

ON THE WIDTH OF THE K-ABSORPTION EDGE OF COBALT

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Plate II

ABSTRACT. The width of the K-absorption edge of cobalt metal and the compounds CoO ; Co_2O_3 ; $\text{Co}(\text{NO}_3)_2, 6\text{H}_2\text{O}$; $\text{CoSO}_4, 7\text{H}_2\text{O}$; CoCl_2 (anhydrous); $\text{CoCl}_2, 6\text{H}_2\text{O}$ in the solid form and in aqueous solutions of $\text{CoSO}_4, 7\text{H}_2\text{O}$; $\text{CoCl}_2, 6\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2, 6\text{H}_2\text{O}$ having different strengths together with a concentrated solution of cobalt nitrate in nitric acid has been studied. It has been observed that so far as the compounds of cobalt in the solid states are concerned the pure metallic element shows the largest width, whereas in solid metallic compounds and their aqueous solutions, the solid has the smallest width. The width of the edge in a concentrated solution of cobalt nitrate in nitric acid deserves particular attention as it is not only appreciably larger than the same obtained in the solid nitrate and in its aqueous solutions but also is largest obtained in this set of investigations.

It has also been found in the case of metallic element and blue oxide CoO that neither the inflection point which determines the wavelength of the edge nor the full width or the idealised width is affected by the screen thickness. The presence of structure edge K' is also reported in the case of cobalt metal and its black oxide Co_2O_3 .

I N T R O D U C T I O N

The measurements of the widths of the X-ray absorption edges have not yet received so much attention as the X-ray emission lines. In the later cases, widths are expressed in terms of the well-defined half-width of the emission lines as in the case of optical spectra. In the X-ray absorption spectra, however, two definitions are generally used to define the width of the edge. The first is defined by the full width and is measured by the distance of two points of maximum and minimum intensity in the photometric curve. The other definition first suggested by Ross¹ measures the distance between the intersection points of the tangent through the inflection point and the two horizontal lines passing through the points of maximum and minimum intensities. Really it is very difficult to ascertain the maximum point, *i.e.*, the long wavelength in the edge with any accuracy mainly because of the smooth decline of the curve. The determination of the wavelength of the edge is now generally made by measuring the middle point of the edge, *i.e.*, the inflection point or really the middle point of

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the straight portion of the edge in the photometric records, as all absorption edges are more or less asymmetrical.

Richtmeyer and Barnes² from theoretical considerations have pointed out that the screen thickness may have a profound influence not only on the shape but also on the position and the widths of the absorption edges.

Sandstrom³ carried out a systematic investigations in the L-absorption edges of 30 Zn to 52 Te, and found that with the varying thickness of the absorber 34 Se there is no systematic variation of the wavelength of the edge. It was also found that the point of inflection, which corresponds with a fair degree of accuracy with the middle portion of the straight part of the photometric curve is unaffected by the screen thickness. Sandstrom has measured the full widths of the most of L_{II} and L_{III} edges and some L_I edges in the region 30 Zn to 52 Te, showing the variation of the width with atomic numbers.

Cioffari⁴ has investigated the width of the edges of Bromine and Iodine in the element itself in solid, liquid and vapour phases and also in chemical combination by the double-crystal spectrometer. He reports that chemical combination seems to have very little effect on the width of the K-absorption edges. Most of the compounds of bromine and iodine showed nearly the same width as that of the pure element, no matter in what phase it was. The only exceptions were shown by IBr vapour which had a slightly narrower width and CH_3Br which had a larger value for the width.

The similarity of the structures of the K-edge of Cobalt, in cobalt metal, in its various compounds and also in aqueous solutions of different strengths of some of these compounds was reported before.⁶ It was also stated there that with only dilute solutions of strengths of the order of N/10 and N/20, a quite different structure of the edges adjacent to the main one was found. In this connection it was thought proper to investigate the effect on the width of the edges under different combinations and also with aqueous solutions of different strengths.

EXPERIMENTS

A Siegbahn Vacuum spectrograph was used with a calcite crystal. The latter was rotated through $2^\circ-30'$ about the mean angle for the K-absorption edge of cobalt. The width of the slit was 0.1 mm. and was covered with thin aluminium foils of thickness .002 cm. to separate the high vacuum part of the X-ray tube from the spectrograph.

The dispersion in the plate was found to be 16.41 X. U. per mm. The photometric records magnified the lines to 6.78. All measurements of the widths of the edge were made with the photometric record.

A large number of plates was taken with absorption screen of varying thickness of cobalt metal and cobaltous oxide (CoO). Although actual measurements of screen thickness were not made, it was found that neither the point of inflec-

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tion which determines the actual position of the absorption edge, nor the "full-width" or "idealised" widths showed any change with varying thickness.

In some absorption spectrum with cobaltous oxide (CoO) as the absorption screen was made very thick, the contrast between the black and white bands on the short-wavelength side of the main edge was so poor that only a continuous white band appeared in the photographic plate without any secondary structures.

Barnes⁵ has found that the K-edges of the elements 25Mn-29Cu have a fine structure in the edge itself. In the element cobalt and in Co₂O₃ similar "structure edge" K' whose wavelength is about 1 X.U. shorter than the primary edge has also been found in our experiments.

As it is extremely difficult to locate the actual position of maximum and minimum intensities preceding and following an absorption jump as well as the direction of the tangent at the point of inflection, an error as high as 20 per cent is quite likely in these measurements. The photometric records of cobalt metal (Fig. 1); Co₂O₃ (Fig. 2); Co-nitrite (Fig. 3); CoCl₂, 6H₂O (Fig. 4); Co(NO₃)₂, 6H₂O (Fig. 5); Co(NO₃)₂, 6H₂O in .3N Sol. (Fig. 6); Co(NO₃)₂, 6H₂O Sol. in HNO₃ (Fig. 7); and CoCl₂, 6H₂O in 1.5N sol. (Fig. 8) are given here.

The following table gives the results on the measurements on the idealised widths.

TABLE I

Solid Substance	Strength.	Idealised Width of the K-edge of Cobalt in X.U.
Cobalt metal (Co)	...	4.1
Cobaltous oxide (CoO)	...	3.0
Cobaltic oxide (Co ₂ O ₃)	...	2.0
Cobalt nitrite	...	2.2
Cobalt sulphate (CoSO ₄ , 7H ₂ O)	...	2.5
Cobalt Nitrate (Co(NO ₃) ₂ , 6H ₂ O)	...	3.6
Cobaltous chloride (CoCl ₂ , 6H ₂ O)	...	3.6
Cobalt Chloride (CoCl ₂) (anhydrous)	...	2.6
Solutions		
Co(NO ₃) ₂ , 6H ₂ O	solid	3.6
Co(NO ₃) ₂ , 6H ₂ O	1.9N	4.1
Co(NO ₃) ₂ , 6H ₂ O	.6N	4.6
Co(NO ₃) ₂ , 6H ₂ O	3N	4.4
Co(NO ₃) ₂ , 6H ₂ O	concentrated sol. in nitric acid	6.8

TABLE I (contd.)

Solution.	Strength.	Idealised width of the K-edge of cobalt in X.U.
CoSO ₄ · 7H ₂ O	solid	2.5
CoSO ₄ · 7H ₂ O	1.7N	3.6
CoSO ₄ · 7H ₂ O	1N	4.8
CoSO ₄ · 7H ₂ O	N/10	4.8
CoSO ₄ · 7H ₂ O	N/20	4.8
CoCl ₂	anhydrous	2.6
CoCl ₂ · 6H ₂ O	hydrated solid	3.6
CoCl ₂ · 6H ₂ O	1.5N	3.0
CoCl ₂ · 6H ₂ O	1N	2.9
CoCl ₂ · 6H ₂ O	N/10	2.9
CoCl ₂ · 6H ₂ O	N/20	3.6

In this region, 4.1 X. U. is equivalent to an energy value of 20 Volts.

From the table I, it is apparent that of all the solid substances investigated, cobalt metal definitely shows the largest width. In Co₂O₃ we have the smallest width. An error in this measurement is quite large because of the presence of a peculiar position of the fine structure in the edge itself. Cobalt nitrate cannot be obtained in the pure form; it is always a mixture of cobaltous and cobaltic nitrites as well as cobaltous nitrate.

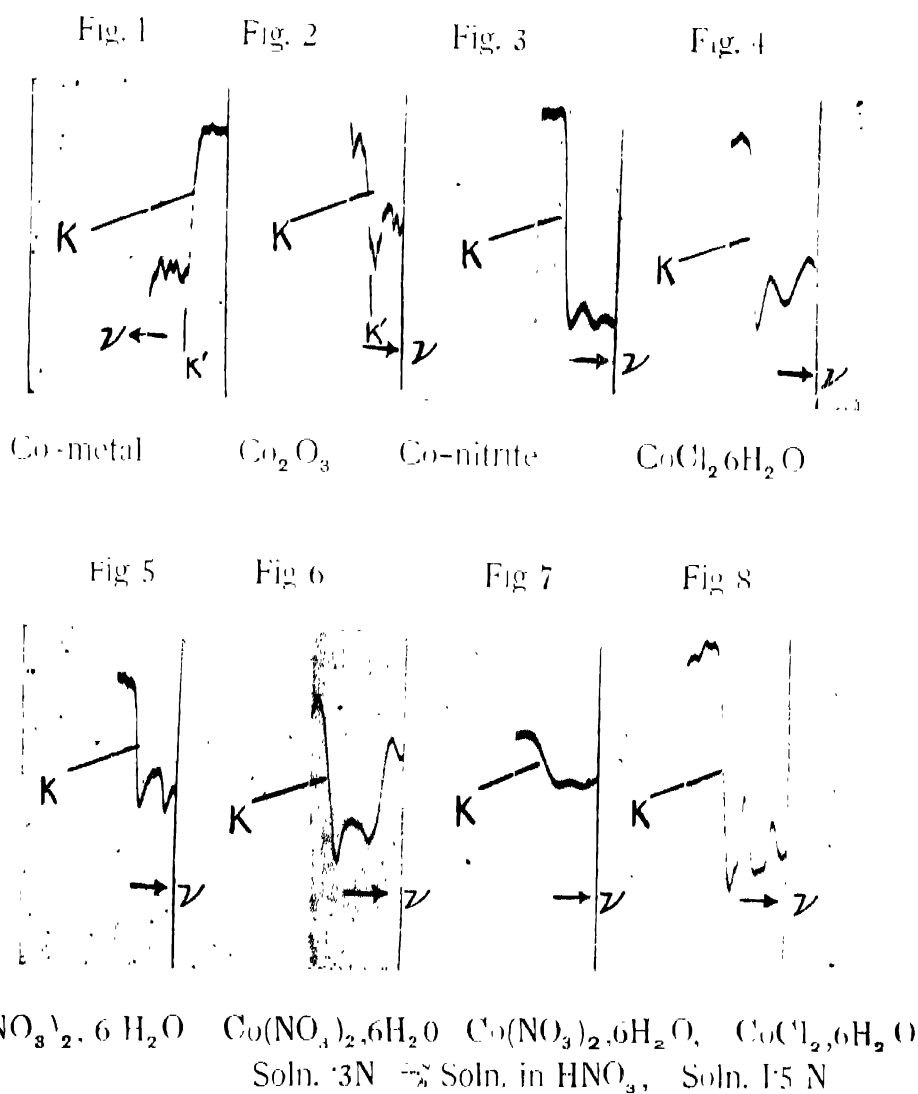
From a survey of the results obtained in the cobaltous nitrate, Co(NO₃)₂ · 6H₂O, in states of solid and aqueous solutions, one can conclude that the solid shows the smallest width, which rises in the case of solution; as a matter of fact from 1N to .3N solutions, the width is fairly constant. Concentrated solution of Co(NO₃)₂ · 6H₂O in strong HNO₃ shows the largest width. (Fig. 7.)

In CoSO₄ · 7H₂O we have an analogous result; the width is definitely smaller in the solid state than in solutions. From 1N to N/20, it is fairly steady with an intermediate value for 1.7N solution.

From the table I, it will be seen that CoCl₂ (anhydrous) has the smallest width and CoCl₂ · 6H₂O (solid) and aqueous solutions of different strengths show the same width within experimental error.

It may be mentioned here that the anhydrous salts of Co(NO₃)₂ and CoSO₄ could not be easily prepared and so in the solid state, Co(NO₃)₂ · 6H₂O and CoSO₄ · 7H₂O only were examined. The widths of the K-edges of these salts in solid

PHOTOMETRIC RECORDS OF SOME ABSORPTION EDGES
MAGNIFICATION 6.78 X



The K edge and some secondaries are shown.
K' - the fine structure with the edge K

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states were definitely smaller than those obtained in aqueous solutions. It is quite likely that the anhydrous salts of CoSO_4 and $\text{Co}(\text{NO}_3)_2$ might possess smaller widths than the hydrated ones ; but unlike $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, K-edges have approximately the same width in $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, as in its aqueous solutions.

It may be concluded that so far as the compounds of cobalt in the solid states are concerned the pure metallic element shows the largest width whereas in the solid metallic compounds and their aqueous solutions the solid has the smallest width.

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R E F E R E N C E S

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