

chennähe befinden, d. h. daß die Konzentration der beim Mahlen des Salzes erzeugten Defekte an der Oberfläche um Größenordnungen höher ist als im Innern.

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## Relative Intensities of $K_{\alpha}$ Satellites in X-Ray Fluorescence Spectra of Na, Mg, Al and Si

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A plane crystal spectrometer was used to measure relative integrated intensities of  $K_{\alpha}$  X-ray satellites in fluorescence spectra of Na in NaF, and of Mg, Al, Si in metals and oxides. A comparison between the measured intensity of the  $K_{\alpha'_{a3a4}}$  satellite group and the intensity obtained from electron excitation measurements indicates that the production probability of KL double-hole states is independent of the excitation mode. The measured intensities in metals are in agreement with calculated intensities based on the sudden approximation theory of x-ray satellites of free neon-like ions. The bond in fluoride and oxides was shown to increase the relative intensity by about 13%. From intensity considerations, the  $K_{\alpha_{5a6}}$  satellite group was attributed to  $KL^2$  triple-hole states.

The K x-ray satellite or non-diagram lines have been extensively studied in electron excitation<sup>1,2</sup>. Their initial states are commonly interpreted as multiple-ionization or more generally as multiple-excitation states<sup>1,3</sup>. It has been widely believed that the K satellites found in electron excitation do not appear in fluorescence<sup>4–6</sup>. However, some recent experimental work<sup>7–11</sup> shows that this is not true. Related to this, it has also been concluded from measurements of charge states of ions formed following photo-ionization that with considerably probability two or more electrons can be ejected when

one photon is absorbed<sup>12–15</sup>. Evidence of excitation and ionization of two electrons simultaneously in the photoabsorption process has been found from the K-photoelectron spectra of neon and argon<sup>16</sup>.

A recent theory of x-ray satellites is based on the sudden approximation<sup>17–19</sup>. If this approximation is valid excitation of KL double-hole states should occur independently of the excitation mode if the excitation energy is high enough. Therefore, the same K satellites should appear with equal intensity in both x-ray and electron excitation. Measured multiple excitation rates in noble-gas atoms have

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<sup>1</sup> For a review, see M. A. BLOKHIN, Physik der Röntgenstrahlen, VEB Verlag Technik, Berlin 1957, p. 334, and F. R. HIRSH, JR., Rev. Mod. Phys. **14**, 45 [1942].

<sup>2</sup> For some recent work, see for example, B. NORDFORS, Arkiv Fysik **10**, 279 [1956]; D. W. FISCHER and W. L. BAUN, Spectrochim. Acta **21**, 443 [1965], J. Appl. Phys. **36**, 534 [1965]; W. L. BAUN and D. W. FISCHER, Spectrochim. Acta **21**, 1471 [1965]; H.-U. CHUN and D. HENDEL, Z. Naturforsch. **22 a**, 1401 [1967].

<sup>3</sup> L. G. PARRATT, Rev. Mod. Phys. **31**, 616 [1959].

<sup>4</sup> A. E. SANDSTRÖM, in Handbuch der Physik, Springer-Verlag, Berlin 1957, Vol. XXX, p. 85.

<sup>5</sup> M. A. BLOKHIN, Physik der Röntgenstrahlen, VEB Verlag Technik, Berlin 1957, p. 336.

<sup>6</sup> E. H. S. BURHOP, The Auger Effect and Other Radiationless Transitions, University Press, Cambridge 1952, p. 69.

<sup>7</sup> V. F. DEMEKHIN and M. A. BLOKHIN, Izv. Akad. Nauk SSSR, Ser. Fiz. **28**, 825 [1964] (Transl.: Bull. Acad. Sci. USSR Phys. Ser. **28**, 733 [1965]).

<sup>8</sup> M. A. BLOKHIN and V. F. DEMEKHIN, Izv. Akad. Nauk SSSR, Ser. Fiz. **28**, 830 [1964] (Transl.: Bull. Acad. Sci. USSR Phys. Ser. **28**, 738 [1965]).

<sup>9</sup> R. D. DESLATTES, Phys. Rev. **133**, A 390, A 399 [1964].

<sup>10</sup> W. L. BAUN, in Discussion of Advances of X-ray Analysis, Vol. 8 [1965], p. 382.

<sup>11</sup> R. A. MATTSON and R. C. EHLERT, in Advances of X-ray Analysis, Vol. 9 [1966], p. 471.

<sup>12</sup> M. O. KRAUSE, M. L. VESTAL, W. H. JOHNSTON, and T. A. CARLSON, Phys. Rev. **133**, A 385 [1964].

<sup>13</sup> T. A. CARLSON and M. O. KRAUSE, Phys. Rev. **137**, A 1655 [1965].

<sup>14</sup> T. A. CARLSON and M. O. KRAUSE, Phys. Rev. **140**, A 1057 [1965].

<sup>15</sup> M. O. KRAUSE and T. A. CARLSON, Phys. Rev. **158**, 18 [1967].

<sup>16</sup> M. O. KRAUSE, T. A. CARLSON, and R. D. DISMUKES, Phys. Rev., to be published.

<sup>17</sup> V. P. SACHENKO and V. F. DEMEKHIN, Zh. Eksperim. i Teor. Fiz. **49**, 765 [1965] (Soviet Phys.-JETP **22**, 532 [1966]).

<sup>18</sup> T. ÅBERG, Phys. Rev. **156**, 35 [1967].

<sup>19</sup> T. ÅBERG, Phys. Letters **26 A**, 515 [1968].



been compared with sudden approximation (shake-off) calculations<sup>12-16</sup> but there are only a few integrated intensity measurements of K $\alpha$  satellites<sup>16, 20-23</sup> admitting a comparison with the theory. As far as we know there are no measurements of integrated intensities carried out in fluorescence, except possibly one<sup>22, 24</sup>.

For this reason we have measured relative integrated intensities of the satellite group K $\alpha'$  $\alpha_3\alpha_4$  in fluorescence for some elements (Mg, Al, Si) and compounds (Na in NaF and Mg, Al and Si in their oxides) in order to: —

1. find out whether there are any significant differences between the relative satellite intensities in x-ray and electron excitation.

2. obtain accurate relative intensity values for comparison with the theory. In fact the measurement system used here is very suitable for accurate intensity measurements.

3. search for solid state effects in relative integrated intensities. In this respect, the advantage of studying the fluorescence spectra instead of the spectra excited by electrons is obvious as there is no temperature rise in the sample which might cause chemical reactions.

Besides this, we have also been able to measure the relative integrated intensity of the K $\alpha_3\alpha_4$  satellite group. The measured intensities are compared with approximate calculations based on the sudden approximation theory of the x-ray excitations.

## 1. Description of Apparatus

A chromium anode x-ray tube with a 0.5 mm thick beryllium window was used in conjunction with the Kristalloflex 4 x-ray generator. The generator has a stability of  $\pm 0.3\%$  in the x-ray beam intensity. Throughout our measurements we kept the tube voltage at 50 kV and the current at 40 mA. A vacuum x-ray fluorescence spectrometer was attached to a horizontal goniometer. The generator, the spectrometer and the goniometer were all manufactured by Siemens. The analyzer crystal used were plane KAP-(KHC $_8$ H $_4$ O $_4$ ) and gypsum-crystals of approximate dimensions 35  $\times$  70  $\times$  2 mm<sup>3</sup>. Some further details are given in Table 1.

A Soller slit between the analyzer crystal and the detector limited the horizontal divergence to 0.15°. As a detector we used a flow counter with a window of

material measured	crystal	2d (Å)	order of reflection	counter window ( $\mu$ )
NaF	KAP	26.6	1	6 and 2
Mg	gypsum	15.2	1	6
MgO	gypsum	15.2	1	6
Al	KAP	26.6	2	6
Al $_2$ O $_3$	KAP	26.6	2	6
Si	KAP	26.6	2	6
SiO $_2$	KAP	26.6	2	6

Table 1. The plane crystals and counter windows used in the satellite measurements.

aluminized hostaphan (6  $\mu$ ) or makrofol (2  $\mu$ ). The rate of gas flow was 3–4 l/h and the mixture used contained 10% methane in argon. The voltage of the flow counter was 2 kV. The recording system consisted of a preamplifier, a linear amplifier, a single channel analyzer, a scaler-timer and a printer, all from Siemens. An essential feature of our method was the use of a step-scanning device which moved the detector step by step over the whole range of  $2\theta$  needed. The step length normally used was 0.02° in  $2\theta$  and the counting time was usually 4 min per step. Counting times as long as 10–20 min were also used in special cases. The long term stability of the whole detecting system was found to be better than  $\pm 0.5\%$  in 24 h.

## 2. Experimental Technique

The NaF and the oxide specimens were prepared from fine-grained pure powder in a polished mould by using considerable pressure. The surfaces of the metal specimens were polished just before attachment to the measurement chamber. Some specimens were also coated with a very thin layer of plastic in an argon atmosphere. It was found, however, that coated and uncoated specimens gave the same results.

One example of a recorded spectrum is shown in Fig. 1. A characteristic of this method is the very good statistics, for example in Fig. 1 the  $\beta'$  satellite, which according to BLOKHIN<sup>25</sup> is very faint, is clearly discernible. The relative intensities were obtained from the recorded spectra by measuring the areas under the curves. In separating the K $\alpha'$  $\alpha_3\alpha_4$  group from the main peak ( $\alpha_1\alpha_2$ ) the latter was assumed to be symmetric. In separating the K $\alpha_3\alpha_4$  group from the K $\alpha'$  $\alpha_3\alpha_4$  group the shape of the high energy side of the latter was assumed to conform with the sym-

<sup>20</sup> L. G. PARRATT, Phys. Rev. **50**, 1 [1936].

<sup>21</sup> B. NORDFORS, Arkiv Fysik **10**, 279 [1956].

<sup>22</sup> V. F. DEMJOCHIN and W. P. SATSCHENKO, in Röntgenspektren und chemische Bindung, VEB Reprocolor, Leipzig 1966, p. 58 (the excitation mode is not given).

<sup>23</sup> D. W. FISCHER, private communication (the works quoted in footnote <sup>2</sup> give the peak intensities).

<sup>24</sup> In Ref. <sup>19</sup>, the statement that KRAUSE et al.<sup>16</sup> have used x-ray excitation is in error.

<sup>25</sup> M. A. BLOKHIN, Physik der Röntgenstrahlen, VEB Verlag Technik, Berlin 1957, p. 344.

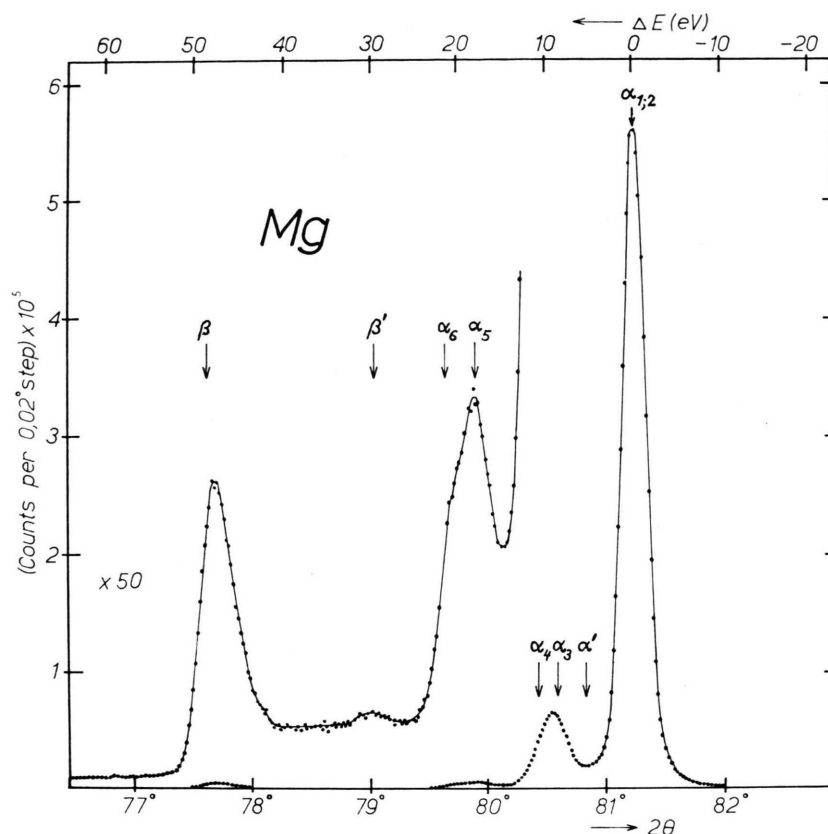


Fig. 1. The K fluorescence spectrum of Mg metal.

metric main peak. This method worked well in the cases of Mg, Al, Si and their compounds, but in the case of NaF, the  $K_\beta$  line is also near to the  $K_{\alpha_5\alpha_6}$  group. The  $K_{\alpha_5\alpha_6}$  group was separated from the  $K_\beta$  by assuming that the former is symmetric. Each spectrum was measured 6–10 times.

The absorption in the flow counter window and the integrated reflection of the analyzing crystal are both dependent on the wavelength. The measured intensity ratios therefore need the corresponding corrections. Fortunately these corrections turn out to be small and besides partly cancel each other. The correction for the absorption in the counter window was determined by measuring the change of intensities as a function of  $\lambda$  when one or two layers of flow counter window material was used. The second correction was determined by assuming that the integrated reflection is proportional to the third power of  $\lambda$ . The final corrections to the relative intensity were  $-1.0$  (Na,  $6\mu$ ),  $0.0$  (Na,  $2\mu$ ),  $-0.1$  (Mg),  $+0.1$  (Al) and  $+0.1$  (Si) for  $K_{\alpha'_3\alpha_4}$  and  $-0.3$  (Na,  $6\mu$ ) for  $K_{\alpha_5\alpha_6}$ . The corrections to the

values for  $K_{\alpha_5\alpha_6}$  for Mg, Al and Si are small and are included in the error estimates.

### 3. Results and Discussion

#### 3.1. The $K_{\alpha'_3\alpha_4}$ Satellite Group

Table 2 gives the corrected ratios of the integrated intensity of the  $K_{\alpha'_3\alpha_4}$  group to that of the  $K_{\alpha_1\alpha_2}$  group together with previous results and calculations based on the sudden approximation theory of the satellites.

According to CARLSON and KRAUSE the probability of the simultaneous ionization of an L and a K electron should be constant in the photoabsorption process and comparable with the sudden approximation probability if <sup>14, 16, 18</sup>

$$(E_{KL} - E_K) t < 0.4 \hbar.$$

Here  $t$  is the time of transit of the K photoelectron past the L shell.  $E_{KL}$  and  $E_K$  are the excitation energies of the KL and K x-ray states, respectively. It can be shown that the time  $t$  in the validity criterion corresponds to an excitation energy of the incom-

element	target material	present work <sup>a</sup>	BF <sup>b</sup>	SD <sup>c</sup>	P <sup>d</sup>	N <sup>e</sup>	KCD <sup>f</sup>	theory <sup>g</sup>
Na	NaF	20.2 $\pm$ 0.4	20.3 $\pm$ 0.8		22			18.2
Mg	metal	14.0 $\pm$ 0.3	16.1 $\pm$ 0.5	12.6				13.6
	MgO	15.8 $\pm$ 0.2	15.9 $\pm$ 0.5	14.1			15.0 $\pm$ 1.5	
Al	metal	10.8 $\pm$ 0.2	10.1 $\pm$ 0.4	10.7		8.0		10.5
	Al <sub>2</sub> O <sub>3</sub>	12.3 $\pm$ 0.2	11.9 $\pm$ 0.4	11.9		8.2	9.3 $\pm$ 1.5	
Si	metal	7.8 $\pm$ 0.3	7.5 $\pm$ 0.4	9.0	11			8.3
	SiO <sub>2</sub>	9.0 $\pm$ 0.4	9.3 $\pm$ 0.4	10.0				

Table 2. Relative integrated intensities of the satellite group K $\alpha'$  $\alpha$  $\beta$  $\gamma$ . The values are in percent relative to the K $\alpha$  $\beta$  line.

<sup>a</sup> Note that the values quoted in Ref. <sup>19</sup> are uncorrected.

<sup>b</sup> Ref. <sup>23</sup>; Electron excitation at 4–5 kV.

<sup>c</sup> Ref. <sup>22</sup>; Excitation mode and energy are not given.

<sup>d</sup> Ref. <sup>20</sup>; Electron excitation at two to five times the satellite excitation potential. The target material for Na was NaCl.

<sup>e</sup> Ref. <sup>21</sup>; Electron excitation at 2.25 kV.

<sup>f</sup> Ref. <sup>16</sup>; From photoelectron spectra of Ne induced by the MgK $\alpha$  and AlK $\alpha$  line excited by electrons.

<sup>g</sup> Ref. <sup>19</sup>; The calculated intensities refer to free neon-like ion.

ing x-rays which is more than two times the K threshold energy  $E_K$ . This criterion is well satisfied in our measurements where the sample was excited by the radiation from a Cr tube operating at 50 kV. Then the CrK lines at 6.0 and 5.4 keV and the continuous spectrum, which is concentrated to higher energies, are responsible for the excitation. Thus, our measurements should be comparable with relative intensities calculated by the sudden approximation.

In the case of electron excitation PARRATT<sup>26</sup>, BAUN and FISCHER<sup>27</sup> have shown that the relative K satellite intensity increases rapidly above the threshold, reaching a saturation value at about twice the threshold. The trend is very similar to the double-ionization probability trend<sup>14</sup> in Ne as a function of the x-ray excitation energy. Consequently it is to be expected that the saturation value should be comparable with the sudden approximation value, in spite of the fact that electron excitation occurs mostly for small momentum transfer<sup>28</sup>.

In all the electron excitation measurements quoted in Table 2 the excitation energy is more than twice the threshold energy, except in the measurement of NORDFORS where the excitation energy is 1.5  $E_K$ . This explains the rather low intensity value obtained by NORDFORS as has been pointed out by BAUN and FISCHER<sup>27</sup>.

PARRATT<sup>20</sup> obtained his values with photographic registration and the values of KRAUSE et al.<sup>16</sup> are not very accurate. As we do not know any details

of the measurements of DEMEKHIN and SACHENKO<sup>22</sup> we confine ourselves to a comparison between the measurements of BAUN and FISCHER<sup>23</sup> and our own where in both cases the analyzing systems were very similar. We see from the third and fourth columns of Table 2 that the agreement is excellent except in the case of Mg metal. Here we are perhaps faced with the difficulty of obtaining pure spectra from metals by electron excitation.

The general agreement between the x-ray and electron excitation measurements justifies the treatment of excitations of KL x-ray states as independent of the excitation mode, in accordance with the sudden approximation. SACHENKO and DEMEKHIN<sup>17</sup> have given a curve of the relative intensity of the corresponding free atoms. However, their curve is based on an extrapolation of the relative KL double ionization value for potassium which has been calculated with wave functions without exchange. Besides this, the change of the oscillator strength and the K Auger width, which is due to the extra hole in the L shell, has not been taken into account. Therefore, we prefer a comparison to the free neon-like ion values<sup>19</sup> given in the last column of Table 2. This should also bring out more clearly possible solid state effects hidden in the relative intensity.

The agreement with the theoretical values is good and we see that the metals give intensity values which are closer to the theoretical values than do the oxides and the fluoride. Oxidation increases the relative integrated intensity and this increase is

<sup>26</sup> L. G. PARRATT, Phys. Rev. **49**, 132, 502 [1936].

<sup>27</sup> W. L. BAUN and D. W. FISCHER, Phys. Letters **13**, 36 [1964].

<sup>28</sup> See, for example, N. F. MOTT and H. S. W. MASSEY, The Theory of Atomic Collisions, 3<sup>rd</sup> ed., Clarendon Press, Oxford 1965, Chapt. XVI.



15% for Si, 14% for Al and 13% for Mg. This may be compared with the findings<sup>29</sup> that the intensity ratio of the K $\alpha_4$  and K $\alpha_3$  peaks increases when we go from element to oxide. The bond in NaF is similar to the bond in the oxides. Consequently it is not surprising that the experimental relative intensity for the Na<sup>+</sup> ion is 11% larger than the calculated value.

### 3.2. The K $\alpha_3\alpha_6$ Satellite Group

The corrected integrated intensity ratios of the K $\alpha_3\alpha_6$  satellite group to those of the K $\alpha_1\alpha_2$  group are given in Table 3 where they are compared with sudden approximation values.

element	observed <sup>a</sup>	theory <sup>b</sup>
Na	3.0 $\pm$ 0.4	1.8
Mg	1.7 $\pm$ 0.2	1.1
Al	1.1 $\pm$ 0.2	0.7
Si	0.7 $\pm$ 0.1	0.5

Table 3. Relative integrated intensities of the K $\alpha_3\alpha_6$  satellite group. The values are given in percent relative to the K $\alpha_1\alpha_2$  line.

<sup>a</sup> Measured from metallic specimens except in the case of Na, where an NaF specimen was used.

<sup>b</sup> T. ÅBERG (unpublished), the values refer to free neon-like ions.

These values are based on the assumption that the initial states of the K $\alpha_3\alpha_6$  lines are KL<sup>2</sup> triple-hole states. The relative production probability has been calculated with a similar method<sup>19</sup> as the production probability of the KL double-hole states. This neglects the correlation between the *two* outgoing L electrons. The fact that almost all the KK states decay via Auger transitions to triple-hole states of KL type has been taken into account. The correlation between the K electrons is included in the calculation of the relative production probability of KK states. The method used here has been previously applied with success to double excitation of helium by photon impact<sup>30</sup>. In electron impact the production probability of the KK states is much smaller than in photon impact, and therefore the K $\alpha_3\alpha_6$  intensity should be lower in electron excitation than in fluorescence. In Al and Si, where the KK

states contribute about 30% to the total intensity in fluorescence, this difference should show up. A comparison between our integrated intensity and the peak intensity given by BAUN and FISCHER<sup>31, 32</sup> indicates this.

The correction factor<sup>19</sup>, which takes into account the change of the frequency, the oscillator strength and the Auger width due to the extra holes in L shell, has been estimated to be about 1.6. In spite of the fact that the correlation between the ejected L electrons has been neglected the agreement is good. This indicates that the K $\alpha_3\alpha_6$  satellite group is due to triple-hole states. This is in agreement with calculations of the energy difference between the satellites and the main line<sup>33</sup>.

## 4. Conclusion

We have shown that accurate relative integrated intensities can be obtained with a plane crystal spectrometer and a flow counter using a step scanning device. Although the x-ray excitation mode is used, there are no intensity difficulties and very good statistics can be achieved. With increased resolution this method will be very powerful in studying, for example, solid state effects in the integrated intensities of various lines in satellite spectra.

The results obtained in this paper are in agreement with the sudden approximation theory of x-ray satellites. It has been shown that the relative intensity of the K $\alpha_3\alpha_6$  satellite group of Na, and Mg, Al and Si increases when they form bonds with F and O, respectively. From intensity considerations, the K $\alpha_3\alpha_6$  group has been attributed to initial triple-hole states.

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<sup>29</sup> D. W. FISCHER and W. L. BAUN in footnote <sup>2</sup>, see also Ref. 7, 21, and 22.

<sup>30</sup> T. ÅBERG, Double Excitation of Helium Atoms by Photon Impact in the Sudden Approximation (Preprint Series in Theoretical Physics, University of Helsinki, 1967), to be published.

<sup>31</sup> D. W. FISCHER and W. L. BAUN, J. Appl. Phys. **36**, 534 [1965].

<sup>32</sup> W. L. BAUN and D. W. FISCHER, Spectrochim. Acta **21**, 1471 [1965].

<sup>33</sup> E. H. KENNARD and E. G. RAMBERG, Phys. Rev. **46**, 1040 [1934].