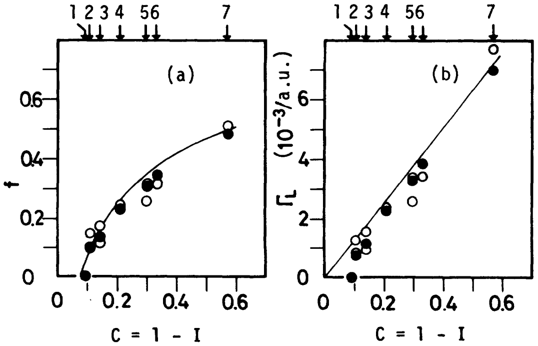

FIG. 4. The L-shell refilling probability f and the L-shell width Γ_L for (1) NaF; (2) LiF and CaF_2; (3) Na_3AlF_6 and MgF_2; (4) AlF_3, (5) NiF_2 and PbF_2; (6) CuF_2, and (7) teflon. ○: photon impact, and ●: electron impact.

structure of the $K\alpha$ x-ray satellites observed. In fact, we have observed large chemical effects reflected in the values of the fluorescence yield ratio ω_2/ω_0 for 84-MeV N^{4+} impact on various fluorides.[14] The good agreements of the values of f and Γ_L estimated from photon and electron impacts, with those obtained for nitrogen bombardment support the validity of the values of ω_2/ω_0 estimated previously, since in the case of photon and electron impacts, the L-vacancy rearrangement probability f was determined independently of ω_2/ω_0.

The linear relationship between the F L-shell width and the covalency can be explained by the nature of the molecular orbitals in the fluorine compound. Based on the molecular orbital (MO) theory, the MO wave function of the valence band of the F-X system is described through the ionic-covalent resonance state as

$$\Psi(\mathrm{MO})=\frac{1}{(1+\lambda^2)^{1/2}}(\lambda\Psi_{X:F}+\Psi_{X^+F^-}), \qquad (6)$$

where $\Psi_{X:F}$ and $\Psi_{X^+F^-}$ are wave functions associated with the covalent and ionic bonds, respectively. These component wave functions are composed of the intrinsic atomic orbitals of the F and X atoms. The F L-shell width Γ_L, which relates to the spatial overlap between the initial and final states of Ψ(MO), can be connected with the strength of the interatomic transition between the F and X atoms. The covalency C is the square of the amplitude of the component $\Psi_{X:F}$. Thus the linear relationship between Γ_L and C indicates that interatomic transitions take place only through the covalent component of Ψ(MO).

IV. CONCLUSION

The results of the present investigations have shown that the relative intensities of the F K^1L^1 satellite to the diagram line are strongly correlated to bond covalency. The primary cause of the observed chemical effect was attributed not to the ionization process but to the F L-shell vacancy rearrangement process through interatomic transitions, which occur prior to F $K\alpha$ x-ray emission. The probability for L-vacancy rearrangement, and the L-shell width were estimated quantitatively for the various F compounds and were found to be nearly the same as those obtained previously for nitrogen impact. The linear relationship between the L-shell level width and the covalency supports the conclusion that the interatomic electron transfer process takes place through the covalent component of the valence band in fluorine compounds. The values of Γ_L estimated by using realistic MO wave functions should be compared with the present results.

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