K_β Satellites in Fluorescence Spectra of Some Mg and Al Compounds

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The high energy K_β satellites β^{III}, β^{IV}, β^{VII}, β^{VIII} have been studied in fluorescence. Their intensities have been correctd for the self-absorption effect by measuring the intensities from Mg and Al compounds having various absorption coefficients. By comparing the energy and intensity of the $\beta^{III}\,\beta^{IV}$ group with the calculations of the sudden approximation theory we have shown that this group is due to double-hole states. It is proposed that the $\alpha_{10}\,\alpha_{11}$ group on the low energy side of the K_β line arises from transitions between quadri-hole states. The line usually designated as $K_{\beta'}$ is thought to arise from a cross transition between the cation and anion in Mg, Al, and Si compounds involving the second period elements.

We have recently presented further evidence that the high-energy K_α satellites α', α_3, α_4, α_5, α_6 are due to KL double- and KL^2 triple-hole states by considering their relative intensities in Na, Mg, Al, and Si [1]. Here we have extended our fluorescence measurements to high-energy K_β satellites in Mg and Al. These faint satellites have apparently not been studied by using x-ray excitation. KARLSSON and SIEGBAHN [2] first found evidence of the satellites $\beta^{III}\,\beta^{IV}$ in both Mg and Al and their oxides whereas KUNZL [3] succeeded in identifying two additional satellites $\beta^{VII}\,\beta^{VIII}$ at shorter wavelengths. We discuss the origin of these satellites in the light both of their energies and intensities. The intensities have been measured relative to the K_β line and have been corrected for the self-absorption effect. The influence of the self absorption is especially large, since the K absorption edge is situated between the satellites and the β line.

In the previous work [1] the region between the $K\alpha_5\alpha_6$ group and the K_β line was not considered in detail although a line denoted $K_{\beta'}$ [2, 3] was found in Mg. Here we discuss the origin of this line and other lines appearing in this region in Mg, Al, and Si compounds. We show that they can be traced back to either cross transitions between the cation and anion or to transitions between quadri-ionized states.

1. Measurements

The apparatus used is described in Ref. [1]. The specimens were excited by radiation from a chromium anode x-ray tube with a 0.5 mm thick beryllium window. The fluorescent radiation was analyzed with a plane KAP or ADP crystal. The counting time was usually 20 min per step. In the measurements of the intensities of the high-energy K_β satellites low dispersion (KAP, 1st reflection) was used whereas in some cases the low energy satellites were investigated with higher dispersion (ADP, 1st reflection).

The spectra of Mg, MgO, MgF_2, Al, Al_2O_3, AlN, and $AlCl_3$ were studied. The integrated intensities of the satellite groups $\beta^{III}\,\beta^{IV}$ and $\beta^{VII}\,\beta^{VIII}$ relative to the $K_{\beta\beta'}$ group are given in Table 1, columns 3 and 5. An example of a recorded spectrum is shown in Fig. 1 where the background is indicated by the dashed line. Column 2 in Table 3 shows the measured energy dif-

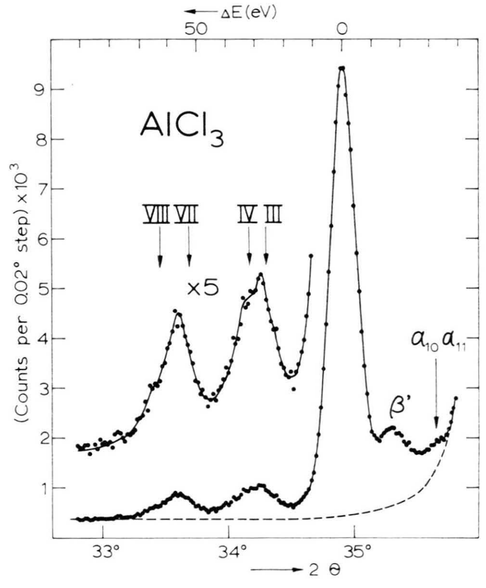

Fig. 1. The K_β spectrum of $AlCl_3$ obtained by using a KAP analyser crystal.

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[1] J. UTRIAINEN, M. LINKOAHO, E. RANTAVUORI, T. ÅBERG, and G. GRAEFFE, Z. Naturforsch. **23 a**, 1178 [1968].

[2] H. KARLSSON and M. SIEGBAHN, Z. Phys. **88**, 76 [1934].

[3] V. KUNZL, Z. Phys. **99**, 481 [1936].

ferences between β and β'. The figures in Table 1 and 3 are mean values of three independent measurements. The error limits in the case of the intensity correspond to the range of the individual measurements. The uncertainty of the energy differences is about ± 2 eV.

2. The Effect of Self-Absorption

The energies of the satellites $\beta^{\mathrm{III}}\beta^{\mathrm{IV}}\beta^{\mathrm{VII}}\beta^{\mathrm{VIII}}$ slightly exceed the energy of the K absorption edge. Hence the satellite photons emanating from the specimen have a much higher probability of absorption than photons of the main line. Following BLOCHIN [4] we get an approximate dependence

$$m/C = (\mu_e + \mu_\beta)/(\mu_e + \mu_s) \tag{1}$$

between the measured intensity m of the K_β satellite group relative to that of the $K_{\beta\beta'}$ group and the corresponding "true" value C. Here μ_e, μ_β, and μ_s are the absorption coefficients of the specimen for the exciting radiation, for the main $K_{\beta\beta'}$ group and the satellite group, respectively.

The relative integrated intensities corrected for self-absorption using Eq. (1) are given in column 4 and 6 of Table 1. The absorption coefficient of the CrK_α line was used for μ_e. The values of the ratio μ_s/μ_β were based on the K absorption jump ratios of COLBY [5] and on the absorption coefficients of HENKE [6]. In Fig. 2 we have plotted C_1 corresponding to $\beta^{\mathrm{III}}\beta^{\mathrm{IV}}$ as a function of μ_s/μ_β. The self-absorption does not affect the intensity ratio if $\mu_s = \mu_\beta$. Thus we have carried out a linear extrapolation to $\mu_s/\mu_\beta = 1$ for the values C_1 obtained from Eq. (1). The extrapolated values are given in Table 2 as final experimental results.

Target	μ_s/μ_β	$\beta^{\mathrm{III}}\beta^{\mathrm{IV}}$ m_1	C_1	$\beta^{\mathrm{VII}}\beta^{\mathrm{VIII}}$ m_2	C_2
Mg	12.4	2.6 ± 0.3	25	<0.3	< 3
MgO	3.4	5.7 ± 0.4	18	0.5 ± 0.3	2
$\mathrm{MgF_2}$	1.9	8.5 ± 0.7	16	3.2 ± 0.2	6
Al	12.0	2.6 ± 0.5	21	1.4 ± 0.1	11
AlN	5.1	3.7 ± 0.3	16	2.3 ± 0.2	10
$\mathrm{Al_2O_3}$	3.1	5.3 ± 1.0	15	2.9 ± 0.4	8
$\mathrm{AlCl_3}$	1.8	8.7 ± 0.3	14	5.7 ± 0.4	9

Table 1. Integrated intensities of the $\beta^{\mathrm{III}}\beta^{\mathrm{IV}}$ and $\beta^{\mathrm{VII}}\beta^{\mathrm{VIII}}$ satellite groups. The intensities are given in percent relative to the $K_{\beta\beta'}$ group. Here m and C denote measured and corrected values, respectively.

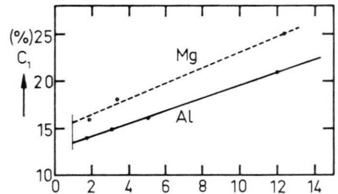

Fig. 2. A plot of C_1 obtained from Eq. (1) as a function of μ_s/μ_β.

3. Discussion

High-energy satellites

From energy considerations it has already been proposed that the $K_{\beta^{\mathrm{III}}\beta^{\mathrm{IV}}}$ group originates in double ionization [2]. In Table 2 we have also extended these considerations to the $\beta^{\mathrm{VII}}\beta^{\mathrm{VIII}}$ group by assuming that the initial states of these lines are triple-hole states. We see that agreement is good between the measurements and the $(Z \rightarrow Z+1)$ approximation of double and triple ionization which follows from the sudden approximation theory of the satel-

Substance	Satellite group	Energy separation (eV) Experimental This work[a]	Previous works[b]		Calculation[c] 2p	2s	Intensity (%) Extra-polation	Calculation
Mg	$\beta^{\mathrm{III}}\beta^{\mathrm{IV}}$	26	21	27	22	28	16	15
	$\beta^{\mathrm{VII}}\beta^{\mathrm{VIII}}$	43	44		43	57	4[d]	~ 1
Al	$\beta^{\mathrm{III}}\beta^{\mathrm{IV}}$	28	25	32	26	31	14	12
	$\beta^{\mathrm{VII}}\beta^{\mathrm{VIII}}$	55	51	62	52	62	8	~ 1

[a] Mean value.

[b] The values for Mg and Al are from Ref.'s [3] and [7], respectively.

[d] Mean value.

[c] The energy separations corresponding to $\beta^{\mathrm{III}}\beta^{\mathrm{IV}}$ have been calculated from $\Delta E = E(Z+1) - E(Z)$ where E is the energy of the 2p or 2s electron. The energy separations corresponding to $\beta^{\mathrm{VII}}\beta^{\mathrm{VIII}}$ have been taken to be $2\,\Delta E$. The energy values are from Ref. [8].

Table 2. The energies and intensities of the high-energy β satellites with respect to the K_β line.

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[4] M. A. BLOCHIN, Physik der Röntgenstrahlen, VEB Verlag Technik, Berlin 1957, p. 249.

[5] J. W. COLBY, National Lead Company of Ohio, Report NLCO-917 [1964].

[6] B. L. HENKE, in Advances in X-ray Analysis, Vol. 7, Plenum Press, New York 1964, p. 460.

[7] I. NAGAKURA, Sci. Rep. Tôhoku Univ., I, **48**, 90 [1964].

[8] J. A. BEARDEN and A. F. BURR, Rev. Mod. Phys. **39**, 125 [1967].

lites[9]. Further evidence of the origin of the $K_{\beta^{\text{III}}\beta^{\text{IV}}}$ group is gained by comparing in the two last columns of Table 2 the measured intensities with the sudden approximation calculations[10]. No conclusions about the origin of the $K_{\beta^{\text{VII}}\beta^{\text{VIII}}}$ group in Mg compounds could be drawn from the intensities. The high intensity of the Al $K_{\beta^{\text{VII}}\beta^{\text{VIII}}}$ group is not in accordance with the triple-ionization calculations. In this region the absorption technique was used to check that multiple reflections from shorter wavelength radiation did not interfere with the high-energy K_β satellites.

Low-energy satellites

We have confined ourselves to the region extending from the $K_{\alpha_5\alpha_6}$ group to approximately 10 eV below K_β. The $K_{\beta'}$ line found in several oxides[11] falls in this region. It has been proposed that this line originates in the quadrupole transition $K-M_{\text{I}}$[12], in Compton scattering[13], and also suggested that it is from the cross transition between the metal K level and an oxide band[11, 14, 15].

In Table 3 we compare measured values of the $\beta-\beta'$ energy separation with data based on the assumption that β' is a cross transition between the cation K and the anion L_{I} levels. Thus, following MENDEL[11], column 4 of Table 3 gives the energy differences $E(2s2p^x)-E(2s^22p^{x-1})$ for N, O, and F ($x=4$, 5, 6) and $E(3s3p^5)-E(3s^23p^4)$ for Cl obtained from optical spectra[16]. In the last column the corresponding differences between the atomic energy levels[8] are shown. The results in Table 3 support the cross transition hypothesis except possibly in the case of $AlCl_3$.

If we determine the energy separation between the $K_{\beta'}$ and $K_{\alpha_1\alpha_2}$ line in Al_2O_3 we get 50.3 eV. On the other hand, FOMICHEV[17] has found a line in the $L_{\text{II, III}}$ spectrum corresponding to 50.5 eV which he interprets as the cross transition $O(L_{\text{I}})-Al(L_{\text{II, III}})$. This gives further evidence that $K_{\beta'}$ can be considered as the cross transition $Al(K)-O(L_{\text{I}})$.

Target	Experimental		From optical spectra[16]	From atomic energy levels[8]
	This work	MENDEL[11]		
MgO	15	15	16	17
MgF_2	18[a]	20	21	22
AlN	12	—	11	—
Al_2O_3	16	15	16	17
$AlCl_3$	17	—	12	11

[a] In this case the β' line overlaps the K_{α_6} line. It was observed by noting an increase of the K_{α_6} intensity when going from MgO to MgF_2.

Table 3. Energy separation between K_β and $K_{\beta'}$ in electron volts in various Mg and Al compounds.

In the K spectrum of Si compounds possible cross transition lines also appear. For example, the $\beta'-\alpha_1\alpha_2$ energy separation[18] in SiO_2 is 79 eV whereas the corresponding line in the $L_{\text{II, III}}$ spectrum has been measured to be 78.5 eV[19] or 76 eV[20]. In SiC the $\beta-\beta'$ separation is 9 eV[18] while the optical spectrum of C gives 8 eV[16].

In addition to β' we have found in MgF_2 and in Al and its compounds (see Fig. 1) a faint line situated at about 10 eV and 30 eV, respectively, from the β line. This line corresponds to $\alpha_{10}\alpha_{11}$ in the notation of KARLSSON and SIEGBAHN[2]. It can be associated with the transition KL^3-L^4 on the basis of approximate energy and intensity calculations. These indicate that the energy separation between α_{11} and α_5 should be almost equal to the $\alpha_5-\alpha_3$ separation and that the intensity of the $\alpha_{10}\alpha_{11}$ group should be about 2 to 6% of the intensity of the $\alpha_5\alpha_6$ group.

According to energy calculations the cross transition line $Mg(K)-O(L_{\text{I}})$ should coincide with the KL^3-L^4 line in MgO. In fact we found only one line in the magnesium oxide. Its intensity was about 20% of the intensity of $K_{\alpha_5\alpha_6}$ whereas the corresponding line in Mg previously called β'[1] had an intensity of about 5%. For an Mg specimen it is hard to say how large is the contribution to β' due to oxidation. However, in other cases like Al, β' should be a very sensitive indicator of oxidation.

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[9] T. ÅBERG, Phys. Rev. **156**, 35 [1967].

[10] T. ÅBERG, Phys. Letters **26 A**, 515 [1968], and unpublished results.

[11] H. MENDEL, Koninkl. Nederl. Akad. Wetensch. Proc. **B 70**, 276 [1967].

[12] D. W. FISCHER and W. L. BAUN, J. Appl. Phys. **36**, 534 [1965].

[13] A. FAESSLER and G. WIECH, Phys. Letters **27 A**, 11 [1968].

[14] M. FICHTER, in Röntgenspektren und Chemische Bindung (Ed. A. MEISEL), VEB Reprocolor, Leipzig 1966, p. 112.

[15] V. I. NEFEDOV, Zh. Strukt. Khim. **8**, 686 [1967].

[16] C. E. MOORE, Atomic Energy Levels, Vol. I, National Bureau of Standards Circular 467, Washington 1949.

[17] V. A. FOMICHEV, Fiz. Tverd. Tela **8**, 2892 [1966]; Transl.: Soviet Phys.—Solid State **8**, 2312 [1967].

[18] B. KERN, Z. Phys. **159**, 178 [1960].

[19] H. M. O'BRYAN and H. W. SKINNER, Proc. Roy. Soc. London **A 176**, 229 [1940].

[20] O. A. ERSHOV, D. A. GOGANOV, and A. P. LUKIRSKII, Fiz. Tverd. Tela **7**, 2355 [1965]; Transl.: Soviet Phys.—Solid State **7**, 1903 [1966].