

Chemical effects on F *KVV* Auger spectra induced by photon impact

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F *KVV* Auger emissions were measured with NaF, MgF<sub>2</sub>, AlF<sub>3</sub>, and Teflon [(CF<sub>2</sub>)<sub>n</sub>], which were induced by photoionization. Chemical effects were reflected in line broadening and change in intensity ratios of the spectra emitted from singly and doubly ionized initial states,  $|K^1L^0\rangle$  and  $|K^1L^1\rangle$ . Reduction in Auger peak intensities which originated from  $|K^1L^1\rangle$  is in the order of the covalencies of the fluorides or the natural widths of F *L* shells. This is caused by the refilling of a F *L*-shell vacancy by one of the ligand electrons prior to Auger emission.

## I. INTRODUCTION

Auger electrons emitted from multiply ionized initial state have been studied in the field of atomic physics.<sup>1</sup> Chemical shifts and line broadening of the Auger lines have also extensively been studied and discussed in the field of chemistry. However, no data are available to compare the line intensities of Auger spectra emitted both from singly and multiply ionized initial states.

Characteristic x-rays induced from these states have satellite lines responsible for the multiply ionized states, together with the diagram line.<sup>2</sup> From a series of experiments the assumption was made that vacancies produced in a valence band were filled with ligand electrons prior to the characteristic x-ray emissions.<sup>3-9</sup> The degree of such refilling was proportional to the natural width of the valence band with electron vacancies. In the case of fluorides, the natural widths were estimated as  $\sim 0$  for NaF to  $\sim 70 \times 10^{-4}$ /a.u. for Teflon.<sup>3</sup>  $\sim 70 \times 10^{-4}$ /a.u. is comparable order to the lifetime of F *KVV* Auger emission or F *K $\alpha$*  radiation.<sup>10</sup> It is very interesting to study the competition between the Auger emission and the electronic rearrangement of valence electrons for a series of fluorides.

Ionization of a F *K* shell may accompany the additional electron ejection from the valence band of fluorides through the shakeoff process, both in the excitation with electrons and x rays. We expect to excite a F atom to the state with one *L* and one *K* vacancy by the photoexcitation, with  $\sim 40\%$  probability of the state with only one *K* vacancy.<sup>11</sup> Such an excitation condition should give rise to simple and clearcut Auger spectra in the fluorides, though the multiply ionized state of the F atom can easily be formed through an ion excitation. The latter gives rather complicated Auger spectra.

## II. EXPERIMENTAL PROCEDURE AND RESULTS

Thin films of NaF, MgF<sub>2</sub>, AlF<sub>3</sub>, and Teflon [(CF<sub>2</sub>)<sub>n</sub>] were evaporated on gold-plated stainless steel, whose thickness was thin enough to liberate surface charge through the tunneling effect, i.e., less than 50 Å. During evaporation, fundamental pressure in a evaporation chamber was kept less than  $1 \times 10^{-8}$  Torr. Auger-electron

spectra in these compounds were measured with a Hewlett-Packard model HP-5050A ESCA (electron spectroscopy for chemical analysis) spectrometer. Al *K $\alpha$*  x ray with 1487 eV energy was used for the excitation. Pressure was kept less than  $1 \times 10^{-9}$  Torr to avoid successive oxidation and adsorption during these measurements.

To facilitate the interpretation of the Auger spectra, the photoelectron spectra in these compounds were also measured. F *1s*<sub>1/2</sub>, *2s*<sub>1/2</sub>, and *2p*<sub>3/2,1/2</sub> expressed in the atomic scheme were shown in Figs. 1-3, respectively. The binding energies of F *1s*<sub>1/2</sub> and F *2s*<sub>1/2</sub> increased with in-

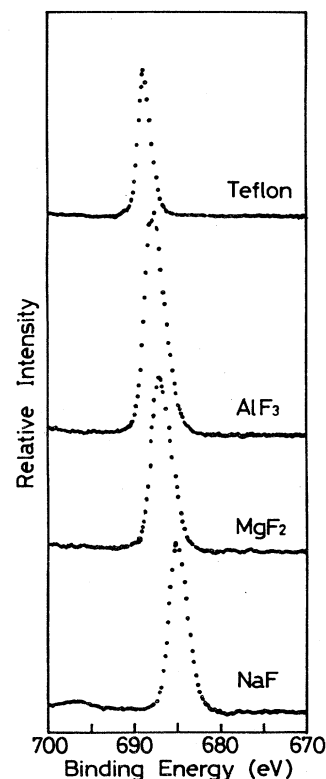


FIG. 1. Photoelectron spectra of F *1s*<sub>1/2</sub> for NaF, MgF<sub>2</sub>, AlF<sub>3</sub>, and Teflon induced by monochromatized Al *K $\alpha$*  x ray.

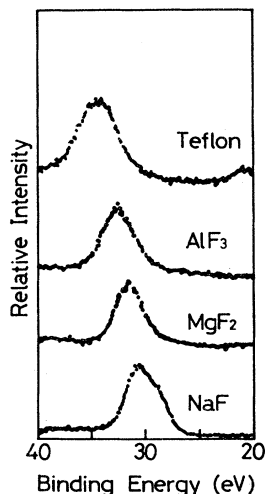


FIG. 2. Photoelectron spectra of F  $2s_{1/2}$  for a series of fluorides excited with Al  $K\alpha$  x ray.

creasing covalency  $C$  of the fluorides ( $C = 1.0 - I$  where  $I$  is the Pauling bond ionicity,<sup>12</sup>  $I = 1.0 - \exp[-0.25(X_A - X_B)^2]$  with  $X_N$  the electronegativity of element  $N$ ). The electronegativities are 0.9, 1.2, 1.5, and 2.5 for Na, Mg, Al, and C, respectively. The relationship between chemical shifts and covalencies for these fluorides is shown in Fig. 4. F  $2s_{1/2}$  and  $2p_{3/2,1/2}$  spectra in these compounds showed fine structures, caused by the mixing of atomic orbitals of F and its partner elements to make molecular orbitals. Structural complexity of the spectra in the compounds will, according to the degree of overlap integrals of the molecular orbitals, increase in the order of NaF, MgF<sub>2</sub>, AlF<sub>3</sub>, and (CF<sub>2</sub>)<sub>*n*</sub>. As can be seen from Fig. 3 NaF is almost ionic because its molecular orbitals seem to be the simple sum of F and Na atomic orbitals. If the covalency increases as in the case of Teflon, the valence bands can be seen as partly resolved lines. This is caused

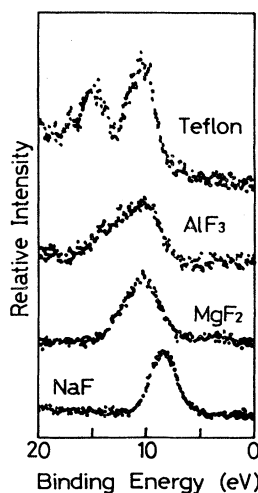


FIG. 3. Photoelectron spectra of valence bands for the fluorides, whose molecular orbitals are mainly composed of F  $2p_{3/2,1/2}$  atomic orbitals.

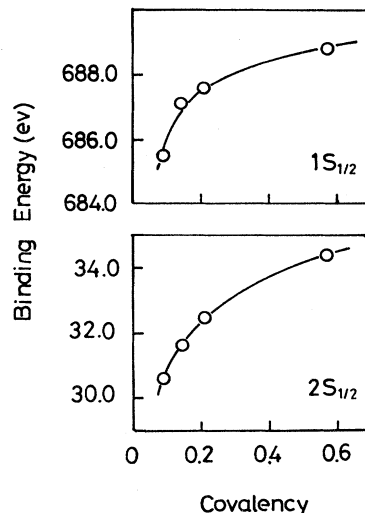


FIG. 4. Relationship between chemical shifts of F  $1s_{1/2}$  and  $2s_{1/2}$ , and covalencies of NaF, MgF<sub>2</sub>, AlF<sub>3</sub>, and Teflon.

by overlapping of atomic orbitals on individual atoms to make molecular orbitals. Binding energies of core and valence electrons that originated from F atoms in the compounds are summarized in Table I.

In Fig. 5 are shown photon-excited Auger spectra in these compounds. These peaks are, referring to the theoretical and experimental results for NaF and MgF<sub>2</sub> studied by Albridge *et al.*,<sup>13</sup> assigned to be  $A = 2s^2 2p^4(^1D) + 2s^2 2p^4(^1S)$ ,  $C = 2s^1 2p^5(^3P)$ ,  $D = 2s^1 2p^5(^1P)$ , and  $E = 2s^0 2p^6(^1S)$ , expressed in terms of final states. Maeda and Uda<sup>14</sup> assigned the peak  $B$  as  $KL_{2,3}(^3P, ^1P) - L_{2,3}^3(^4S, ^2D, ^2P)$  Auger peak, where the initial state has each one vacancy in  $K$  and  $L_{2,3}$  shells. The peak  $B$  is then originated from the doubly ionized initial state  $|K^1 L^1\rangle$ , and is completely distinguished from the other peaks  $A$ ,  $C$ ,  $D$  and  $E$  that originated from the singly ionized initial state  $|K^1 L^0\rangle$ . Here  $K^1 L^n$  denotes that one and  $n$  electrons are ionized by the photon impact from  $K$  and  $L$  shells, respectively.

Fluorides with high ionicity or low covalency give sharp Auger peaks. This is because the atomic-orbital components of F  $1s_{1/2}$ ,  $2s_{1/2}$ , and  $2p_{3/2,1/2}$  in the molecular orbitals in question are, as can be seen from Figs. 1–3, localized almost only on the F atom itself. On the other hand, Auger peaks from fluorides with high covalency become broad because of broadening of the F  $2s_{1/2}$  com-

TABLE I. Binding energies of electrons (relative to Fermi level).

Compounds	F $1s_{1/2}$ (eV)	F $2s_{1/2}$ (eV)	F $2p_{3/2,1/2}$ (eV)
NaF	685.0	30.6	8.3
MgF <sub>2</sub>	687.1	31.6	10.4
AlF <sub>3</sub>	687.6	32.5	14.0, 10.3
Teflon [(CF <sub>2</sub> ) <sub><i>n</i></sub> ]	688.8	34.4	16.8, 14.6, 10.4

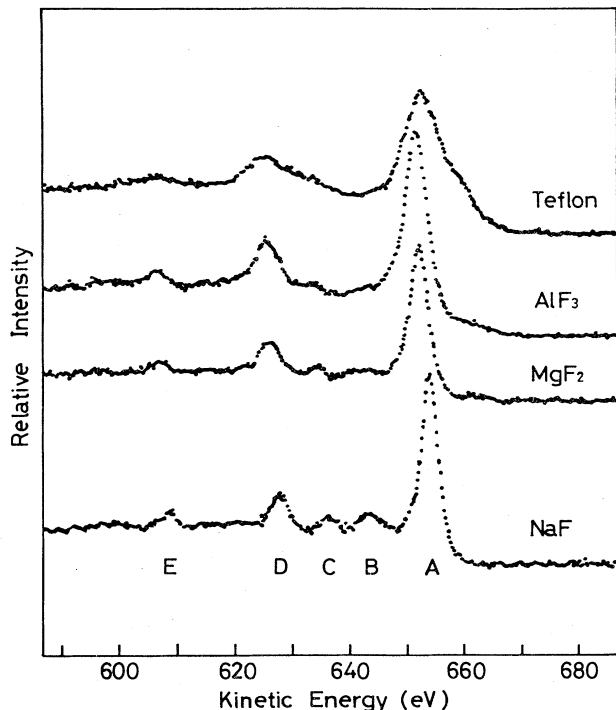


FIG. 5. Auger spectra of F  $KVV$  or  $KLL$  for fluorides induced by Al  $K\alpha$  x ray.

ponent, and broadening and splitting of the F  $2p_{3/2,1/2}$  components. Albridge *et al.*<sup>13</sup> observed that the bonding effects on the relative Auger intensities are seen from the spectra taken from LiF, NaF, and  $MgF_2$  to be small or nonexistent. Such a trend can also be seen in the present spectra from the fluorides with a wide range of covalencies. However, the most important difference seen in the intensity distributions of Auger spectra is in the explicit and implicit presence of the Auger peak  $B$  that originated from the doubly ionized initial state for NaF and  $MgF_2$  with high ionicity, and Teflon with high covalency, respectively.

### III. DISCUSSION

A series of papers<sup>3-5</sup> deals with the electronic rearrangement of valence electrons prior to the F  $K\alpha$  emission when F in a fluoride is multiply ionized, and then the  $|K^1L^n\rangle$  state is formed. In this case assumptions were made that the electron vacancies in the  $FL$  shell would be filled, one by one, by the ligand valence electrons, and that the probability of simultaneous multielectron transfers would be negligibly small. Hence the probability for an  $L$ -shell-vacancy rearrangement by one electron  $f_{n,n-1}$  is expressed, for a  $K^1L^n \rightarrow K^1L^{n-1}$  transition, as

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

Here  $\Gamma_L(K^1L^n)$  and  $\Gamma_K(K^1L^n)$  denote  $L$ - and  $K$ -shell widths for a vacancy configuration state of  $K^1L^n$ . From the experimental results<sup>3</sup>  $\Gamma_L(K^1L^n)$  is determined to be  $\sim 0, 26.9,$  and  $67.3 \times 10^{-4}/\text{a.u.}$  for NaF,  $AlF_3$ , and Teflon, respectively. By use of  $\Gamma_L(K^1L^n)\tau \approx \hbar$ , the lifetime  $\tau$  of a  $FL$ -shell vacancy, when it is filled with one of ligand valence electrons, is estimated to be  $\infty, 9.5,$  and  $3.6 \times 10^{-15}$  sec for these fluorides, respectively. On the other hand, the F  $|K^1L^0\rangle$  lifetime can be estimated to be  $3.3 \times 10^{-15}$  sec if we use the atomic data of fluorine  $\Gamma_K(K^1L^0) = 73.8 \times 10^{-4}/\text{a.u.}$ <sup>10</sup> Then we expect to see no electronic rearrangement for F in NaF with the  $|K^1L^1\rangle$  state prior to F  $KVV$  Auger emission.  $\Gamma_K(K^1L^0)/\Gamma_L(K^1L^n)$  for Teflon is almost unity, and then the refilling of fluorine  $L$ -shell vacancies with the ligand electrons and F  $KVV$  emission are in competition. In such a case the peak  $B$  should become weak.  $MgF_2$  and  $AlF_3$  lie between these two extreme cases. Experimental results reproduced such predictions completely.

The conclusion can be drawn from the experimental results that if the time necessary for the valence electron rearrangement and the lifetime to emit Auger electron are the same order, we can see quite different intensity distributions of Auger spectra emitted from the singly and multiply ionized states. Then such a technique should become a powerful tool to distinguish the difference in chemical bondings.

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