

THE K X-RAY ABSORPTION OF CALCIUM IN
CALCITE, GYPSUM, AND FLUORITE*

BY GEO. A. LINDSAY AND GEO. D. VAN DYKE

ABSTRACT

Fine structure of the K x-ray absorption edge of calcium.—The K x-ray absorption edge of calcium has been photographed with the object of studying the fine structure of the edge. The absorption occurred in the reflecting crystal itself, thus rendering unnecessary any absorbing material other than the crystal. Three crystals were used—calcite, gypsum, and fluorite. The fine structure of the edge shows as many as four subdivisions. The explanation is probably, as suggested by Kossel, that the electron ejected from the K orbit by the absorption stops in some of the unoccupied orbits, and in case of a calcium ion which we undoubtedly have in these crystals, the energy difference of these different virtual orbits is sufficient to show as a fine structure of the edge.

IT IS now well known that the wave-length of the x-ray absorption edge, due to a certain element, depends upon the compound in which the absorption occurs. The fine structure of the edge has also been found to present a different appearance in different compounds. For elements which have more than one valence, the wave-lengths of the edge fall into groups, in general, according to the valence. For the most part the longest wave-lengths are associated with the lowest valences, the uncombined element generally exhibiting the longest wave-length of all. Lindh¹ found, for example, that in the case of chlorine the wave-length of the K absorption edge varies as in Table I.

TABLE I

<i>Wave-length of K absorption edge of Cl (Lindh).</i>	
	λ in X.U.
Cl ₂ (element alone)	4393.8
Cl _I	4382.9
Cl _{IV}	4376.9
Cl _{VII}	4369.8

Similar results were found for sulfur. He also found a variation in the fine structure even within groups of the same valence. Thus a few selected from the divalent sulfur compounds investigated by Lindh showed wave-lengths for the K absorption edge as given in Table II.

* A portion of this paper was presented at the Montreal meeting of the American Physical Society, February, 1926.

¹ Lindh, Dissertation, Lund, 1925.

TABLE II

Wave-length of K absorption edge of sulfur compounds (Lindh).

Compound	λ in X.U.
CS ₂	5011.4
Na ₂ S	5009.6
MgS	5005.6
CoS	5010.9
BaS	5007.5

This variation over a range of about 6 X.U. is evidently beyond the limits of experimental error.

Fricke² investigated the K absorption edges of the elements from Mg to Cr inclusive, and found a variety of fine structure, and it may be noted that the most complicated edges occurred in the cases of compounds. The free elements, magnesium, aluminum, and argon gave a simple edge, while for sulfur and the others, which were in compounds, the edges showed a fine structure. For calcium, which he used in the form of a screen of calcium carbonate, Fricke found at the absorption limit a single white line, i.e., a narrow region where the absorption was especially great. Later Lindh³ found for absorption in the calcite crystal used as a grating the same single white line, evidently much like that observed by Fricke, while for an absorbing strip of calcium metal he found a simple absorption edge with no noticeable white line. Lindh remarks that the white line might appear with a thinner screen. His values of wave-length for the edge are

Ca	3064.3 X.U.
CaCO ₃	3060.5 X.U.

We have obtained edges for calcium by absorption in the reflecting crystal itself and they show in all cases a structure considerably more complicated than that found by either Fricke or Lindh. Three different crystals were used as gratings: calcite (CaCO₃), gypsum (CaSO₄ · 2H₂O), and fluorite (CaF₂). Figs. 1, 3, and 5 show absorption edges due to the calcium in these three crystals respectively. The curves in Figs. 2, 4, and 6 are photometer records taken with a Moll microphotometer. These curves were copied by tracing through a sheet of white paper and the slight irregularities due to the grain of the photographic plates were omitted. The points *A*, *B*, *C*, and *D* indicate corresponding points on the plate and on the photometric curve. The point *A* on each plate is the principal edge. *B* is the secondary edge, very distinct in the case of calcite, less so for fluorite, and so faint as to be rather doubtful in the case of gypsum. *C* is the beginning of a broader region of absorption, while

² Fricke, Phys. Rev. **16**, 202 (1920).

³ Lindh, Ark. för Mat. Ast. och Fys., Vol. 18, No. 14.

D is probably a fourth absorption band which is not well separated from the *C* band for calcite and gypsum but is more distinct for fluorite.

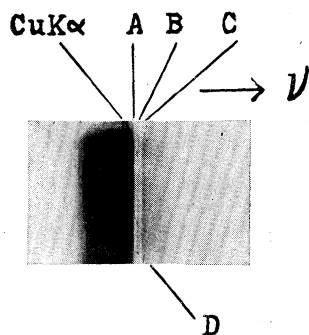


Fig. 1. Fine structure of K absorption limit of Ca from CaCO_3 crystal.

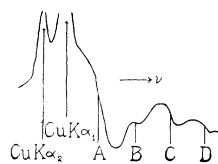


Fig. 2. Microphotogram of plate shown in Fig. 1.

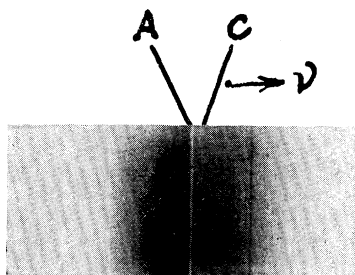


Fig. 3. Fine structure of K absorption limit of Ca from gypsum crystal.

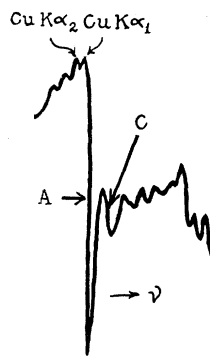


Fig. 4. Microphotogram of plate shown in Fig. 3.

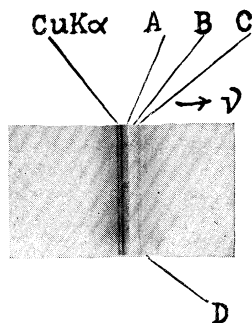


Fig. 5. Fine structure of K absorption limit of Ca from CaF_2 crystal.

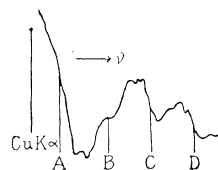


Fig. 6. Microphotogram of plate shown in Fig. 5.

Table III gives the wave-lengths of these four points. Table IV gives the differences in volts between the points designated, and the corresponding differences in the values of ν/R .

TABLE III

Wave-lengths of absorption edges in calcium compounds.

	CaCO ₃	CaSO ₄ ·2H ₂ O	CaF ₂
	λ in X.U.	λ in X.U.	λ in X.U.
A	3060.3	3059.1	3059.9
B	3050.2	3047.5	3047.8
C	3037.9	3035.3	3034.6
D	3023.3	—	3025.3

TABLE IV

Equivalent volt differences and differences in ν/R between absorption edges.

	Volts	$\frac{\Delta\nu}{R}$	Volts	$\frac{\Delta\nu}{R}$	Volts	$\frac{\Delta\nu}{R}$
A to B	13.3	0.99	15.3	1.13	16.0	1.18
B to C	16.2	1.20	16.3	1.20	17.7	1.30
C to D	19.6	1.46	—	—	12.5	0.93
A to D	49.1	3.65	—	—	46.2	3.41

The width of the first white line which extends from *A* to a point about half way to *B* is, for CaCO₃, 6.7 volts or $\Delta\nu/R=0.51$, the second white line has a width of about $\Delta V=5.4$ volts, or $\Delta\nu/R=0.41$, while the width over both white lines is 26 volts or $\Delta\nu/R=1.9$. Fricke's results show $\Delta\nu/R=2.2$, indicating that Fricke's single white line is, on our plates, resolved into two. The width of the slit has been subtracted both in Fricke's and our values given above. As we measured the extreme limits of the white line, we have assumed that the true value should be one-half the width of the slit towards the middle of the line from each side.

There is no doubt that this fine structure is due to the absorption and not to any emission lines which occur in this region, because there are no lines of the first order in x-ray spectra falling at the regions of greater blackening on the plates, and on some of the plates the voltage was kept low enough so that the CuK α_1 and K α_2 lines from the copper target did not show. These strong copper lines in the second order fall only about 1 mm to the long wave-length side of *A*, as shown in Figs. 1 and 5, and hence are in a very favorable region where there is little absorption in the crystal. If they do not appear, it is certain that no other second order lines will. On the plates taken at voltages so low that these lines did not appear, the fine structure of the edge was just as distinct as in the ones reproduced here. It is, therefore, evident that the absorption edge due to calcium is much more complicated than has been observed hitherto.

It was first suggested by Kossel⁴ that the white line shown in absorption edges was due to the ejected electron's stopping in the unoccupied orbits in the exterior part of the atom. He also remarked that, in case the atom were ionized, this white line should be wider or probably

⁴ Kossel, Zeits. f. Physik 1, 119 (1920).

resolved into several components. Coster⁵ has also considered the possibility of the simultaneous ejection of a K electron and one of the outer electrons as proposed also by Wenzel in explanation of the fine structure. In the experiments of the former with argon, however, this double ionization was judged to be improbable. The appearance of the fine structure on our plates would demand multiple ionization, or several different kinds of double ionization. The distance between the components of the fine structure would also be difficult to account for on the theory of the simultaneous ejection of two or more electrons. For if we use the notation of Wenzel in which N represents the energy of the atom when one electron is missing from the N group, N^2 the energy when two are missing from the N group, KN when one is lacking in each of the K and N groups, then, assuming the calcium in the crystals used to be in the form of the calcium ion, Ca^{++} , we should represent the work required to remove a K electron from this ion by $KN^2 - N^2$. To remove simultaneously a K and an M electron (there are no more N electrons left) the work is $KMN^2 - N^2$. The difference between these two energies is $KMN^2 - KN^2$, which is seen to be the work required to remove an M electron when the atom already lacks one K electron and two N electrons. The second ionizing potential of Ca is 11.22 volts, and if an outer electron were removed at the same time as a K electron, the edge corresponding to this should differ from the main edge by about the fourth ionizing potential of Sc(21), the next element above Ca(20), for when one K electron is removed, the center of the atom could be considered to act about the same as that of the neutral atom of the next higher number. The fourth ionizing potential of scandium would certainly be much greater than the difference between our first and second edges, which was about 15 volts.

We may then consider the case in which the ejected K electron stops in various unoccupied orbits. Such orbits for Ca^{++} are from the 3_{32} orbit inclusive outward. If the selection rules hold for this semi-optical phenomenon, the K electron would be limited in its final position to the 4_{21} , 4_{22} , 5_{21} , 5_{22} , 6_{21} , 6_{22} , etc., orbits. Although we have no data on which to base a judgment as to the difference in energy corresponding to the stopping of the electron in the 4_{21} or the 4_{22} orbit, it is probably much smaller than the 14 volts observed as the difference between first two components of the edge. We should rather suppose that the components of the fine structure correspond to the N group, the O group, etc., possibly limited to the sub-levels in those groups indicated above.

⁵ Coster and Van der Funk, *Nature* **117**, 586 (1926).

We may also notice that in Bohr's and Stoner's tables of electron groupings, the electron added on passing from Ca to Sc is placed in the 3_{32} orbit. If the nucleus, together with the absence of one K electron in the Ca atom, acts like the Sc nucleus, then we might think it possible, ignoring the selection rule, that the K electron would stop in the 3_{32} orbit, the system then resembling the doubly ionized Sc atom. However, as Bohr and Coster have emphasized, and as x-ray spectra and also optical spectra indicate in analogous cases, there is in this region of the periodic table very little difference in the binding energy of an electron whether it is in the 3_{32} orbit or the 4_{11} orbit. Hence there would be very little difference in the wave-length whether the electron stopped in the M group or in the N group.

On the other hand, if we consider the distances separating the points *A*, *B*, *C*, *D* in Fig. 5 for fluorite, we see that these do not agree with the relative steps that we should have between the N, O, and P groups. There is apparently no reason why the difference between the O and P levels should be 18 volts while that between the N and O levels should be only 16 volts.

The extreme difference between the points *A* and *D* is nearly 50 volts. The point *D* probably corresponds to a removal of the electron entirely from the influence of the Ca^{++} ion, and the 50 volts represents the difference of potential necessary to remove an electron probably from the valence orbit of the ion to infinity, the atom meantime lacking two other of its 20 electrons, one from the K orbit and one from the valence orbit. 50 volts seems too large, for it should be like the 3rd ionizing potential of scandium. The latter has not yet been measured, but if we consider the similar element, Al(13), for which the 3rd ionizing potential is 28.3 volts, we might suppose that for scandium to be somewhere between 25 and 30 volts instead of 50.

The gypsum crystal has a much larger grating space than calcite or fluorite. For calcite, $d=3.029\text{A}$; for gypsum, $d=7.578\text{A}$. The grating space of the (111) planes of fluorite taken from Bragg's⁶ measurements is 3.132A, and other investigators, using the powder method, have found a somewhat higher value. From a measurement of the constant of the fluorite crystal used we obtain in the first order, $d=3.1446\text{A}$. The second and third orders gave increasingly higher values for d as has been found by several other observers who have investigated the departure from the Bragg law. The spectrum from gypsum, then, falling at a much smaller glancing angle, has a much smaller dispersion than that from the

⁶ Bragg, Proc. Roy Soc. 89A, 468 (1914).

other two crystals, and the fine structure is necessarily crowded into so small a region as to render it less distinct. Figs. 3 and 4 each show but two white lines. The other irregularities towards higher frequencies are probably due to faint emission lines. The two portions, *A* and *C*, are, however, unmistakable. The second one is lettered *C* because it is at about the same wave-length as *C* in the plates for calcite and fluorite. On close examination of the original plates, one can see a trace of a faint white line at about the same wave-length as *B* in Figs. 1 and 5. This faint edge was measured approximately and is included in Table I, though it is invisible in the reproductions. It can easily be seen that *B* is relatively more pronounced in calcite than in either of the other two, and that *C* is relatively stronger in fluorite, so that the compound has some influence on the relative intensities of the different portions of the fine structure. The wave-lengths of the various edges could be measured very conveniently by comparison with the $\text{CuK}\alpha_1$ and α_2 lines in the second order which are about 1 mm away, as shown in Figs. 1 and 5.

The Ca^{++} ion undoubtedly presents more favorable conditions for the appearance of the fine structure than does the neutral atom, because the electric field in the outer region of the ionized atom is much stronger. This idea of Kossel is supported by the extended fine structure shown by our plates and by the general lack of fine structure in the work of Fricke and Lindh, referred to above in the cases in which they used the uncombined elements.

It has been shown that the fine structure of the CaK absorption edge is more complicated than previous observations have indicated. If selection rules are valid for the transition of the electron ejected from the K orbit, it is difficult to account for the number of parts of the edge as well as for their relative locations and intensities. We expect to continue the work with other crystals containing calcium.

PHYSICAL LABORATORY,
UNIVERSITY OF MICHIGAN,
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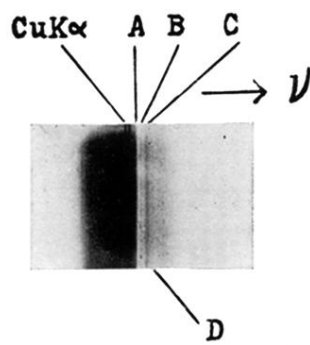


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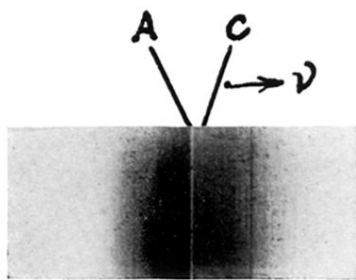


Fig. 3. Fine structure of K absorption limit of Ca from gypsum crystal.

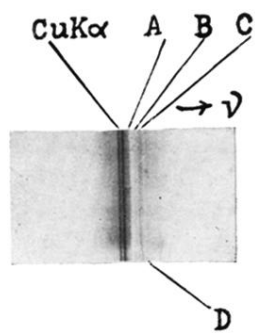


Fig. 5. Fine structure of K absorption limit of Ca from CaF_2 crystal.