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Chemical-state Analysis by Means of Soft X-Ray Spectroscopy. III. O *K*α Emission Spectra for Oxyanions in Different Salts

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The oxygen *K*α spectra of the oxyanions in different salts are obtained by secondary excitation. The obtained spectra are affected by the cations, the central atom, and the chemical-bond condition. Generally, there are four components in the spectra, but one small component may originate from the anomalous reflection of an analyzing crystal. The spectra are discussed from the point of view of chemical-state analysis.

Until a few years ago valence-band spectra originating from the electron transition from the valence-band orbitals to the inner-core level were interpreted by studying the complex interactions involving an isolated atomic model or by using solid-state-band models. Because X-ray emission involves two levels, the chemical effect is the result of the shift of the core level and of the structure of the valence-band orbital levels. Therefore, the X-ray-emission spectra can be directly applied, using standard sample systems, for the identification of an unknown valence state and for investigations of the electronic structures of chemical compounds.

In previous papers[1,2] and companion papers,[3,4] we have studied the valence-band spectra, that is the $L_{2,3}$ emission and $K\beta$ spectra for phosphorus, sulfur, and chlorine, in various compounds and discussed the spectral profile from the point of view of chemical-state analysis. It is concluded that the spectral features of the $K\beta$ or $L_{2,3}$ emission spectra are especially influenced by the oxygen of the ligand. In the ground state, two 2s-electrons and four 2p-electrons are present in the valence band, but they will obviously be directly involved in bonding. The O*K*α spectrum yields information only about the valence orbitals containing the O-2p population, because the spectra reflect the p-like symmetry on account of the dipole-selection rule. In general, the O-2p electron is related to valence-band orbitals when oxygen combines with another atom. Therefore, one can expect to get information about the electronic structure and be able to apply it to the chemical-state analysis from the results of the analysis of the O*K*α spectra.

The first evidence in studies of the O*K*α spectra in various oxide compounds that the X-ray spectra were influenced by the chemical combination was reported on the 1940's;[5,6] using the direct electron bombardment. As samples are decomposed under such electron bombardment, however, fluorescence excitation is frequently used in the region of soft X-rays.[7–11] Recently, O*K*α spectra have been obtained using low-energy-electron-induced X-ray spectroscopy,[12] a high-resolution concave-grating-grazing incidence spectrometer,[13] synchrotron radiation as a light source for the excitation of substances,[14,15] or the ion-induced X-ray excitation method.[16] Andermann *et al.* have measured the O*K*α spectra for the oxide compounds with a grating spectrogaph and discussed the C–O bond on the basis of the spectra thus obtained[17] by applying spectral techniques of such efficiency as to minimize the effects of radiation decomposition. Kosuch *et al.* have shown that the comparison of the O*K*α spectrum with the other X-ray spectra is a useful technique for the investigation of the electronic structures of chemical compounds.[14,15]

In this and in companion papers[3,4] we present the results of chemical-state analysis by means of soft X-ray spectroscopy; in this paper we will also try to make clear the relationship between the character of the chemical state and the O*K*α emission spectra.

Experimental

Measurements of the oxygen *K*α spectrum were carried out using the single flat-crystal spectroscopic method with a TAP($2d$=25.8 Å) analyzing crystal. The basic spectrographic approach that is used in this laboratory is shown in Fig. 1. The X-ray spectrometer is a vacuum type equipped with a fine Soller collimator 10 cm long and with 0.08 mm spacing. It has a simple close-coupling of a high-intensity, demountable, low-energy X-ray excitation source. The most intense and practical line source in the oxygen *K* excitation is Cu*L*α (13.3 Å). It is generated in a demountable Henke-type tube[18] using a copper anode. The source is stable for many hours of operation, typically at 9 kV and 220 mA. The X-ray tube window is constructed of 6 μm polycarbonate film with an aluminum coating a few hundred angstroms thick. Propane gas at a pressure of 65 mmHg (1 mmHg≈133.322 Pa) is used as the proportional counting gas, and the counting gas in the counter is isolated from the vacuum chamber with poly(vinyl formal). This spectroscopic approach has been described in detail elsewhere.[18,19] As the oxygen *K*α emission spectra analyzed with a KAP crystal show a strong anoma-

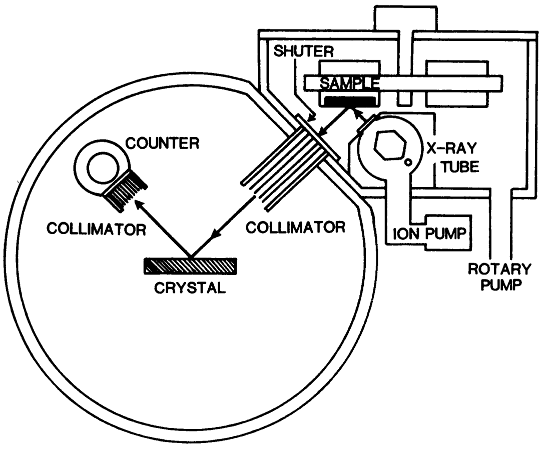


Fig. 1. A single-crystal spectrographic approach for low energy X-ray spectroscopy applying closely coupled demountable X-ray source.

lous peak on the high-energy side of the main peak,[8,20] a flat TAP was used as the analyzer crystal. The solid specimens were prepared by pressing a fine powder into a smooth aluminum ring in order to keep the target sample pure and at a constant pressure. In order to insure that the radiation decomposition effect upon these measurements was negligible, the measurement was done twice for each spectrum with two identical samples. The total counting times were 30 s per point, and the counter was scanned, step by step, by 0.05° of 2θ arm.

Results and Discussion

The spectral features of the O$K\alpha$ spectra for Li_3PO_4, Li_2SO_4, and $LiClO_4$ are compared in Fig. 2. The anions of these compounds all have the T_d molecular symmetry, but with different central atoms. There are mainly four components. These components are probably related to the molecular orbital in the valence band. There are seven occupied orbitals ($4a_1$, $3t_2$, $5a_1$, $4t_2$, 1e, $5t_2$, and $1t_1$) in the valence band for these T_d molecular symmetries. The main peak C originates from the electron transition from the O-2p lone-pair level ($1t_1$) to the O-1s core level. The hump B on the lower-energy side of the main peak probably orignates from the $5t_2$ and 1e molecular orbitals, whose molecular orbitals consist mainly of the oxygen-2p and the central atom-3d population. The peak A on the lower-energy side should be assigned to $4t_2$, with its comparatively high 3p population of the central atom and its relatively poor 2p population of the oxygen. The peak C and the hump B shift to the higher-energy side, and the peak A shifts to the lower-energy side, in proportion to the increase in the atomic number of the central atom with the T_d molecular symmetry. Thus, the domain of the spectra of interest is expanded in proportion to the increase in the atomic number of the central atom.

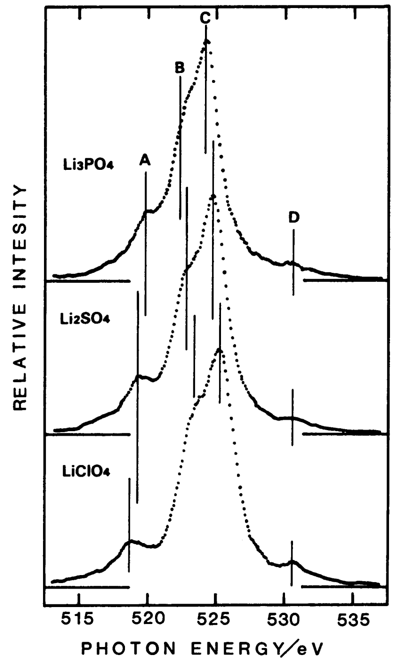


Fig. 2. Comparison of the O$K\alpha$ emission spectra for Li_3PO_4, Li_2SO_4, and $LiClO_4$. O$K\alpha$ spectra have been excited by Cu$L\alpha$ radiation and analyzed by TAP crystal.

In general, there are similar features of the $L_{2,3}$ emission spectra or the $K\beta$ spectra for all anions having the T_d molecular symmetry, though with different central atoms, although the energy ranges of the emission spectra are different,[3,4] and the domain of spectra of interest is expanded in proportion to the increase in the atomic number of the central atom. It should be noted that the peak position of D reveals scarcely no influence of the central atom. It seems reasonable to say that the peak D is due to an enhanced reflectivity of the analyzed crystal with the local continuum background in this energy region.[8]

In companion papers,[3,4] the $L_{2,3}$ emission spectra of the central atom are reported to reveal scarcely no influence of the cations for the phosphate, sulfate, or perchlorate compounds, but the $K\beta$ spectra of the central atom are affected just a little by the cation for these compounds. Kosuch *et al.* conclude that the oxygen $K\alpha$ spectra of oxyanions from different salts do not show any influence of the cation within the limits of accuracy of the measurements.[14] The oxygen $K\alpha$ spectra for lithium sulfate, sodium sulfate, and potassium sulfate are compared in Fig. 3 in order to consider the influences of the cations. Here, the intensity (in arbitrary units) is presented as a function of the 2θ of the Bragg angle θ. Each of the experimental spectra was resolved into its component lines in order to consider

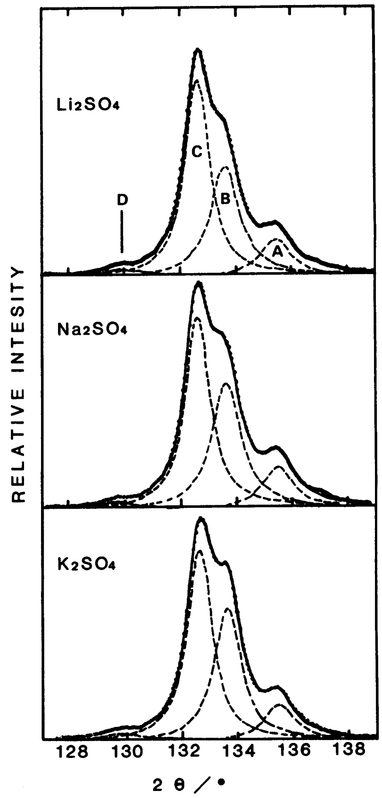


Fig. 3. Comparison of the O$K\alpha$ emission spectra for Li_2SO_4, Na_2SO_4, and K_2SO_4 in order to consider the influences of cations. O$K\alpha$ spectra have been excited by Cu$L\alpha$ radiation and analyzed by TAP crystal. Fit through the experimental points is the sum of convolution function of Lorentzian components with Gaussian function.

it more efficiently. The outmost line is the fitting curve, which is the sum of the emission components, which are also plotted here. Each line component is used as the convolution function, alone the with Lorentzian and Gaussian functions. It can be seen that the peak component B is affected little by the cation. As the main peak C originates from the lone-pair orbital $1t_1$, it seems reasonable to say that the peak C reveals scarcely no influence of the cation. On the other hand, the peak B and the peak A should be affected by the cations, because the oxygen atom is directly related to the cation. It seems that the hump B grows in proportion to the atomic number of the cations. The intensity ratios of the peaks C and B are 0.56, 0.65, and 0.75 for lithium sulfate, sodium sulfate, and potassium sulfate respectively.

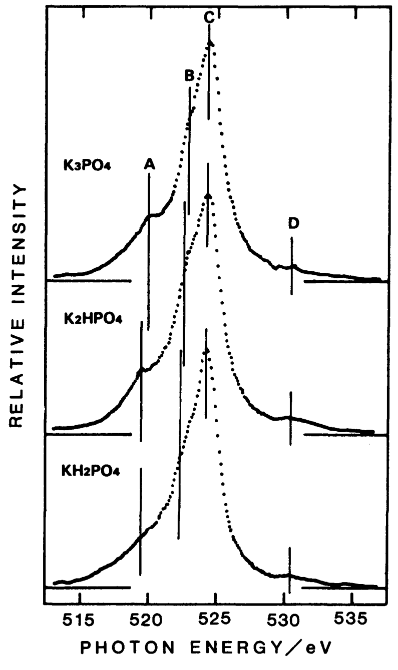


Fig. 4. Comparison of the O*Kα* emission spectra for K_3PO_4, K_2HPO_4, and KH_2PO_4. O*Kα* spectra have been excited by Cu*Lα* radiation and analyzed by TAP crystal.

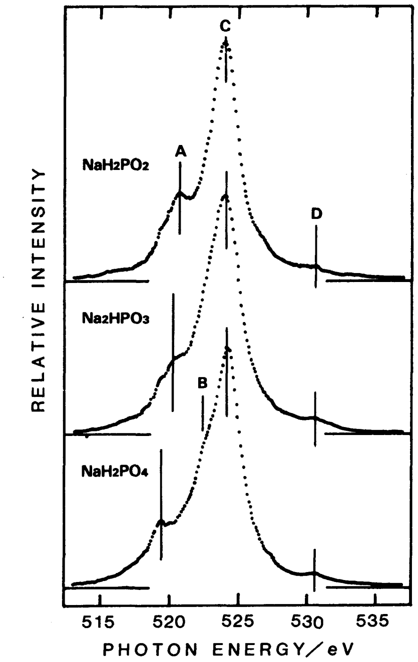
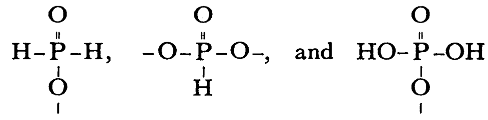


Fig. 5. Comparison of the O*Kα* emission spectra for NaH_2PO_2, Na_2HPO_3, and NaH_2PO_4. O*Kα* spectra have been excited by Cu*Lα* radiation and analyzed by TAP crystal.

The O*Kα* spectra for K_2HPO_4, and KH_2PO_4, in each of which the metallic cation is replaced by hydrogen, are compared with K_3PO_4 in Fig. 4. The spectral features of the O*Kα* spectra for their compounds are especially influenced by hydrogen, as are the $L_{2,3}$ emission spectra (in Ref. 3). The peaks A and B shift to the lower-energy side, and the peak A decreases in proportion to the relation with hydrogen. This phenomenon is very different from the *Kβ* spectra (in Ref. 4), because the peak on the lower-energy side of the main peak of *Kβ* shifts to the higher-energy side and increases in proportion to the relation with hydrogen. It can be noted from the *Kβ* spectra that the molecular level concerning the O–H bond is created on the lower-energy side of the $4t_2$ level, which consists mainly of the 3p population and which is and shifted to near the $4t_2$ level in proportion to the relation with hydrogen. On the other hand, the electron population of oxygen-2p diffuses to lower-energy molecular orbitals with the relation with hydrogen. Figure 5 shows the same phenomenon in the O*Kα* spectra for NaH_2PO_2, Na_2HPO_3, and $NaHPO_4$. The O*Kα* spectrum for NaH_2PO_4, consists of three components A, B, and C. However, the O*Kα* spectra for NaH_2PO_2 and Na_2HPO_3 consist of only two components, A and C. Moreover, the peak A of NaH_2PO_2 shifts to the higher-energy side as compared with the cases of NaH_2PO_4 and Na_2HPO_3. The structural formulas for $H_2PO_2^-$, HPO_3^{2-}, and $H_2PO_4^-$ are;



$$\mathrm{H{-}\underset{\underset{\underset{|}{O}}{|}}{\overset{\overset{O}{\|}}{P}}{-}H},\quad \mathrm{{-}O{-}\underset{\underset{H}{|}}{\overset{\overset{O}{\|}}{P}}{-}O{-}},\quad \text{and}\quad \mathrm{HO{-}\underset{\underset{\underset{|}{O}}{|}}{\overset{\overset{O}{\|}}{P}}{-}OH},$$

respectively. In the structural formula of $H_2PO_4^-$, the central P atom combines directly with oxygen only, but the partial oxygen atoms combine with hydrogen. In the structural formulas of $H_2PO_2^-$ and HPO_3^{2-}, on the other hand, the central P atom combines directly with oxygen and hydrogen, but the oxygen atom does not combine with hydrogen. In the case of the O*Kα* spectra for NaH_2PO_2, and Na_2HPO_3, the hump B does not appear. Therefore, it seems that the hump B appears when the central atom combines directly with O ions (including OH ions). In the structural formulas of $H_2PO_2^-$ or HPO_3^{2-}, the central P atom combines directly with only two or three oxygen atoms respectively. It may be seen that the peak A is related with the number of the oxygen which is combined with the central atom of the oxyanion, and is shifted to the lower-energy side in proportion to the number of the directly combined oxygen atom with the central atom. Moreover, the peak A for these compounds shifts to the higher-energy side compared with the case of K_3PO_4. It is reasonable that the peak A is related with the number of oxygen which is combined with the central atom of the oxyanion and is shifted to the lower-energy side in proportion to the number of oxygen.

Figure 6 compares of the O$K\alpha$ spectra for sodium sulfite (Na_2SO_3) and sodium sulfate (Na_2SO_4) with their hydrogensulfite ($NaHSO_3$) and hydrogensulfate ($NaHSO_4$). There are two components in the O$K\alpha$ spectra in the case of SO_3^{2-}, but three components in the case of SO_4^{2-}. The spectral domain of SO_4^{2-} expands compared with that of SO_3^{2-}. The sharpness of the spectra for $NaHSO_3$ or $NaHSO_4$ is inferior to that for Na_2SO_3 or Na_2SO_4 respectively. It seems that the spectral components are broadened a little with the relation to hydrogen.

In Figs. 7 and 8, the relations between the spectral features and the coodination number of oxygen are shown. In both cases, the main peak C shifts to the higher-energy side and the peaks A and B shift to the lower-energy side according to the coodination number of oxygen. However, each peak component shifts to the higher-energy side in the case of the $K\beta$ spectra, and the middle peak only shifts to the higherenergy side, but the higher-energy peak increases in the case of the $L_{2,3}$ emission spectra in proportion to the coordination number of oxygen.

As the chemical effect of the X-ray spectra is the result of the shift of the core level and of the structure of the valence-band orbitals, the variation in the spectral profile will give us information about valence-band orbitals, because the core level is shifted simply with differ chemical states.

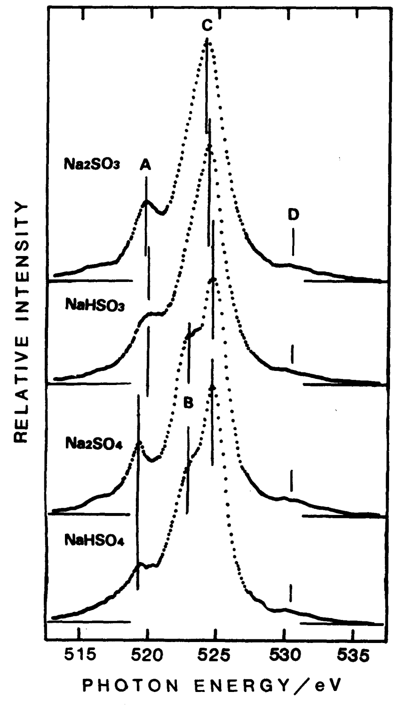


Fig. 6. Comparison of the O$K\alpha$ emission spectra for Na_2SO_3, and Na_2SO_4, with $NaHSO_3$ and $NaHSO_4$. O$K\alpha$ spectra have been excited by Cu$L\alpha$ radiation and analyzed by TAP crystal.

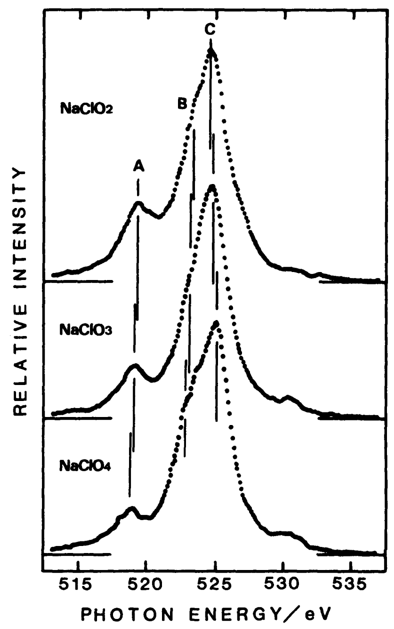


Fig. 7. Comparison of the O$K\alpha$ emission spectra for $NaClO_2$, $NaClO_3$, and $NaClO_4$. O$K\alpha$ spectra have been excited by Cu$L\alpha$ radiation and analyzed by TAP crystal.

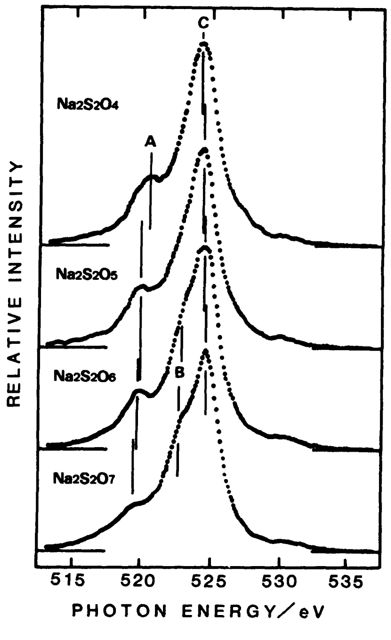


Fig. 8. Comparison of the O$K\alpha$ emission spectra for $Na_2S_2O_4$, $Na_2S_2O_5$, $Na_2S_2O_6$, and $Na_2S_2O_7$. O$K\alpha$ spectra have been excited by Cu$L\alpha$ radiation and analyzed by TAP crystal.

Conclusion

In this work, it has been shown that a spectral feature is closely affected by the chemical state and that the O$K\alpha$ spectra give us not only information for studies of molecular orbitals, but also provide a useful technique for application to chemical-state analysis, because oxygen 2p is related in almost all molecular orbitals of the valence band. The following properties have been found:

1) The O$K\alpha$ spectra for oxyanions are expanded in proportion to the increase in the atomic mumber of the central atom.

2) The O$K\alpha$ spectra are affected a little by the cations, because oxygen atom is directly related to the cation. This conclusion is very different from that is the case of the $L_{2,3}$ emission spectra for the central atom, and also from the conclusion of Kosuch *et al.* about the O$K\alpha$ spectra.

3) The O$K\alpha$ spectra are especially influenced by hydrogen. It seems that the electron population of oxygen 2p diffuses to the lower-energy molecular orbitals in the relation to the hydrogen.

4) The O$K\alpha$ spectral profile is affected by the quantity of oxygen, the lower-energy peak shifts to the lower-energy side, and the main peak at a higher-energy shifts to the higher-energy side in proportion to the quantity of oxygen, and the hump B appears only when the central atom combines directly with the O (including OH) ions.

In this work, we can not interpret the spectra quantitatively as transitions from the molecular orbital with the help of a molecular orbital calculation. However, it seems that it will be very useful in studying the electronic structure and molecular orbital in chemical compounds in combination with the results of the $L_{2,3}$ emission spectra, the $K\beta$ spectra, and the O$K\alpha$ spectra from various compounds with the help of a molecular orbital calculation. These are subjects for future study in our work.

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References

1) K. Taniguchi and B. L. Henke, *J. Chem. Phys.*, **64**, 3021 (1976).

2) K. Taniguchi, "Advances in X-Ray Analysis," Plenum, New York (1980), Vol.23, p. 193.

3) K. Taniguchi, *Bull. Chem. Soc. Jpn.*, **57**, 909 (1984).

4) K. Taniguchi, *Bull. Chem. Soc. Jpn.*, **57**, 915 (1984).

5) F. Tyren, *Nova Acta Regiae Soc. Sci. Ups.* **12**, 7 (1940).

6) H. M. O'Bryan and H. W. B. Skinner, *Proc. R. Soc. London, Ser. A*, **176**, 229 (1940).

7) R. A. Mattson and R. C. Enlent, "Advances in X-Ray Analysis," Plenum, New York (1966), Vol. 9, p. 471.

8) B. L. Henke and R. E. Lent. "Advances in X-Ray Analysis," Plenum, New York (1969), Vol. 12, p. 480.

9) D. G. W. Smith, R. K. O'Oions, and K. Norrish, *Spectrochim. Acta, Part B*, **29**, 63 (1974).

10) D. W. Fischer, *J. Phys. Chem. Solids*, **32**, 2455 (1971).

11) A. S. Koster, *J. Phys. Chem. Solids*, **32**, 2685 (1971).

12) R. Bador, "Advances in X-Ray Analysis," Plenum, New York (1981), Vol. 24, p. 351.

13) E. Gilberg, M. J. Hanus, and B. Foltz, *Rev. Sci. Instrum.*, **52**, 662 (1981).

14) N. Kosuch, E. Tegeler, G. Wiech, and A. Faessler, *Chem. Phys. Lett.*, **47**, 96 (1977).

15) N. Kosuch, E. Tegeler, G. Wiech, and A. Faessler, *J. Electron Spectrosc. Relat. Phenom.*, **13**, 263 (1978).

16) K. Kawatsura, K. Ozawa, F. Fujimoto, and M. Terasawa, *Phys. Lett. A*, **58**, 446 (1976).

17) G. Andemann, F. Burkard, F. Fujiwara, and R. Kim, "Inner-Shell and X-Ray Physics of Atomic and Solids 2," Plenum, New York (1981), p. 727.

18) B. L. Henke and M. A. Tester, "Advances in X-Ray Analysis," Plenum, New York (1975), Vol. 18, p. 76.

19) B. L. Henke and K. Taniguchi, *J. Appl. Phys.*, **47**, 1027 (1976).

20) K. Maeda and M. Uda, *Spectrochim. Acta, Part B*, **35**, 561 (1980).