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THE K ABSORPTION EDGES OF POTASSIUM AND CHLORINE IN VARIOUS COMPOUNDS

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Abstract

The *K* absorption edges of potassium and of chlorine were photographed by means of a vacuum spectrometer of the type designed by Siegbahn. Four compounds were used for the absorption of potassium; namely, sylvine, orthoclase, lepidomelane, and phlogopite. In the first two, the absorption occurred in the reflecting crystal itself; in the last two, in thin sheets of the substance placed in the path of the beam which was dispersed by a calcite crystal. The chlorine of the sylvine also gave an excellent Cl *K* absorption edge. In these photographs as many as five secondary edges were observed. The fine structure of the potassium edge thus extended in wave-lengths from 3429 to 3365 x.u, or over a range of about 67 volts. The fine structure of the chlorine edge extended from $\lambda = 4383$ x.u. to $\lambda = 4341$x.u., or about 27 volts. That portion of the fine structure which is more remote from the principal edge is not satisfactorily explained by Kossel's original hypothesis, and is perhaps best accounted for by double ionization of the atoms absorbing the x-radiation.

IT IS now well known from the work of Bergengren[1], Lindh[2], Fricke[3] and others that the wave-length of the x-ray absorption edge of an element depends on the chemical compound in which the absorption occurs. The main feature of the results of these observers is that the position of the absorption edge varies with the valence of the atom, the longest wave-length being associated with the lowest valence. The absorption edge for the pure element has the longest wave-length of all.

In addition to this shifting of the principal absorption edge, a certain amount of fine structure is observed on the short wave-length side of that edge, i.e., there are secondary effects represented by white lines and dark lines which may be looked upon as edges of greater frequency than that of the principal edge. This fine structure has been observed by Lindh[2] and Fricke[3] in the edges of the lighter elements, and by Nishina[4] in the *L* edges of the heavier elements.

The difficulty of experimentally observing the fine structure lies largely in the preparation of absorbing screens of suitable or optimum thickness. The general evidence would appear to show that if the screen is too thick, then the fine structure is not observed. There is one method of avoiding the difficulty of preparing suitable absorbing screens, viz., the use of a reflecting crystal which itself contains the element whose absorption edge is required. This method is necessarily limited in its application to the cases where a crystal can be found with a suitable lattice constant for investigation of the

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[1] Bergengren, Zeits. f. Physik **3**, p. 247 (1920).

[2] Lindh, Dissertation, Lund. 1923.

[3] Fricke, Phys. Rev. **16**, 202 (1920).

[4] Nishina, Phil. Mag. **49**, 521 (1925).

desired region. Lindsay and Van Dyke[5] have used this method to investigate the K absorption edge of calcium in the crystals calcite, gypsum, and fluorite. In all cases their observations revealed a much more complicated fine structure than that found by previous observers. This has been confirmed by the present investigation of the K edges of potassium and chlorine in various compounds. The photographs were taken with an x-ray vacuum spectrograph of the Siegbahn type in which the crystal-plate distance was 182.2 mm. The x-ray tube was evacuated by a mercury diffusion pump preceded by an oil pump. A piece of thin gold beater's skin covered the slit, and separated the x-ray tube from the camera chamber which was evacuated by the oil pump alone. The voltage applied to the tube was supplied by a transformer and was in general regulated so as to prevent the excitation of second order emission lines in the region under investigation.

The average time of exposure was about five hours with a current of approximately 20 m.a. through the tube. The K absorption edge of potassium has been examined in the crystals sylvine (KCl) lepidomelane $(K, H)_2(Mg, Fe)_2(Al, Fe)_2(SiO_4)_3$, phlogopite $(K, H)_3Mg_3Al(SiO_4)_3$ and orthoclase $(KSiO_4)$.

In the case of sylvine the dispersion was 14.59 x.u. per mm on the plate, and the position of the principal edge could easily be fixed within 1/10 mm, so that the error in the determination of this edge was about one x.u. The secondary edges in the fine structure are much fainter and could not be determined so accurately as the principal edge, but the probable error was not greater than 2 x.u. As the dispersion in the crystals lepidomelane and phlogopite was about 55 x.u./mm, the fine structure was crowded close to the principal edge and on account of the poor resolution, it was difficult to measure accurately the positions of the secondary edges. Both these crystals, however, are micas and can readily be split into thin uniform sheets a few hundredths of a mm in thickness. Therefore, in the cases of these two crystals the photographs were taken with thin absorbing screens and with *calcite* as the reflecting crystal. The dispersion in the neighborhood of the K edge of potassium with a calcite crystal was 13.7 x.u./mm, so that the resolution was about the same as in the case of sylvine and approximately the same order of accuracy was obtained in determining the edges.

In the measurements with orthoclase the absorption was in the reflecting crystal itself and the dispersion (33.7 x.u./mm) did not allow such an accurate determination of the fine structure as in the previous cases.

Throughout the work the $K\beta$ line of potassium was photographed on the plates as a reference line. In all cases the photographs of the K edge of potassium show a fine structure which is somewhat similar to that found by Lindsay and Van Dyke in the case of calcium. The main features of the potassium K edge as shown by the photographs (See Figs. 1, 2, 3) are as follows. First, a strong principal edge A—then an edge B so close to the principal edge that its position is only fixed with some difficulty. These are followed by edges C, D, E, which owing to their spacing are not difficult to

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[5] Lindsay and Van Dyke, Phys. Rev. **28**, 613 (1926).

fix in lepidomelane and phlogopite, though in the case of sylvine I was unable to locate edge *D*. Succeeding these edges comes a region of more or less uniform blackening on the plate in which it is difficult to see any fine structure then finally a very weak absorption edge *F* which I have attempted to measure on most plates. These main features of the photographs were confirmed by photometer records taken with a Moll microphotometer. Table I gives the wave-lengths of the absorption edges in the different crystals, and Table II the separation in volts between the principal edge and the various secondary edges.

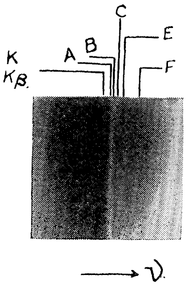

Fig. 1. Fine structure of *K* absorption edge of potassium from sylvine crystal.

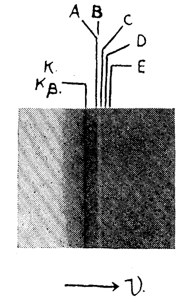

Fig. 2. Fine structure of *K* absorption edge of potassium from lepidomelane.

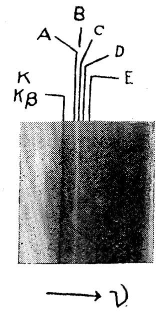

Fig. 3. Fine structure of *K* absorption edge of potassium from phlogopite.

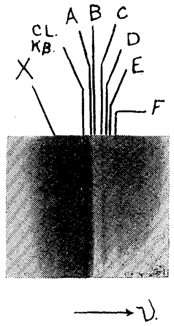

Fig. 4. Fine structure of *K* absorption edge of chlorine from sylvine crystal.

TABLE I. *Wave-lengths of absorption edges of potassium in various compounds*

Edge	Sylvine	Lepidomelane	Phlogopite	Orthoclase
A	3429.0 *x. u.*	3426.6 *x. u.*	3426.8 *x. u.*	3427.5 *x. u.*
B	3424.3	3423.6	3424.1	—
C	3414.1	3415.9	3414.6	3414.0
D	—	3408.8	3408.4	—
E	3402.7	3401.7	3401.9	3401.3
F (weak)	3366.0	3363.0	3365.0	3372.0?

TABLE II. *Separation (in volts) principal edge—secondary edges*

Edges	Sylvine	Lepidomelane	Phlogopite	Orthoclase
$A-B$	4.9 volts	3.2 volts	2.8 volts	— volts
$A-C$	15.6	11.3	12.8	14.2
$A-D$	—	18.9	19.5	—
$A-E$	27.8	26.4	26.4	27.7
$A-F$	67.4	67.7	65.7	59.2

The figures of Table I show that there is a marked similarity in the fine structure in the different crystals. The edge *D* could be distinctly seen in the photographs with lepidomelane and phlogopite but not in the case of sylvine. Edge F was weak in all the photographs.

The K absorption edge of chlorine was examined in the sylvine crystal and the fine structure was most marked in all the photographs (See Fig. 4). Rocksalt was the only other crystal containing chlorine which was examined but here unfortunately the photographs were indistinct and were not measured. Lack of time prevented any further examination of the chlorine edge.

The results for chlorine are given in Table III with the corresponding separations of secondary edge from principal edge. The fine structure extended beyond edge F (to approximately 50 volts) but was faint and was not measured.

TABLE III. *Wave-lengths of absorption edges of Cl in sylvine.*

A	B	C	D	E	F
4383.2	4377.0	4366.3	4359.3	4353.5	4341.4 x. u.
	$A\rightarrow B$	$A\rightarrow C$	$A\rightarrow D$	$A\rightarrow E$	$A\rightarrow F$
	4.0	10.9	15.5	19.2	27.3 volts

Lindh[2] has examined the K edge of chlorine in a number of compounds but in no case did he obtain so complicated a structure as that given above. His observations were made with different compounds in which the chlorine had a valence of one, five, or seven.

A remarkable feature of all the photographs of the chlorine edge in the author's experiments with sylvine was the presence of a white line absorption band at approximately 4444 x.u. This is apparently the same phenomenon which has been observed by Berg,[6] and explained by him as being due to the simultaneous reflection of that wave-length from two or more sets of planes in the crystal. The wave-length found for this white line (Fig. 4) was 4444 x.u. For the sylvine crystal the corresponding glancing angle θ is $45°-0'$. This is an excellent confirmation of Berg's theory, for in the case of a cubic crystal, we should have a strong reflection at $\theta=45°$ from the set of planes at right angles to the surface being used as the reflector. The angle for this set of planes would then also be 45°; thus the (100) planes and the (010) planes would share about equally in the reflection of this particular wave-length and at the position in the continuous spectrum corresponding to $\lambda=4444$ x.u. we should have about 1/2 the intensity of adjacent positions. This would result in the white line shown at x (Fig. 4).

It is evident from the results of the foregoing experiments that the structure of these K absorption edges is very complicated. The first possible explanation to account for the fine structure is due to a suggestion originally put forward by Kossel[7] that the ejected electron may possibly stop in the various unoccupied or virtual orbits of the outer part of the atom. On this view the frequency of the principal K absorption edge corresponds to the energy required to remove a K electron to the surface of the atom or to the

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[6] Otto Berg, Wiss. Veröff. aus dem Siemans-Konzern, Vol. V, p. 89.

[7] Kossel, Zeits. f. Physik **1**, 119 (1920).

first occupied orbit, and the limiting frequency of the fine structure is the energy corresponding to the work of removal of an electron entirely from the influence of the atom. Between these two frequencies separated by a small quantity $\delta\nu$ we have the whole of the fine structure corresponding to the ejected electron stopping in various virtual orbits. In this event one would expect that the frequency differences between the secondary absorption edges would become less as we moved away from the principal edge. Moreover the extreme difference in energy from principal edge to the limit of the fine structure should correspond (in the case of these experiments) to the work of removal of an electron from the valence orbit of a potassium ion. Assuming that the potassium ion has for the moment had one of its K electrons removed to the valence orbit, then the *additional* energy required to completely remove that electron will be somewhat similar to the energy required to remove an outer electron from a Ca^+ ion. In other words, the energy is comparable with the 2nd ionizing potential of calcium which is known to be 11.8 volts. However, the fine structure certainly extends beyond this point to at least 27 volts and probably to over 60 volts. The suggestion by Kossel may account for the first part of the fine structure, say up to and including edge C (mean value 13 volts) but could hardly account for the full extent observed in these experiments. The second possible explanation is to assume that the fine structure arises from some form of multiple ionization. This means that the same quantum of incident x-radiation ejects not only a K electron but also another electron, say one from the M shell. Clearly a quantum of primary radiation which produced such double ionization would lose additional energy and a secondary absorption edge would be produced. Assuming such a process did occur, then we must conclude that the chance of double ionization by a quantum is much less than that of single ionization of the K shell alone since the secondary edges are not so strong as the principal edge. Coster[8] has considered the possibility of double ionization and made observations on the K absorption of argon with negative results. He obtained a secondary edge very *close* to the principal edge and concluded that double ionization was improbable. On the other hand, Wenzel[9] has assumed the occurrence of double ionization to account for the so-called non diagram or spark lines in x-ray emission spectra. In the case of the present experiments it is extremely difficult to test the theory of double ionization, owing to an absence of data of M energies in the required region. Further, if we had the necessary data, uncertainty arises in the calculation of the energy required simultaneously to remove the two electrons. Assuming that the fine structure is in part due to double ionization of the KM type, then following the scheme proposed by Wenzel, the energy difference between the principal edge and a secondary edge should correspond to the energy required to remove an M electron from an atom of next higher atomic number—in the present case, a calcium atom. As emphasized above, we have no knowledge of M levels of calcium but the

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[8] Coster and van der Tuuk, Zeits. f. Physik **37,** 367 (1926).

[9] Wenzel, Ann. d. Physik **66,** 437 (1921); **73,** 647 (1924).

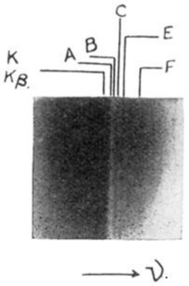
mean difference obtained in the present observations between the main edge of potassium A and the secondary edge E, about 27 volts, is probably of about the right order.

In the case of the K edge of chlorine in sylvine, it seems reasonable to suppose that it would require less energy to remove an electron from a Cl^- ion than that required to ionize a neutral argon atom (15.4 volts). In other words, 15.4 volts represents the limit of the fine structure of the Cl edge on the Kossel assumption of the ejected electron stopping in an outer unoccupied orbit. Again the observations show that the fine structure in this case extends beyond this point and perhaps represents some form of double (KM) ionization.

It has been shown that the structure of the K absorption edges of potassium and chlorine in various crystals is of a complicated nature and it would seem that the theory of the ejected electrons stopping in an outer orbit is inadequate fully to explain the nature of the edges.

In conclusion, I should like to express my thanks to Professor H. M. Randall for providing the facilities for the research which was carried out at the University of Michigan, Ann Arbor, and also to Dr. G. A. Lindsay for much helpful advice during the progress of the work.

MANCHESTER, ENGLAND,
December, 1927.



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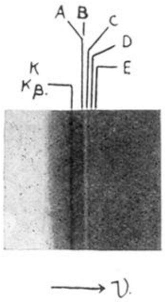

Fig. 2. Fine structure of *K* absorption edge of potassium from lepidomelane.

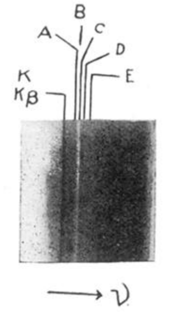

Fig. 3. Fine structure of *K* absorption edge of potassium from phlogopite.

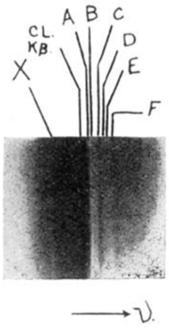

Fig. 4. Fine structure of *K* absorption edge of chlorine from sylvine crystal.