

SECONDARY K-ABSORPTION EDGES OF COBALT SALTS IN SOLID AND LIQUID SOLUTIONS*

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ABSTRACT. The paper deals with the experimental measurements on the primary and secondary K-absorption edges of cobalt metal, its oxides, and its compounds both in the forms of solids and solutions. It is found that

(a) Though the primary K-edge of cobalt shifts to the shorter wavelength side of the spectrum as one passes from the metallic form of the element to its compounds, the secondary structures of all the solid compounds of cobalt show a similarity with that of the metal itself.

(b) The similarity between the structures in cobalt metal and that in anhydrous cobaltous chloride is significant. Though both these substances form hexagonal crystals, the metallic cobalt is non-ionic while the other is of the ionic type.

(c) CoO and Co₂O₃ (cubic and hexagonal respectively) show the same type of structures.

(d) Near the K-absorption edge, the relative intensity of the structures (*i.e.*, contrast between the white and dark lines) are quite prominent, and it decreases gradually at first with increasing separation from the main edge, and afterwards increases again before it vanishes.

(e) On passing from the solid polar compounds to solutions up to 1N the similarity of the secondary structures in all cases is noteworthy. It is suggested that in solutions up to 1N, most of the molecules are not at all dissociated.

(f) In the case of dilute solutions of strengths of the order of N/10 and N/20, the structure near the primary is quite different from what has been observed with strong solutions (e). Here it is suggested that only a small percentage of the molecules are dissociated. The positions of the secondary structures show that they originate from undissociated molecules.

(g) The solution of Co(NO₃)₂ · 6H₂O in conc. HNO₃ shows the same structure as is exhibited by strong solution of the same substance in water (e).

INTRODUCTION

Experiments on the K-absorption edges of lower elements by Lindsay and Van Dyke¹ have clearly shown that after the K-absorption edge, there are fluc-

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tuations of the intensity (Maxima and Minima) in the general absorption spectra in the short wavelength region of the main K-edge. These white and dark lines (or bands) in addition to the main edge form the complete X-ray absorption spectra. Later works by Lindsay and Voorhees,² Lindsay and Keivit,³ Lindh,⁴ Hanawalt,⁵ Coster⁶ and his associates have definitely shown such structures in the K and L series of many elements in different compounds having different crystalline modifications. For the origin of these secondary edges Ray,⁷ Coster,⁸ Lindsay⁹ and others put forward the theory of simultaneous transition of two electrons by a single encounter of an X-ray quantum. But this theory could not satisfactorily explain the dependence of absorption spectra (1) on chemical and physical state, (2) on the nature of crystals of the compound, and (3) on the effect of temperature on the position of the secondary edges.

Further it cannot explain the absence of secondary structure in the case of an isolated atom. The theoretical explanation of the origin of these structures (secondary) was first given by Kronig¹⁰ who investigated the energy spectrum of an electron moving in the lattice of the crystal. He was able to show that under the influence of a crystalline field the electron cannot have all the values of energy but it possesses an energy spectrum consisting of allowed and forbidden energy zones. This spectrum extends to a large energy distance (of the order of several hundred electron volts) from the first optical level. For the zones low in the energy spectrum, the allowed zones are much sharper than the forbidden ones. But reverse is the case as we go upwards and finally there remains no forbidden energy zones.

During the process of X-ray absorption, the electrons ejected from the deeper energy levels (the X-ray limits) accommodate themselves in these allowed energy zones following certain selection principles. In the case of a simple atom and 'ions' we obtain only sharp fine structure lines in the absorption spectrum, whereas in the case of crystal and polyatomic molecules the secondary absorption spectrum extends to very high energy distances from the primary edge.

Kronig has shown that in the case of metals or the cubic crystals the energy values of the mean positions in the forbidden zones are given by

$$E_n = \frac{n^2 h^2}{8md^2}$$

where E_n = mean energy of the n th forbidden zone, n = an integer similar to quantum number, d = the side of the unit cell of a cubic crystal and h = Planck Constant.

Kronig¹¹ has further developed his theory for the existence of secondaries in the case of polyatomic gases. Hartree, Kronig and Patersen¹² calculated the numerical values of the position of the structures of the K-edges of Ge in GeCl_4 by considering the chlorine ions situated at the corners of a regular tetrahedron.

Though Kronig's theory of secondary structure has explained many of the experimental results concerning the X-ray absorption by the atoms in pure metal and in non-polar compounds, yet there are certain difficulties with which it is faced in the case of the ionogenic compounds. Coster and Klammer¹³ have studied the secondary structures to the K-edges of potassium and chlorine in an ionic crystal KCl and have found that the structures of potassium and chlorine are totally different though according to Kronig's theory they would be similar. Similar observations were made by G. P. Brewington¹⁴ which bear the evidence that although Kronig's theory holds good in the case of elements and their compounds involving non-polar bonds it fails in the case of the polar compounds.

Although the results, stated up till now, have thrown considerable light on X-ray absorption spectrum and the electron energy states in crystalline solids including metals and their compounds, no systematic investigation has been carried out for a detailed study in the case of ionic crystals and solutions. So far as the absorption spectra of a solute in a solvent are concerned, mention may be made of the attempts of Yost,¹⁵ Meyer¹⁶ and Hanawalt.⁵ In a short note in *Philosophical Magazine*, Yost has shown that the primary K-edges of Manganous and Chromate ions in ionic crystals $MnCl_2$ and K_2CrO_4 are the same as they are obtained with solutions. Mayer also found no detectable difference in the position of the K-edge of bromine in $NaBrO_3$ in the solid states and in aqueous solutions. Hanawalt also obtained the structure to the K-edge of Br in solid $NaBrO_3$ and in its solution and found that there was no appreciable change except that one structure near the primary K-edge of Br in the solid substances was absent in the case of solutions. Stelling¹⁷ obtained the primary K-edge of chlorine in NaCl in the form of solid and solution and found that the wavelength in solution is a little greater than that for solid NaCl. Owing to difficulties in obtaining an extended structure in case of substance in solution no further work is known to have been done in this line.

Though the preliminary works by Hanawalt⁵ showed no appreciable change of the position of the primary K-edge of bromine in $NaBrO_3$ in solid and in solutions of different strengths, it was thought proper to study systematically the absorption spectra of an element in different chemical combinations both in the solid state and in a state of solution.

For a detailed study of the influence of polar crystals on the absorption spectrum and the influence of water molecules in the ionic solutions of different strengths on primary and secondary absorption spectra, we have chosen cobalt and its compounds because of the fact that

(a) The K-absorption edge of cobalt is not placed either in the very soft or in the very hard region.

(b) The dispersion in this region of the spectrograph is quite sufficient for our purpose.

(c) Cobalt gives two series of compounds and forms hydrated ionic salts, which in some cases may be obtained in the anhydrous form though with much difficulty.

ABSORPTION SCREENS AND CELLS FOR ABSORPTION SPECTRA AND THEIR PREPARATIONS

The preparation of absorption screens and cells for obtaining extended secondary structures associated with the main edge is of prime importance and causes great difficulty. The thickness and uniformity of the absorbing screen always play an important part in these investigations. There is some optimum range of thickness of the screen for which a good record can be obtained. It is found that if the thickness of the screen is below or above a certain range of thickness, all the structures associated with the main edge do not come in prominently. Up till now, theoretically no definite relation has been put forward for the screen thickness, although it is found experimentally that a thickness which reduces the intensity of the general radiation to half its original value gives satisfactory results (Johnson's formula is applied here to find the screen thickness).

(a) Solids

Several methods were tried for obtaining screen of a suitable thickness, but the following proved to be convenient.

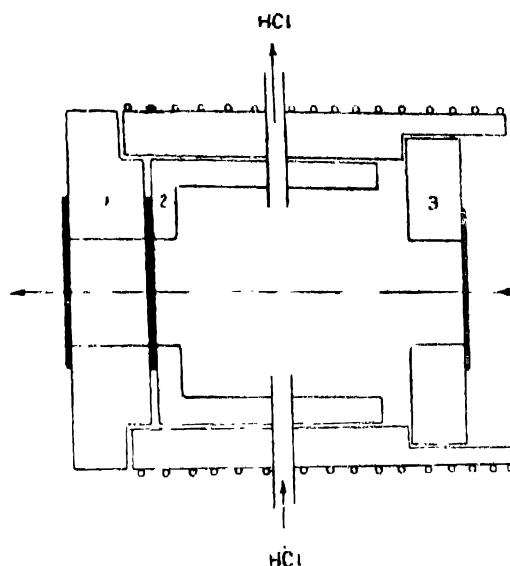
In the case of absorption spectra for solids the following methods were adopted :

(a) The substance is finely powdered in a mortar and the powder is then pressed in uniform thickness over a piece of zig-zag paper or ordinary filter paper. In the case of hydrated salts the substance is pressed on filter paper.

(b) For solid substances which are not soluble in water the following method is particularly suitable. The substance is finely powdered in a mortar and a drop of secotine is then added to it. After mixing it uniformly, a little quantity of water is added and an emulsion is obtained. This emulsion is allowed to pour on a piece of ordinary paper resting on a plate which is levelled. On drying, a screen of uniform thickness is obtained.

(c) For the study of the absorption edges of anhydrous CoCl_2 , a cell holder of special design was used. The cell holder consists of cylindrical syndanio tube in the interior of which another tube was fitted over three-fourths of the length of the former. The two ends can be fitted on the cap attached to the cone carrying the slit. Inside the inner tube there are three circular rings of syndanio plates having rectangular openings in them which are parallel to the length of the slit. There are two perforations in the body of the tube through which a current

of dry gaseous HCl can be passed. The cell is shown diagrammatically in the following figure.



On the second ring an absorbing screen of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, prepared by dipping a filter paper in a saturated solution of the substance, is pressed with secotine. The first ring is pressed on this ring, the outer end of which is covered with thin cellophane. On the third ring another piece of cellophane paper is mounted and between 2 and 3 a supply of dry gaseous HCl is made. On the outer syndanio tube is wound an electrical heater.

The two extreme circular rings were cemented with the outer syndanio tube by Plaster of Paris, so that the cell could be air-tight. The inlet and exit tubes of the cell for passing HCl gas could be sealed at the constrictions. The screen was heated at a temperature of 120°C in a constant supply of dry HCl gas and the temperature was recorded by a thermocouple.

(b) Solutions

In order to obtain absorption spectra of a substance in solution, one must use a cell which will not be attacked by the solution and at the same time will transmit the radiation. In the case of solution the proper thickness was attained by placing the solution between two thin films separated by a rubber sheet of requisite thickness. When the strength of the solution was altered, the thickness of the rubber sheet was also changed accordingly. The walls of the absorbing cell consisted of extremely thin celluloid on one side and aluminium foil $.007\text{ mm.}$ thick on the other in the case of solutions of cobalt nitrate and cobalt sulphate. But in the case of cobalt chloride solutions, the aluminium window must be dispensed with, as aluminium is found to be attacked by the solution. Thinner films of mica or

extremely thin pieces of celluloid were tried in some exposures but none of these methods led to the desired results. The use of cellophane as cell walls was also tried but in that case the uniformity of the thickness of the cell was lost. By coming in contact with the liquid, the cellophane bulges inward in some positions and outwards in others. With gold beater's skin as cell wall, there was no question of non-uniformity but the solution was found to be coloured blue. Thinner films for cell walls were prepared by dissolving celluloid in acetone and pouring the solution on a clear glass plate resting on a levelled platform. The preparation of thin films of uniform thickness by this method, is a very difficult task, and often it was found that as the films became thinner there was a greater chance of non-uniformity, which in many cases resulted in a leak in the films. Moreover, the films prepared in this way seemed to be porous, and air bubbles entered into the cell after some hours and the liquid leaked out. This difficulty could not be avoided and the presence of solution in the cell was examined thrice a day and the cell freshly filled up whenever air bubbles were found inside the cell.

THE CELL HOLDER

The cell holder consisted of a rectangular brass plate, 4 cm. \times 2.5 cm., in which a rectangular slot, 2 cm. \times 0.7 cm., was cut out. Another plate was prepared having the dimensions, and with a rectangular opening having the same area, so that when one was placed on the other, they coincided. The two brass plates can be screwed at the four corners. The lower plate was fitted with a cylindrical cap attached to the cone carrying the slit of the spectrograph. Absorbing screens could be placed between the two brass plates for exposure. The cell holder is indispensable in the case of solutions.

EXPERIMENTAL ARRANGEMENTS

A Siegbahn Vacuum spectrograph fitted with an electron tube was used. The slit through which the X-rays from the electron tube falls on the analysing calcite crystals is 0.1 mm. in breadth. The high vacuum of the electron tube is separated from the comparatively low vacuum in the spectrograph by thin aluminium foils. The heating filament is a spiral of tungsten wire fed by a low tension transformer. The crystal was oscillated at random through $2^{\circ} 30'$ in a few cases by the hand but frequently by the following device.

A low-speed motor was connected to two wheels. In the bigger one was fitted a cam whose groove was cut in the form of a Caseni's spiral. One end of a long brass rod was fixed to the crystal holder and the other to a pin which moved in the groove of the cam, the motion of the rod being controlled by a guide.

After the preliminary adjustment of the crystal and the plate holder, their zero positions were determined. For the reference lines in this connection the W L 1, W L α_1 α_2 and Cu K α_1 α_2 emission lines were chosen. The Cu K α lines, which are highly absorbed by cobalt, were not very strong in the photograph

and did not cause any great inconvenience, though they fell in the secondary absorption region.

In the case of absorption spectroscopy, choice of photographic films and developers is of utmost importance. In our case best results were obtained with double-coated Agfa Sino Films with which a good contrast in the intensity of the absorption spectrum is obtained. Agfa Röntgen developers of constant strength were always used, and the plate was finally fixed in hypo solution.

Agfa Sino Films are very sensitive to temperature, and at temperatures above 20°C there is the possibility of the film being damaged by heat. The film was dried under a fan and in some cases dust particles settled on the film, which when analysed by the microphotometer show several kinks. In order to eliminate these spurious maxima and minima in the photometer curves, photometers were taken at different positions of the plate and in almost all cases by using more than one film.

The X-ray tube was run at 10 K.V. The time of exposure as well as the current in the X-ray tube was not the same in all the cases. Experiments showed that an exposure of 50 to 70 hours and a current of 20 to 35 milliamperes gave in general good results, with a screen of proper thickness. As is well known, the thickness of the screen plays a very important part in these investigations and it is difficult to obtain a good plate in which the contrast between the white and dark lines appears prominently. The screen was placed between the X-ray tube and the crystal. An interesting feature found in this investigation is that all compounds of cobalt do not give the extended structure with the same ease. In some cases they are obtained with greater difficulty than in others. As for example, we can cite the case of cobaltous oxide where some fifteen exposures were tried in vain in order to obtain a good record of extended structures, whereas in the case of the other oxide, cobaltic oxide, the edges are quite prominent.

A dispersion of 2.4 X.U. per mm. was obtained on the photometric record of the absorption spectrum. There are several absorption bands which show a 'fine structure,' that is, if these bands are noticed very carefully under suitable light and magnification, or are analysed by the microphotometer, the presence of bright and dark lines of faint intensity may be detected, which cannot be easily measured by a glass scale. The exact position of any edge in the secondary spectrum being impossible to locate, there may be a maximum error of 2.0 X.U. in the measurements of weak maxima and minima in the photometer curve. In the positions of the primary K-edge and the more prominent dark and white lines, the maximum error that can be expected may not exceed 1 X.U.

MEASUREMENTS AND DISCUSSIONS

In the measurements of the primary and secondary absorption edges, the dispersion in each photometric record was obtained from known emission lines

W L α_1 (1473.4 X.U.), Cu K α_1 (1537.4 X.U.) and W L β_1 (1675.0 X.U.) and position of these edges was determined with W L α_1 line as the standard of reference.

As the exact position of the "Edge" is very difficult to determine, different observers chose different positions of the photometric curve for calculating the wavelength of the primary edge. Thus, some use the point of inflection, others use the middle portion of the jump in the curve as the exact position of the primary edge. But in our measurements, we have followed the procedure adopted generally by Lindh and Sandstrom,¹⁸ *i.e.*, the primary edge was measured from the middle point of the straight portion of the primary absorption jump in the photometric curve. The points of inflection of the maxima and minima in the photometric curve were considered to determine the position of the "dark" and "white" bands.

It may be remarked here that our results on cobalt metal are in good agreement with the values given by Keivit and Lindsay who have also found some of the structures found by us for this element.

It may be remarked here that Swada¹⁹ has followed an entirely novel procedure in the measurement of the absorption edges, and it seems that he has succeeded in measuring the beginning and the end of each of the dark bands in the secondary edges; his values are thus very difficult to compare with those of other investigators.

The absorption edges of the following substances are investigated.

- | | | | |
|-----|-------|--|--|
| (a) | (i) | Cobalt Metal | (Hexagonal) |
| | (ii) | CoO | (Blue Oxide, Cubic) |
| | (iii) | Co ₂ O ₃ | (Black Oxide, Hexagonal) |
| | (iv) | CoSO ₄ , 7H ₂ O | (Crystal type unknown, though the CoSO ₄ is orthorhombic) |
| | (v) | Co (NO ₃) ₂ , 6H ₂ O | (Cobaltous Nitrate) |
| | (vi) | CoCl ₂ , 6H ₂ O | (Structure unknown and CoCl ₂ (Anhydrous) |
| | (vii) | Cobalt Nitrite. | |

All these compounds except cobalt metal are ionic.

(b) Solution in water—

- (i) 1.7N, 1N, N/10, and N/20 Solns. of CoSO₄, 7H₂O.
- (ii) 1.5N, 1N, N/10, N/20 Solns. of CoCl₂, 6H₂O.
- (iii) 1.9N, .64N, .32N Solns. of Co (NO₃)₂, 6H₂O

(c) Solutions in acids—

Saturated Solns. of Co (NO₃)₂, 6H₂O in strong HNO₃

TABLE II
Co(NO₃)₂ · 6H₂O

k_2	a_3	k_3	a_4	k_4	a_5	k_5	a_6	k_6	a_7	a_8	k_8	a_9	k_9	a_{10}	k_{10}	a_{11}
1590	1586	1582	1579	1575	1572	1568	1563	1557	1551		1523			1517	1513	1505
13	17	21	24	28	31	35	40	46	52		80			86	90	95
573.13	574.57	676.06	577.12	578.59	579.69	581.17	583.02	585.27	587.74		598.34			600.71	602.33	605.5
4.65	6.09	7.58	8.64	10.11	11.21	12.67	14.54	16.79	19.06		20.86			32.33	33.85	37.12
63.08	82.58	102.8	114.5	137.1	152.0	172.0	197.2	227.7	258.4		403.0			437	459.0	502

TABLE IV

k_2	a_3	k_3	a_4	k_4	a_5	k_5	a_6	k_6	a_7	a_8	k_8	a_9	k_9	a_{10}	k_{10}	a_{11}	k_{11}
1590	1586	1582	1579	1575	1572	1568	1563	1557	1551		1523			1517	1513	1505	
13	17	21	24	28	31	35	40	46	52		80			86	90	95	
573.13	574.57	676.06	577.12	578.59	579.69	581.17	583.02	585.27	587.74		598.34			600.71	602.33	605.5	
4.65	6.09	7.58	8.64	10.11	11.21	12.67	14.54	16.79	19.06		20.86			32.33	33.85	37.12	
63.08	82.58	102.8	114.5	137.1	152.0	172.0	197.2	227.7	258.4		403.0			437	459.0	502	

1501	1586	1582	1576	1572	1569	1563	1560	1558	1553		1512	1506	1502
12	17	21	17	31	34	40	43	45	50		91	97	101
572-76	574-57	576-06	578-22	570-60	580-8	583-02	584-15	584-89	586-74		602-69	605-09	606-7
4-28	6-99	7-28	9-74	11-21	12-32	14-54	15-67	16-41	18-26		34-21	36-61	38-22
58-04	82-58	101-8	131-0	152-0	167-0	197-2	212-5	222-5	247-7		463-8	496-5	518-3
1591	1585	1583	1577	1574	1571			1560	1556		1514	1510	1507
12	18	20	26	29	32			43	47		89	93	96
572-76	574-93	575-66	577-92	578-95	580-06			584-15	585-5		601-9	603-49	604-69
4-28	6-45	7-18	9-4	10-47	12-58			15-67	17-0		33-4	35-01	36-21
58-04	87-0	97-25	128-0	141-9	159-2			212-5	230-5		452-0	474-6	491-0
1591	1585			1579	1573	1570	1564	1553	1550		1516	1510	1504
16	22			28	34	37	43	54	57		91	97	103
572-76	574-93			577-12	579-34	580-43	582-65	586-74	587-92		601-1	603-49	605-90
5-69	7-86			10-05	12-25	13-36	15-58	16-67	20-85		34-03	36-42	38-83
77-16	106-6			136-6	166-0	181-2	211-2	266-8	282-0		461-5	484-0	526-5
1590	1585	1581	1579	1574	1571			1563	1556		1512	1506	1503 ?
17	22	26	28	33	36			44	51		95	101	104
573-13	574-93	576-39	577-12	578-95	580-06			583-02	585-5		602-69	605-09	606-30
6-06	7-86	9-32	10-05	11-88	13-0			15-05	18-43		35-62	38-02	39-23
82-3	106-5	126-4	136-6	161-2	176-3			216-3	250-0		482-9	515-6	532-0

Cu Ta & Krypton

6000 1 42
2000 5 11

Table I shows the position of the primary and secondary edges of cobalt (Metal) and various cobalt compounds in the solid state including anhydrous cobalt chloride.

Table II the same in $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in forms of solid, aqueous solutions of different strengths and in saturated solutions in concentrated nitric acid.

Table III the same in $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, in forms of solids and aqueous solutions, while, table IV in $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, in solid forms, in aqueous solutions and also in anhydrous state.

The figures (k, k_1, k_2 , etc.) refer to white lines, the primary edge being denoted by k , while (a_1, a_2, a_3 , etc.) denote black bands. The secondary structures extend beyond the Cu.K $a_1 a_2$ lines (1537 and 1511 X.U.) in all cases. In the region between Cu.K $a_1 a_2$ and W.L. $a_1 a_2$ the structures are quite prominent.

(A) SOLIDS

The table I shows clearly how the primary K-edges of cobalt shift to the shorter wavelength side of the spectrum as we pass from the metallic form of the element to its compounds. This shift of the primary K-edge is outside the limits of experimental error and is similar to the earlier observations made by Lindh and others on the shift of the K-absorption edges of an element in its pure form and its compounds.

Pauling²⁰ has put forward a qualitative explanation for the shift of the primary K-edges by considering the following factors in his calculations. The work required to remove an electron is influenced by the external screening exerted by the external ions in the vicinity of the parent ion. This energy of course will depend on the sign of the ions.

He also assumes the law of inverse squares between the ions and introduces the idea that the crystal itself will have an electron affinity which will aid in the process of photoionisation. With these ideas he has attempted to account for the shift of the primary K-edges in a very general way.

The similarity between the structure in cobalt metal and that in anhydrous cobaltous chloride is significant as well as interesting (Table I). Here the two substances form hexagonal crystals, the metallic cobalt being non-ionic while the others are of the ionic type. The positions of all the secondary bands are the same with the exception of that of the primary one. For cobalt ($a=2.54, c=4.10$) while for CoCl_2 ($a=6.14, c=33.26, U=0.25$). Perhaps the influence of the chlorine ions at a definite distance from the cobalt ion in the lattice of CoCl_2 , and the peculiar shape of this crystal (Rhombohedral Hexagonal) affect the field near the cobalt ion in such a way that the values of the allowed and the forbidden zones for the K-electron do not change appreciably from those observed for cobalt metal.

Another interesting feature is that the structures and their positions do not

change in passing from CoO to Co_2O_3 which are respectively cubic and hexagonal in structure. Coster has pointed out (*Physica*, Vol. II, p. 604) that cubic close-packed and hexagonal crystal lattices give the same secondary X-ray absorption edge if we confine ourselves to the positions of the maxima and minima, relative to the main edge. As regards the form of the maxima and minima, some typical difference in the form of the secondary structures in the substances still persists. This he has shown in the case of the copper-zinc alloys known as α and ϵ brass; α brass has the same structures as Cu (face centered cubic) and ϵ brass is hexagonal just as pure zinc. After reducing the values of α and ϵ brass in terms of the close-packed cubic and hexagonal forms, he has verified the relations stated above. Coster's work is confined only to non-ionic crystals but in the case of CoO and Co_2O_3 , the crystals are polar and they are not close-packed but the similarity found in our experiment in the positions of the secondary bands is very significant. As the colours of the two oxides are different it was easily seen that one was not converted into the other during exposure.

A peculiar feature of the secondary structures of all solid compounds of cobalt (Table I) lies in their similarity with those of the metal itself, although in some cases one or two structures are found to be absent. Near the absent edges, the deviation from the corresponding secondary is large. These differences may be caused by the missing band. It should be mentioned here that the microphotometric records, which could not bring out the absent edges as mentioned above, exhibited a flatness of the curve in the region where they would have appeared. This flatness may introduce the above-mentioned discrepancy in the values of the band positions in the neighbourhood of the absent bands. It is quite probable that in such cases the so-called absent bands are not really absent but owing to some unknown factors the contrast between the consecutive dark and white bands has been so much reduced that their separate existence could not be recorded with certainty by the photometer curves. The observed flatness of the curve and also the discrepancy about the band positions may be explained in this way.

The relative intensities of the black and white bands as revealed in the original plate and also in the photometric records, shows a peculiarity which is not yet understood properly. It has been found that near the K-absorption edge, structures and their relative intensities decrease gradually with the increasing separation from the main edge beyond which there is again a marked rise in relative intensity which persists even beyond the Cu K $\alpha_1\alpha_2$ lines (1537.4, 1541.2.) and in some cases it extends even to a distance of 480 volts from the main edge. It is generally found that the contrast between the white and dark bands lying just on the longer wavelength side of the Cu K α lines is generally feebler than that of those on the shorter wavelength side of those emission lines. This peculiarity is not only confined to the structures in solids but is present also in dilute solutions and may be regarded as a general effect. In very dilute solutions only, it has been observed that the first white band of the secondary (*i.e.*, the second white

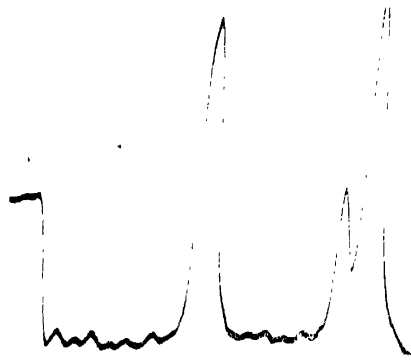


Fig. 1. $\checkmark \rightarrow$

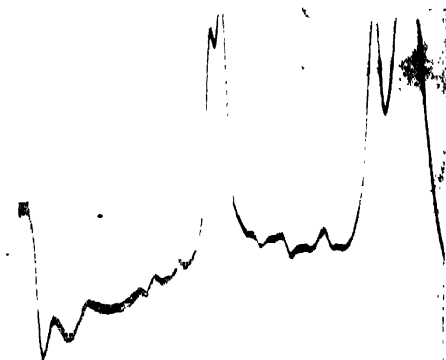


Fig 2. $\checkmark \rightarrow$

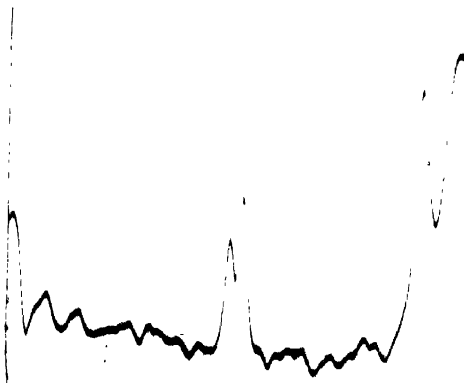


Fig. 3. $\checkmark \rightarrow$

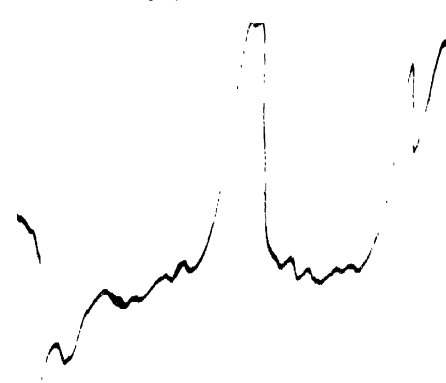


Fig. 4. $\checkmark \rightarrow$

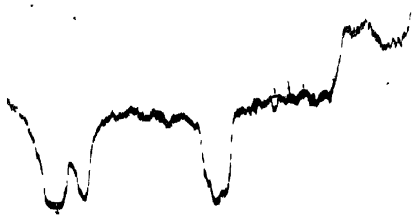


Fig. 5. $\checkmark \rightarrow$

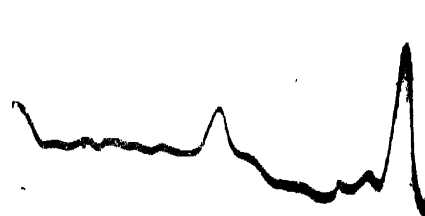


Fig. 6. $\checkmark \rightarrow$

Description of figures

- | | |
|---|---|
| Fig. 1 Cobalt nitrite | Fig. 4 $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ sol ⁿ 0.3N |
| Fig. 2 $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ | Fig. 5 $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ sol ⁿ N.10 |
| Fig. 3 $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ sol ⁿ 1 N | Fig. 6 Saturated sol ⁿ of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in HNO_3 |

line in the plate) is as strong as, and sometimes even stronger than, the primary K-edge. This point raises some interesting questions about the nature of the absorbing medium and will be discussed in the last section. Hanawalt remarked that the secondary discontinuities near to the principal edge are always sharper than those further from the edge. The diffuseness of these further out, makes it impossible to state their positions accurately. In our observations, we have found that some of the bands, which are away from the main edge, are sharper than those near it.

STRONG SOLUTIONS (*i.e.*, Strength up to 1N)

On passing from the solid polar compounds to solutions up to 1N, the similarity of the structures in all cases is not only striking but interesting as well (Tables II, III, IV). This raises some speculations about the nature and binding of the 'Cobalt' ion in strong solutions, and we are now in a position to discuss them one by one.

(a) The substance when dissolved in water may form "ions" which are free in the sense that they are not influenced by one another, and are similar to "pure or isolated atom." If this view is accepted, two states of affairs are expected in the X-ray absorption spectra.

(1) The ion being doubly charged (Co^{2+} ion), the primary K-edge will be shifted to the shorter wavelength side of the absorption spectra and will almost coincide with the primary K-edge of an element with an atomic number greater than it by two units (Cu-K-edge).

(2) The ions will resemble an isolated atom in which the K-electron can travel with all values of kinetic energy, *i.e.*, no secondary edges are expected. Fine structures, as defined before, may be found up to distance of about 20 volts only from the primary.

But it has been found experimentally that the K-edge of strong solution nearly coincides with that of Co-K-edge of the metal (difference about 4 volts) and the secondaries have not only the same wavelength as in the solid compound itself but also extend to a distance about 400 volts from the main edge. The facts clearly point out that the suggestion made in (a), *i.e.*, the hypothesis of free ion in the solution, is not satisfactory.

Prins, ²¹ from his diffraction experiments in Uranium nitrate and Thorium nitrate solutions of different strengths, has concluded that in solutions the ions of Uranium and Thorium are not absolutely free in the sense as mentioned above but they exert force on each other. He further suggests that, as with the increase in dilution the distance between the neighbouring atoms increases, the ions in the solutions form groups among themselves as conceived by the Cybotactic hypothesis of Stewart in long-chain organic liquids. Though the suggestion of Prins seems very reasonable, we have tried in vain to have diffraction pattern of strong solutions of Cobalt compounds with the Nickel radiation. Only the

haloes of water appeared in the photographic plate, which shows that the semi-lattice structure of cobalt ions in solutions in our case is absent though it may be present in the solutions of the compounds of heavier metals as mentioned by Prins.

(a) The trend of thought at the present moment is directed towards the idea that crystals of many simple salts are not dissociated completely in water or in any other solvent. If the positive and negative ions present in the crystals go to the solutions separately and all of them remain as separate positive and negative ions, there would be no neutral solute molecules present at all. But the experimental results of both the conductivity and osmotic pressure methods appear to indicate the presence of a large number of neutral molecules in solutions (even in the dilute solutions of the substances). Thus from the experiments on the osmotic pressure of MgSO_4 solution in water, one can see that even in the case of 1/500 molar solution there are at least 20% of the neutral molecules. Other substances also show the same phenomena (Gurney, *Ions in Solution*, Chapter XI).

It has been shown by Hanawalt⁵ that secondary structures of a crystalline solid and the vapours* of the same compound have the same secondary structure though there are some differences in the structures near the main edge. As for example, AsCl_3 in the solid form shows an additional structure near the main edge which does occur in its vapour. From our experiments on the similarity of the secondary structures both for the solid compound and the solutions up to 1N, we may easily conclude that the structures in these strong solutions must have been due to the presence of a very large number of neutral molecules in the solution. If really there are dissociated molecules in the solutions, their percentage must be small.

WEAK SOLUTIONS (*i.e.*, Strength lower than 1N)

In the case of dilute solutions of the order of N/10 and N/20, we are presented with an entirely different picture of the absorption edges near the primary edge. It has been mentioned before that the second white band, *i.e.*, the first secondary, is as strong as, if not stronger than, the real primary edge and the latter is again shifted towards the longer wavelength side of the corresponding edge for solid compounds.

In the case of dilute solutions[†] we know from the experiments on conductivity and osmotic pressure that a certain portion of the molecules is really dissociated into ions. But, as mentioned previously, these ions cannot remain in the "Free state." We may assume here that these ions are surrounded by water molecules, giving us a picture of the "Complex ionic group." In this case,

[†] It may be mentioned here that the temperature effect on the secondary structure of the molecules in the vapour state has been neglected.

the water dipoles influence the cobalt ions and thus set up a field of force which brings about allowed and forbidden zones as contemplated by Kronig. Thus, in dilute solutions, we have to consider the effects of undissociated cobalt salts in water and also of the "Complex ionic group" as mentioned before. As the secondary edges, excepting the first edge in dilute solutions, have the same structure as found in strong solutions, it is hereby concluded that even in dilute solutions a large percentage of molecules really remains undissociated.

As for change observed near the primary K-edge of the dilute solutions, we may offer the following explanations. The "Complex ionic group" as contemplated above has a field of force inside it, restricting the motion of the K-electrons only to a number of allowed zones. These big "ionic complexes" will therefore produce primary edges. We assume that the number of such complexes in the solutions examined by us is rather small compared to that of the undissociated molecules. We further assume that the whole absorption spectrum, due to the "Complex ionic group," is shifted towards the long wavelength side of the spectrum. Thus in the absorption spectra of dilute solutions, we have to consider the superpositions of two types of spectra :

- (i) One due to the undissociated molecules in the solution, and
- (ii) the other due to the "Complex ionic group" in the solution.

The edge due to the latter is shifted towards the long wavelength side relative to the former.

As the intensity of the former is much greater than that of the latter, it is to be expected that the intensity of the secondary spectrum due to the ionic complexes will be extremely poor and the secondary structures in dilute solutions will be practically produced entirely by the undissociated molecules. The experimental data support this contention. But near the primary edge we have to consider the superposition of the primary and the first secondary of the "Complex ionic group" with reference to the primary of the undissociated molecules.

As is well known, the intensities of the primary absorption are very much stronger than those of the secondary edges and we should naturally expect two strong primary white lines, of which one is due to the undissociated molecules and the other coming from the complex ionic groups. As suggested before, the wavelength of the K-edge of the latter is longer than that of the former. The difference in wavelength ($\delta\lambda$) between the edges is (2X U.) and is easily separated in our plate. Hence we should expect two strong white lines (of which the second one is perhaps the stronger, as the percentage of undissociated molecules has been assumed to be large) near the primary edge. The breadth of the dark line separating the two white lines, depends evidently on the shift of one system with respect to the other. In the case where the separation of the primary K-edges of the two systems is small, there would appear only one broad white band, the intensity within which will be of a fluctuating nature. In our experiments on

cobalt compounds, primary edges are resolved by the spectrograph and the nature of the absorption spectra as revealed on the photographic plates supports our contention about the superposition of the two systems of edges.

Further investigations on other metal compounds in the solid states and in solutions are necessary before any definite interpretation could be given as to the mode of existence of solute particles in solution. Experiments are being continued in this direction.

R E F E R E N C E S

- 1 Lindsay and Van Dyke, *Phys. Rev.*, 2, **27**, 28 (1926).
- 2 Lindsay and Voorhees, *Phil. Mag.*, **6** (1928) *Phys. Rev.*, (2) **31** (1928).
- 3 Keivit and Lindsay, *Phys. Rev.*, **36** (1930).
- 4 Lindh, *Zett. f. Phys.*, **3** (1920).
- 5 Hanawalt, *Journal of the Franklin Inst.*, **214** (1932).
- 6 Coster and Veldkamp, *Zett. f. Phys.*, **70** (1931).
- 7 Ray, *Nature*, **122**, 771 (1928).
- 8 Coster, *Zett. f. Phys.*, **25**, 83 (1924).
- 9 Lindsay, *Zett. f. Phys.*, **71**, 5-6 (1931).
- 10 and 11 Kronig, *Zetts. f. Phys.*, **70**, 5-6 (1931); *Zetts. f. Phys.*, **75**, 3-1 (1931), **75**, 7-8 (1932).
- 12 Hartree, Kronig and Patersen, *Physica*, **1** (1934).
- 13 Coster and Klammer, *Physica*, **1** (1934).
- 14 Brewington, *Phys. Rev.*, **46** (1934).
- 15 Yost, *Phil. Mag.*, **8**, 845 (1929).
- 16 Mayer, *Wissenschaftliche veroffentlichungen aus dem Siemens-Konzern*, **7**, 101 (1929).
- 17 Stelling, *Zeits. f. Phys. Chem.*, **19**, Abt. B 6 (1932).
- 18 Sandstrom, *Phil. Mag.*, **22** (1936).
- 19 Swada, *Kyoto Coll. Sci. Mem.*, **14** (1931).
- 20 Pauling, *Phys. Rev.*, **34** (1929).
- 21 Prins, *Physica*, **2** (1935).

Some photometric records are shown in plate 1.

Fig. 1. Cobalt nitrite.

Fig. 2. $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$.

Fig. 3. $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ Solution 1.0N.

Fig. 4. $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ Solution 0.3N.

Fig. 5. $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ Solution N/10.

Fig. 6. Saturated Solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in nitric acid.

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