Resonant Electron-Transfer Relaxation Observed in Fluorine K Auger Spectra

O. Benka[a] and M. Uda
The Institute of Physical and Chemical Research, Wako-shi, Saitama 351, Japan

(Received 5 March 1986)

Fluorine K Auger spectra were measured for a series of alkali-metal and alkaline-earth fluorides excited by Al $K\alpha$ x rays. A new line was observed in some Auger spectra, and the highest intensity of this line was found for KF. The energy and intensity variations of this line depending on the metal ion are explained by a resonant electron-transfer relaxation mechanism following the Auger transition.

PACS numbers: 32.80.Hd

It is well established that the energy of Auger electrons emitted from atoms bound in solids is higher than that of Auger electrons emitted from free atoms.[1] The main cause of this energy shift is extra-atomic relaxation of the environment screening the created double-hole final state. For metals, where conduction electrons are most effectively screening the holes, this shift is largest, about 10–15 eV.[1] For ionic solids this relaxation shift due to polarization is much smaller.[2] Other relaxation mechanisms are not yet reported. Recent measurements[3] of the relative intensity of the first KL_1 satellite line in fluorine K x-ray spectra of ionic fluorine compounds gave evidence for a resonant electron-transfer (RET) mechanism following $1s2p$ double ionization of the fluorine ion. The final state after Auger-electron emission by a fluorine ion is also a double-hole state. When this RET is now interpreted as a special relaxation mechanism of the ionic crystal in response to the created double hole, RET might also be seen in K-Auger-electron spectra of ionic fluorine compounds if this RET relaxation process is fast enough to affect the emitted Auger electrons. Measuring x-ray spectra and the most intense Auger line of fluorine for a series of fluorine compounds, Deconninck and Van Den Broek[4] found some irregularities in the Auger spectra of KF, SrF_2, and BaF_2 which may indicate the influence of RET, but they could not give an explanation for these irregularities.

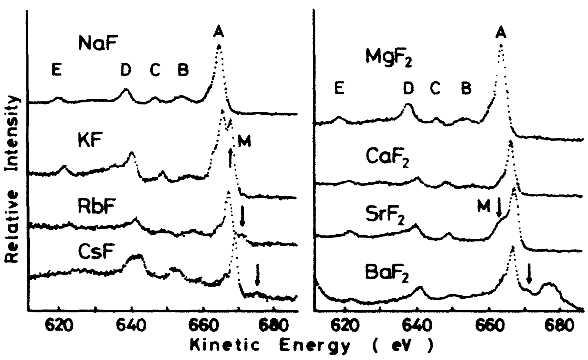

FIG. 1. Fluorine K Auger spectra induced by Al $K\alpha$ x rays. The position of the M line is indicated by arrows. The energy is given with respect to the Fermi level of the spectrometer.

In this Letter we report the results of a systematic investigation of the K Auger spectra of fluorine for the alkali-metal and alkaline-earth fluorides. We shall show that the found anomalous structure of the main line ($KL_{2,3}L_{2,3}$) can be explained by a new resonant electron-transfer relaxation mechanism between the outer np level of the metal ion and the $2p$ level of the fluorine ion.

The fluorine K Auger spectra of NaF, KF, RbF, CsF, MgF_2, CaF_2, SrF_2, and BaF_2 were measured with a HP-5050A ESCA spectrometer. Monochromatized Al $K\alpha$ x rays were used for excitation. The pressure in the analyzer chamber was kept less than 2×10^{-9} mbar and no contaminations were found during measurements. The fluorine compounds were evaporated on gold-plated stainless-steel backings and brought directly into the analyzer chamber without breaking the vacuum. To avoid charging, the samples were flooded with electrons from an electron gun establishing a single vacuum energy level for all samples.[5]

The measured spectra are compared in Fig. 1. Most of the shown spectra have a high background coming from energy-loss electrons of photoelectrons and Auger electrons with high energies. The NaF and MgF_2 spectra are equal to the ones measured and analyzed by Uda *et al.*[6] The spectra can be described by five lines or line groups in terms of final-state holes in the $n=2$ shell: $A=pp(^1D+^1S)$, $C=sp(^3P)$, $D=sp(^1P)$, and $E=ss(^1S)$. The peak B comes from an initial double-hole $(K+L)$ state. In addition to these lines there is in some spectra near to the A line another line indicated by M. The broad high-energy line of BaF_2 is an energy-loss peak of $3d_{3/2}$ and $3d_{5/2}$ Ba photoelectrons. By comparison with the energy-loss structure of fluorine $1s$ photoelectrons of BaF_2, additional contributions of the energy-loss structure are expected in the region of the B and C lines, but not in the region of the A and M lines. For CsF_2, Cs MNV

Auger transitions are overlapping the *C* and *D* lines, but no Auger transitions are expected near to the *A* and *M* lines. The main point of interest in comparing the spectra is the *M* line, which is discussed in the following. For KF the *M* line has the largest intensity, about the same as the *A* line. It can also be seen that the relative height of the *A* line is decreased, compared to NaF, and so for KF it looks like that the *M* line is not an additional line, but that the *A* line is split into two lines, the *A* and *M* lines. In Table I the energies of the *A* and *M* lines are given with respect to the *A* line of NaF. In addition the relative energies of the *E* line are also given.

To explain the *M* line we propose a RET relaxed mechanism. After Auger-electron emission the final state is normally, in ionic compounds, a state with two $2p$ holes localized at the F ion. These two holes reduce the potential around the F ion. If R is the distance between the F and metal (M) ion the potential well separating the F and M ions will be reduced by about $4e^2/R$. If the binding energy of the outer np electrons of the M ion relative to the vacuum level $[B_M^V(np)]$ has about the same value as the reduction of the potential well, a transfer of an electron from the M to the F ion might be possible. For KF, $B_M^V(np)$ is about 21.2 eV and $4e^2/R = 21.6$ eV and therefore nonlocalization of a $2p$ hole might be possible. If the energy of a state I, $M^+(\text{g.s.}) + \text{F}^+(2p^{-2})$, is E_I compared to a state without holes and of a state II, $M^{2+}(np^{-1}) + \text{F}(2p^{-1})$, is E_II, where $M^+(\text{g.s.})$ represents a M^+ ion in the ground state and $\text{F}^{(n-1)+}(2p^{-n})$ represents a F^- ion with n holes in the $2p$ shell, we get a resonance condition for the transfer of an np electron of the metal to the F ion for $\epsilon = E_\text{I} - E_\text{II} = 0$. Because of the level-noncrossing rule a split into two states with different energies is expected corresponding to bonding (N) and antibonding (T) states separated by an energy $\delta = S$, as shown in Fig. 2(a). For increasing $|\epsilon|$ this energy splitting δ is expected to decrease, and we used then a simple approximation $\delta = S\exp(-\epsilon/S)$. The total energy difference Δ between the levels N and T is then $\Delta = \epsilon + \delta$ [Fig. 2(b)],

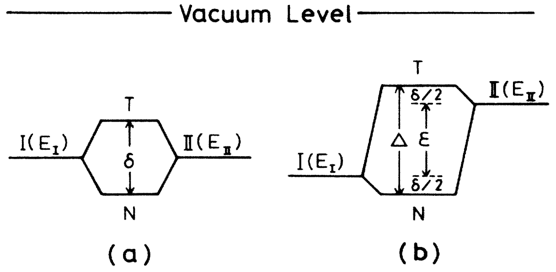

FIG. 2. Schematic diagram of energy levels. (a) Resonance condition $\epsilon = E_\text{I} - E_\text{II} = 0$. (b) Partial resonance condition. E_I, E_II, ϵ, Δ, and δ as defined in the text.

$$\Delta = \epsilon + S\exp(-\epsilon/S). \tag{1}$$

For $\epsilon = 0$ states N and T are symmetric with respect to states I and II, and an equal occupation probability for states N and T is expected. In the KF spectrum lines A and M have almost the same intensity, and we took therefore $\epsilon = 0$ for KF and found $S = \Delta_\text{expt.}(\text{KF}) = 2.4$ eV. For $\epsilon > 0$ [Fig. 2(b)] state N is closer to state I, corresponding to the unrelaxed final state after the Auger transition. Therefore, a higher occupation probability is expected for state N than for state T. Because of the higher binding energy of state I ($\epsilon > 0$), the line with higher intensity (line A) is then expected at lower energy and an additional line (line M), with smaller intensity, at higher energy. For $\epsilon < 0$ state T will be closer to state I and the additional line (line M) is expected at lower energy than the main line (line

TABLE I. Experimental energies of the *A* and *M* lines relative to the *A* line of NaF, and of the *E* line relative to the *E* line of NaF and energies which are defined in the text (units are electronvolts).

Compound	E_A	E_M	E_E	Δ [a]	δ [b]	E_A^c [c]	$\epsilon_\text{expt.}$ [d]	ϵ_th [e]	ϵ_th^c [f]
NaF	0	···	0	···	···	···	···	−14.7	−12.5
KF	0.9	3.3	2.4	2.4	2.4	2.1	0	−2.2	0
RbF	2.6	6.6	3.6	4.0	0.6	2.9	3.4	0.6	2.8
CsF	3.8	10.3	···	6.5	0.2	3.9	6.3	3.5	5.7
MgF_2	−1.4	···	−1.1	···	···	−1.4	···	−34.8	−32.6
CaF_2	1.3	···	1.2	···	···	1.3	···	−10.5	−8.3
SrF_2	2.1	−0.6	1.6	−2.7	1.3	1.5	−1.4	−3.2	−1.0
BaF_2	1.5	5.8	2.6	4.3	0.5	1.8	3.8	1.6	3.8

[a] $\Delta = E_M - E_A$.

[b] $\delta = 2.4\exp(-\epsilon_\text{expt.}/2.4)$.

[c] $E_A^c = E_A \pm 0.5\delta$.

[d] $\epsilon_\text{expt.} = \Delta - \delta$.

[e] ϵ_th = result of Eq. (3).

[f] $\epsilon_\text{th}^c = \epsilon_\text{th} + 2.2$.

A), representing now the relaxed state T. From experimental Δ values, experimental $\epsilon_{\text{expt.}}$ and δ values, were evaluated with use of Eq. (1) and $S = 2.4$ eV, and they are given in Table I.

The chemical environment is normally changing the energies for all core-level Auger transitions by the same amount. Because of the high ionicity of all compounds considered here, the F L shell can be considered as a localized core shell. When we compare the energy shifts of the A and E lines, where the E line involves only the $2s$ shell and is therefore the best core-level Auger line, in Table I, there are discrepancies. But if we take the additional splitting of the A line due to the RET relaxation into account and compare corrected energies $E_A^c = E_A \pm 0.5\delta$ of the A line, agreement is much better.

In order to show the plausibility of the proposed RET relaxation, it is also necessary to calculate $\epsilon_{\text{th}} = E_{\text{I}} - E_{\text{II}}$. This calculation is performed in a similar manner as those of Ref. 3 using a point-charge model.[7] E_{I} is then given by

$$E_{\text{I}} = 2B_{\text{F}}^V(2p) + [E(2p, 2p^{-1}) - E(2p)] - 4R_{\text{F}}, \tag{2}$$

where $B_{\text{F}}^V(2p)$ is the F^- $2p$ binding energy, $E(2p)$ and $E(2p, 2p^{-1})$ are the $2p$ free ion binding energies of F^- and F, and R_{F} is the fluorine polarization energy for one hole. E_{II} is given by

$$E_{\text{II}} = B_M^V(np) + B_{\text{F}}^V(2p) + e^2/R - R_M - R_{\text{F}} - R_M^V - R_{\text{F}}^M, \tag{3}$$

where e^2/R takes the Coulomb interaction of the two holes into account and R_M is the polarization energy for a hole at the M ion. R_M^{F} and R_{F}^M are the extra-atomic cross-polarization energies, discussed by Citrin, Rowe, and Christman,[8] and account for the relaxation energy of a F or M hole due to polarization induced by a M or F hole, respectively. If the approximation $R_M^{\text{F}} = R_M$ and $R_{\text{F}}^M = R_{\text{F}}$ is used, ϵ is given by

$$\epsilon = B_{\text{F}}^V(2p) - B_M^V(np) + [E(2p, 2p^{-1}) - E(2p)] - e^2/R - 2(R_{\text{F}} - R_M). \tag{4}$$

For the evaluation of Eq. (4), $B_{\text{F}}^V - B_M^V$, R_{F}, and R_M values were taken from the work of Poole *et al.*,[9,10] e^2/R from Ref. 3, and $E(2p, 2p^{-1}) - E(2p)$ from the CRC Handbook.[11] The resulting ϵ values ϵ_{th} are listed in Table I. On comparison of these values with $\epsilon_{\text{expt.}}$, there is for all values a difference of about 2 eV. This discrepancy is not unreasonably large, as also binding energies calculated within this point-charge model show differences of about 1 eV from experimental values.[9] If a corrected ϵ_{th}^c is used, $\epsilon_{\text{th}}^c = \epsilon_{\text{th}} + 2.2$ eV, setting $\epsilon_{\text{th}}^c(\text{KF}) = 0$, we get very good agreement for all other ϵ values, as can be seen in Table I. It can also be seen that for NaF, MgF_2, and CaF_2 no M lines are expected because $|\epsilon|$ is too large and far away from the resonance condition.

Here we want to mention that an interatomic Auger transition[8] of the type AAB, where a hole in atom A is filled by an electron of atom A and an electron of atom B is emitted, would also give an additional M line separated by the same energy ϵ as in this RET model. But with use of the interatomic Auger transition model there are the following problems: (a) The probability for AAB transitions is always much lower than for intra-atomic AAA transitions,[8] so that the high intensity of the M line in KF cannot be explained. (b) The AAB transitions have no resonance condition, so that in first approximation all M lines from these fluorides should have the same relative intensity and this is not in agreement with the experiment. (c) An additional splitting δ is not expected, and the measured energy separation Δ between the A and M lines which is different from ϵ cannot be explained. To point the difference, in this RET model always intra-atomic Auger transitions of the type AAA are considered with a subsequent RET relaxation.

In conclusion, a new line is observed in some fluorine K Auger spectra and for KF a split of the main Auger line in two lines of almost the same intensity is found. This is one of the largest chemical effects on Auger spectra yet observed. The energy and intensity variations of this line depending on the metal ion are consistent with a new proposed resonant electron-transfer relaxation mechanism. This relaxation process describes a resonant electron transfer between the outer np level of the metal ion and the fluorine $2p$ level, if the total energies of the two configurations match. The electron is then forming a molecular orbital-like state between the metal and the fluorine ion. This RET relaxation process may also be important and should be considered in the interpretation of Auger spectra of other ionic solids involving outer-shell electrons.

---

[a] Present address: Institut für Experimentalphysik, Universität Linz, Linz, Austria.

[1] S. Aksela, R. Kumpula, H. Aksela, and J. Väyrynen, Phys. Scr. **25**, 45 (1982).

[2] S. P. Kowalcyk, L. Ley, F. R. McFeely, R. A. Pollack, and D. A. Shirley, Phys. Rev. B **9**, 381 (1974).

[3] O. Benka, R. L. Watson, and R. A. Kenefick, Phys. Rev.

Lett. **47**, 1202 (1981).

[4] G. Deconninck and S. Van Den Broek, J. Phys. C **13**, 3329 (1980).

[5] R. T. Lewis and M. A. Kelly, J. Electron. Spectrosc. **20**, 105 (1980).

[6] M. Uda, K. Maeda, A. Koyama, and Y. Sasa, Phys. Rev. A **29**, 1258 (1984).

[7] P. H. Citrin and T. D. Thomas, J. Chem. Phys. **57**, 4446 (1972).

[8] P. H. Citrin, J. E. Rowe, and S. B. Christman, Phys. Rev. B **14**, 2642 (1976).

[9] R. T. Poole, J. Liesegang, R. C. G. Leckey, and J. G. Jenkin, Phys. Chem. Lett. **23**, 194 (1973).

[10] R. T. Poole, J. Szajman, R. C. G. Leckey, J. G. Jenkin, and J. Liesegang, Phys. Rev. B **12**, 5872 (1975).

[11] *CRC Handbook of Chemistry and Physics,* edited by Robert C. Weast (CRC Press, Boca Raton, Fla., 1980), 61st ed.