Studies on the Chemical Shifts of Auger Electron Energies for Magnesium and Zinc in Their Compounds

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The energy shifts of X-ray excited Auger electrons and photoelectrons for zinc and magnesium in their metals, oxides, halides, and chelate compounds are analyzed in terms of the relaxation effect. Zn $2p_{3/2}$, 3d photoelectron, Zn $L_3M_{45}M_{45}{}^1G$ Auger electron, Mg ls, 2p photoelectron and Mg $KL_{23}L_{23}{}^1D$ Auger electron peaks were provided for the investigation. The quantitative estimation of the extra-atomic relaxation energies for core electron emission was performed by combining atomic spectral data, XPS and AES data of the compounds. For zinc compounds, extra-atomic relaxation energies increase in the order of $ZnF_2 < ZnCl_2 < ZnBr_2 \approx ZnO < ZnI_2 \approx ZnS <$ $Zn(acac)_2$, whilst the values are not fairly systematic for magnesium compounds. The nearest neighbored atom is found to be the important function for the extra-atomic relaxation energies.

Few investigations on the XPS for inner shell electrons of magnesium or zinc atoms in their compounds have been undertaken[1-3] because of the small chemical shifts in these binding energies. For zinc halides, shifts of zinc 3d bands have been discussed in terms of the ionic character of the zinc–halogen bonds[4] measured in vapor phase in UPS. For zinc, Auger spectra were measured for atom,[5,6] zinc metal, oxide, and fluoride.[7] Kowalczyk[7] *et al.* have given a theoretical interpretation of Auger energies and discussed the shifts of extra-atomic relaxation energies for zinc in metal, oxide, and fluoride. Hoogewijs *et al.*[8,9] have given a similar but improved results for the analysis of Auger electron energies of zinc atom and metal. No data have been explored about the Auger emission of magnesium compounds other than that of magnesium atom,[10] metal, and oxide.[11]

In this paper, we report on the chemical shifts of the core level electron binding energies and Auger electron energies for zinc and magnesium in their metals and compounds. Atomic spectral data for these elements are applied here to elucidate the extra-atomic relaxation energies in Auger electron emission. For oxides, sulfides and halides, extra-atomic relaxation energies were corelated with polarizabilities of ligands. In both elements, common ligands give the same extent of contributions to the extra-atomic relaxation energy shifts of host atoms.

Experimental

Spectra of photoelectrons and Auger electrons were recorded by AEI ES 200 type spectrometer with the Al $K\alpha_{1,2}$ X-ray source. The pressure in the sample chamber was maintained at about 5×10^{-8} Torr (1 Torr=133.322 Pa) during the measurements.

Magnesium and zinc metal films were provided for the investigation by evaporating them onto the sample holder.

Testing samples for zinc chloride, bromide, and iodide were deposited onto a stainless holder plate by using a platinum filament. The XPS spectra of these halides were free from the background O ls and C ls photoelectron peaks. Original magnesium chloride and magnesium bromide were obtained by pyrolysis of their double salts with ammonium chloride and ammonium bromide. The dehydration of magnesium iodide was carried out with heating in vacuum.

8-Quinolinolate complexes for zinc and magnesium were prepared by the ordinary method[12] and dehydrated by heating at 150 °C for a few hours.

All the other samples were obtained from commercial sources without further purification.

Solid samples other than halides and metals were powdered and pressed onto the cellophane tape placed on the metal holder to provide for the X-ray exposure.

The energy scale of the spectra was calibrated with reference to the photoelectron energies of the following levels of standard materials: Pd $4d_{5/2}$, Au $4f_{7/2}$, Pd $3d_{5/2}$, Ag $3d_{5/2}$, and Ag $3p_{3/2}$ of highly pure metallic palladium, gold, and silver. From a knowledge of the spectrometer constant thus obtained,[13] the measured values of kinetic energies for various levels in samples were corrected. The binding energies of $4f_{7/2}$ photoelectron peak of gold (83.8 eV) deposited onto each sample were measured and used to evaluate the extent of charging of the respective solid.

Results

The binding energies of 1s and 2p photoelectrons and $KL_{23}L_{23}$ Auger electron energies for all of the measured magnesium compounds are summarized in Table 1.

For zinc compounds, the binding energies of $2p_{3/2}$, 3d and $L_3M_{45}M_{45}$ Auger peaks are summarized in Table 2. Each value for the shifts of these energies referred to those of the respective fluorides is also listed in the tables.

In the photoelectron and the Auger electron spectra for magnesium metal film, peaks due to the partially oxidized magnesium are observed, but no such oxidized peaks were observed for zinc metal in both photoelectron and Auger electron spectra. A satellite peak due to the plasmon loss is observed at the 10.8 eV lower kinetic energy side of the main peak in both photoelectron and Auger electron spectra for magnesium metal. The absence of the O 1s peak in zinc halides gives the evidence of the complete dehydration of these samples by the evaporation method.

In spite of the careful preparations, O 1s photoelectron peak was slightly observed in magnesium chloride, bromide and iodide spectra. For a zinc 8-quinolinolate compound, O 1s peak with rather high intensity was observed compared with the intensity of N 1s peak, despite of the heating at 150 °C for a few hours. On the other hand, the spectrum for magnesium 8-quinilinolate showed appropriate intensity of O 1s photoelectron peak to the predicted stoichiometric value for its structure.

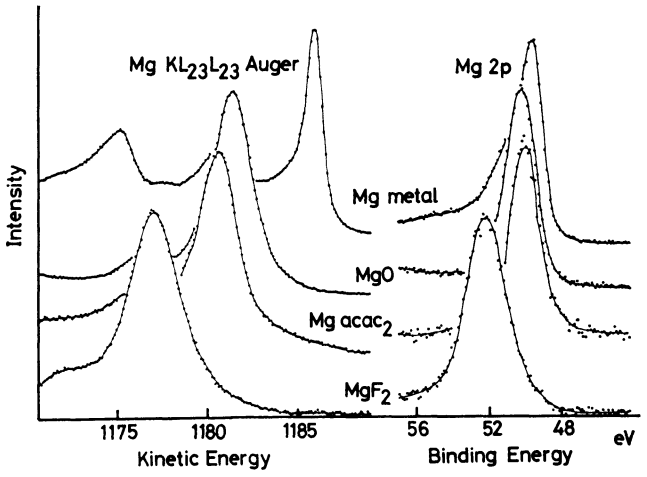

Fig. 1. Magnesium 2p photoelectron and $KL_{23}L_{23}$ Auger electron spectra for various magnesium compounds.

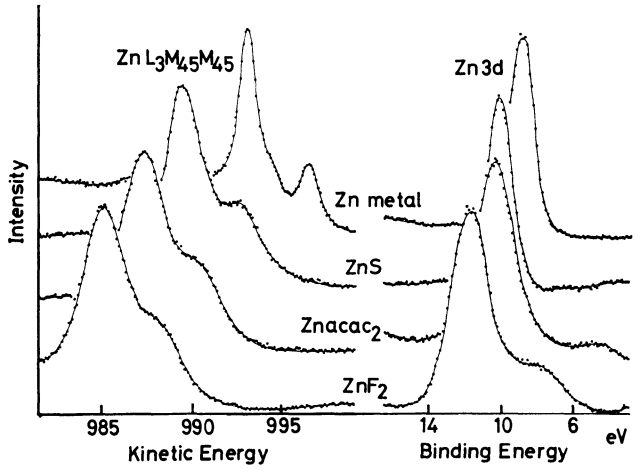

Fig. 2. Zinc 3d photoelectron and $L_3M_{45}M_{45}$ Auger electron spectra for various zinc compounds.

For the other chelate compounds of magnesium and zinc, the intensity ratios in each photoelectron peak give good agreements with the predicted ratios from their structures.

In Fig. 1 the spectra of Mg $KL_{23}L_{23}$ Auger electron and 2p photoelectron for magnesium metal, magnesium oxide, magnesium acetylacetonate, and magnesium fluoride are shown. Also those of Zn $L_3M_{45}M_{45}$ Auger electron and 3d photoelectron for zinc compounds are shown in Fig. 2.

The chemical shifts of Auger lines are larger than those of photoelectrons for both elements in all the compounds.

The magnitudes of the shifts of these lines for each metal referred to their fluorides are the largest of the compounds investigated for both elements. The energy separations of the binding energies between magnesium 1s and 2p photoelectrons are as constant as those between zinc 2p and 3d orbital electrons in all the compounds.

Discussion

As shown in Tables 1 and 2, chemical shifts of Auger electrons are larger than those of photoelectrons. This

Table 1. Chemical shifts of photoelectron binding energies (ΔE_b), Auger electron energies (ΔE_{Auger}) and extra-atomic relaxation energies (R^{ea}) for magnesium compounds

Sample	Mg 2p		Mg $KL_{23}L_{23}(^1D)$		R^{ea}
	E_b	ΔE_b	E_{Auger}	ΔE_{Auger}	
Mg metal	49.7	2.5	1185.9	8.9	15.2
MgF_2	52.2	(0.0)	1177.0	(0.0)	8.8
$MgCl_2$	51.7	0.5	1179.5	2.5	10.8
$MgBr_2$	50.5	1.7	1180.8	3.8	10.9
MgI_2	49.6	2.6	1181.1	4.1	10.3
MgO	50.3	1.9	1181.0	4.0	10.9
[Mg(oxine)[a]$_2$]	49.2	3.0	1182.0	5.0	10.8
[M(acac)[b]$_2$]	50.0	2.2	1180.6	3.6	10.2
Na_2[Mg(edta)]	50.2	2.0	1180.6	3.6	10.4

a) oxine=8-quinolinolate ion. b) acac=acetylacetonate ion=2,4-pentanedionate ion. c) edta=ethylenediaminetetraacetate(4−) ion.

can be interpreted in terms of the larger relaxation energy due to the final state after two-electron ejection in Auger process, as described in the following equation.[7,14–16]

$$E_{Auger}(KLL) = E(K) - 2E(L) + R - F, \quad (1)$$

where $E(K)$ and $E(L)$ are the photoelectron binding energies of 1s and 2p orbitals, respectively, and F is a two-electron interaction term, for which Asaad and Burhop[17] have made a theoretical analysis by taking into account the effect of intermediate coupling in the two-hole final state for KLL Auger transitions. R is a so-called static relaxation energy according to the definition after Shirley.[7] It may be separated into two parts, atomic and extra-atomic static relaxation energies. Static atomic relaxation energy should be twice the dynamic relaxation energy, E_R,[18] accompanied with photoelectron emission. Extra-atomic static relaxation energy, R^{ea}, is the relaxation energy due to surrounding atoms in the electron emission process. Then, Eq. 1 is expressed as follows.

$$E_{Auger}(KLL) = E(K) - 2E(L) + 2E_R + R^{ea} - F. \quad (2)$$

For a free atom, R^{ea} value in Fig. 2 is zero and the following equation will be established.

$$E^A_{Auger}(KLL) = E^A(K) - 2E^A(L) + 2E^A_R - F, \quad (3)$$

where E^A means the energy term for a free atom. The photoelectron binding energy for a free atom is referred to the vacuum level, and the kinetic energy of an Auger electron is independent of the excitation energy. When a measurement is carried out using characteristic X-ray with the energy of $h\nu$, Eq. 3 is expressed as follows.

$$2E_R - F = (E_b(K) - E_b(L)) + (E_{kin}(L) - E_{Auger}(KLL)) - h\nu, \quad (4)$$

where $E_b(K) - E_b(L)$ is equivalent to the value $E_{kin}(L) - E_{kin}(K)$. Then, $2E_R - F$ can be obtained directly from the observed kinetic energies for each peak. Here, the energy level for an Auger electron could be defined with just the same reference as that for photoelectron binding energy.

TABLE 2. CHEMICAL SHIFTS OF PHOTOELECTRON BINDING ENERGIES (ΔE_b), AUGER ELECTRON ENERGIES (ΔE_{Auger}) AND EXTRA-ATOMIC RELAXATION ENERGIES (R^{ea}) FOR ZINC COMPOUNDS

Sample	Zn $2p_{1/2}$		Zn 3d		Zn $L_3M_{45}M_{46}(^1G)$		R^{ea}
	E_b	ΔE_b	E_b	ΔE_b	E_{Auger}	ΔE_{Auger}	
Zn metal	1020.6	2.8	8.9	2.8	993.1	8.1	14.7
ZnF_2	1023.4	(0.0)	11.7	(0.0)	985.1	(0.0)	9.5
$ZnCl_2$	1022.5	0.9	10.8	0.9	987.2	2.1	10.7
$ZnBr_2$	1022.6	0.8	10.9	0.8	987.8	2.7	10.4
ZnI_2	1022.3	1.1	10.6	1.1	989.0	3.9	12.3
ZnO	1022.2	1.2	10.5	1.2	988.0	2.9	11.2
ZnS	1021.9	1.5	10.2	1.5	989.5	4.4	12.4
[Zn(acac)[a]$_2$]	1022.1	1.3	10.4	1.3	987.3	2.2	10.4
[Zn(oxine)[b]$_2$]	1022.5	0.9	10.8	0.9	987.1	2.0	10.6
[Zn(pc)][c]	1021.8	1.6	10.1	1.6	988.6	3.5	11.4

a) acac: acetylacetonate ion (2,4-pentanedionate ion). b) oxine: 8-quinolinolate(2−) ion. c) pc: phthalocyanine.

In a similar fashion for a solid sample, both photoelectron binding energy and Auger electron kinetic energy must be referred to the same level.

Then, the electron energy values can be scaled from the reference level, that is, electrons at the reference level are to be photoejected with the kinetic energy of $h\nu$. In this paper, both photoelectron and Auger electron energies are referred to the Fermi level.

Using Eq. 3 the numerical values of $2E_R^A - F$ term can be estimated for magnesium atom on the basis of the following data; the energy value, 1167.3eV for Mg KL_{23}-$L_{23}{}^1D$ in magnesium atom measured by Breuckmann and Schmidt,[10] the binding energy of 2p orbital electron, 57.64 eV, estimated from the atomic spectral data[19] and 1s orbital binding energy, a sum of the binding energy of 2p orbital and magnesium $K\alpha$ X-ray energy 1256.6 eV[20] being equal to 1311.24 eV. Then the value for $2E_R^A - F$ term is calculated to be −28.66 eV. The result is graphically shown in Fig. 3.

For magnesium, the sum of $2E_R - F$ in Eq. 2 is considered to be equal for all the compounds and then the extra-atomic relaxation energy, R^{ea}, a parameter for the characterization of molecular environment surrounded by a host atom, could be estimated with the following method. As magnesium in its compounds under investigation exists as cation with oxidation number +II, no 3s orbital electrons are assumed to contribute to the atomic relaxation effect. Then, the atomic relaxation of magnesium ion, $2E_R$, was calculated by subtracting the relaxation energy due to 3s orbital electrons and we obtained the value of 3.9 eV by using Slater's orbitals and equivalent core model.[21,22]

$$-F + 2E'_R = -33.02\ \text{eV}$$

where E'_R is dymanic relaxation energy ignoring 3s electrons.

On the other hand, as shown in Fig. 4, the value of $2E_R - F$ can be directly estimated from atomic data[19] for magnesium ion with a similar fashion for magnesium atom. That is, the value can be obtained as a difference between ionization potentials of the spectroscopic MgIII(Mg^{2+}) and MgIV(Mg^{3+}) states, −29.17 eV. As the lowest energy state of $MgV(2s)^2(2p)^4$ is $^3P_2$ in optical term, $-F+2E_R'$ value corresponding to ^1D state can be obtained from a energy difference between $^3P_2$ and ^1D states, 3.8 eV, as follows:

$$-F + 2E'_R = -32.97\ \text{eV}$$

The value is in good agreement with the former results. Utilizing this value with the observed Mg $KL_{23}L_{23}{}^1D$ Auger electron energy, and 1s and 2p photoelectron binding energies, extra-atomic relaxation energy, R^{ea}

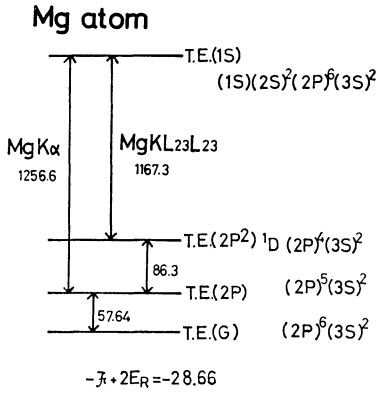

Fig. 3. Total energy (T.E.) level diagram of a free magnesium atom for various core-ionized electron configurations (eV).

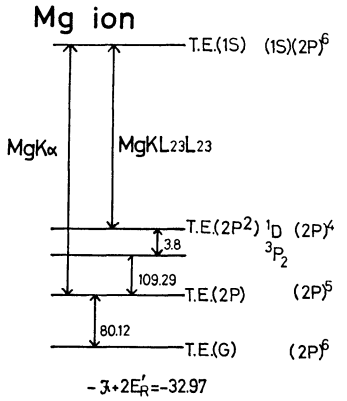

Fig. 4. Total energy (T.E.) level diagram of magnesium ion (+2) for various core-ionized electron configurations (eV).

could be calculated for various magnesium compounds.

For zinc Auger electrons, $L_3M_{45}M_{45}{}^1G$ electron with the highest intensity is adopted to calculate the extra-atomic relaxation. For the fourth ionization potential of zinc atom, the value obtained by Lotz[23] was used and the energy separation between ^1G and $^3F_4$, the lowest energy state of $Zn(Zn^{4+})$ ion ($3d^84s^0$), has the measured value of 3.75 eV for the free zinc atom.[5] The result obtained from these data is graphically shown in Fig. 5.

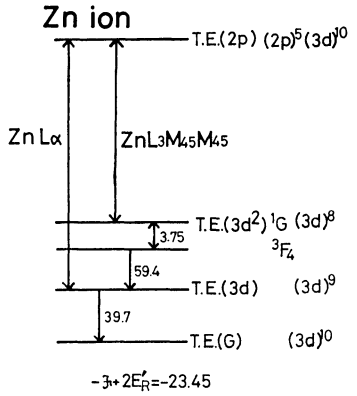

Fig. 5. Total energy (T.E.) level diagram of zinc ion (+2) for various core-ionized electron configuration.

In Tables 1 and 2, the extra-atomic relaxation energies obtained by the above mentioned method (Eq. 2) for various magnesium and zinc compounds are shown, respectively.

The distance between Auger electron and photoelectron peaks is independent of the reference level. The ambiguity of reference level or charging effect can be canceled out. Wagner[24] has also noted this energy difference and defined a parameter for Auger chemical shift. He found out that the shifts of this parameter qualitatively obey the trend of Pearson's concept of soft-hard acid and base character of bonding atoms to host atom. The shift of Auger parameter can be identified with the change of the magnitudes R^{ea}, assuming $E(K)-E(L)$ and $-F+2E_R$ to be constant for all the compounds.

For zinc halides, the electron binding energies of Zn $2p_{3/2}$ are nearly the same for all the compounds but fluoride, whereas the shifts in R^{ea} are clearly progressive and the order of the magnitudes of R^{ea} is quite coordinated with polarizabilities of halide ions. Although the Zn $2p_{3/2}$ binding energies in zinc oxide are the same with that of zinc iodide, R^{ea} in zinc iodide is larger than that in zinc oxide. This corresponds to the fact of the larger polarizability of iodide ion than that of oxygen ion. Sulfide ion with a large polarizability shows a large relaxation energy in zinc sulfide. For three zinc chelate complexes, the order of magnitudes in extra-atomic relaxation energies obeys the donicity of the coordinated atoms, that is, is in the order of O–O, O–N, and N–N.

A plot of the measured relaxation energy *vs.* the product of polarizability[25,26] for a neighbored surrounding atom and the inverse of the nearest neighbor distance[27] for various zinc compounds is shown in Fig. 6. It is seen that the extra-atomic relaxation energies are linearly related to the polarization energies due to nearest neighbored surrounding atoms. A value obtained by extrapolating the line, the intercept of the line with the ordinate, 8.8 eV, means the residual relaxation energies which are commonly contributed to all the compounds. A part of this residual relaxation energies may be due to contributions from all the atoms in crystal except the host and nearest neighbored atoms. The second important contribution may be the participation of 4s orbital electrons. In order to calculate the extra-atomic relaxation energies for zinc compounds, the assumption has been made for 4s orbital electrons to be absent from the host atom, leaving it ideally in Zn^{2+} ion state. Thus, the relaxation energies due to the charge density on zinc atom may be considered as the sum of those localized to the host atom, the values dependent on the bonding character being proportional to the polarizability of surrounding atoms.

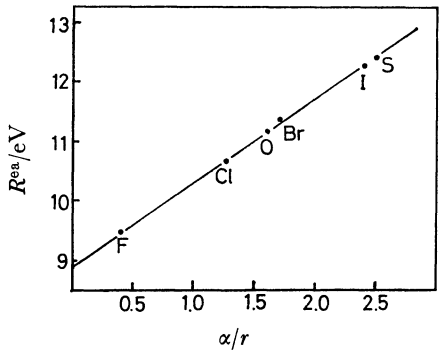

Fig. 6. Corelation between extra-atomic relaxation energies and polarizabilities of neighbor atoms divided by nearest neighbor distance for zinc compounds.

For magnesium halides except for fluorides, the extra-atomic relaxation energies are nearly the same and the order of the magnitude does not correspond to that in zinc halides. Ambiguity exists on the electron emission data sources because of the hydroscopic character of these compounds. For three magnesium chelate compounds investigated, magnesium bonding with nitrogen and oxygen in 8-quinolinol shows the largest relaxation energy. This means that the contribution of nitrogen to relaxation energy may be larger than that of oxygen, like the case of zinc chelate complexes.

The extra-atomic relaxation energies due to the same ligand in both magnesium and zinc compounds are in good agreement with each other except for the bromide and iodide, as shown in Tables 1 and 2.

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