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Structure of the X-Ray *K* Absorption Limits of the Elements Manganese to Zinc

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The double crystal spectrometer was employed to investigate the main absorption edge of the free elements Mn, Fe, Co, Ni, Cu, and Zn, and the oxides Mn_2O_3, Fe_2O_3, Co_2O_3, Ni_2O_3, CuO, and ZnO. Definite structure was exhibited by all the free elements except Zn, and all the oxides except ZnO. The oxide edges were all displaced toward shorter wave-length. The observed width of the edges varied from 15 volts in the case of Zn to 23 volts for Fe.

PREVIOUS investigations of the x-ray absorption edges have been made for the most part with the single crystal spectrometer, and usually for the purpose of inspecting either the position of the main edge or the secondary structure on the short wave-length side. The principal contributions in this field have been made by Lindh,[1] Coster,[2] Lindsey,[3] and Hanawalt.[4]

Davis and Purks[5] have shown that the greater resolving power of the double crystal spectrometer provides a more effective means of examining absorption limits. With this instrument Hull[6] has recently studied the *L* limits of mercury and its compounds.

In the present work the double crystal spectrometer was employed in an investigation of the *K* absorption edge of the elements Mn, Fe, Co, Ni, Cu, and Zn, together with Mn_2O_3, Fe_2O_3, Co_2O_3, Ni_2O_3, CuO and ZnO.

Apparatus

The double x-ray spectrometer was of the universal type crystal mounting described by Spencer.[7] This type of instrument has two advantages: first, by making use of the focussing effect and placing the absorption screen at the position of the focus, behind the second crystal, the movement of the x-ray beam across the sample is reduced to a minimum; and, second, by locating the position of certain emission lines on the divided circle the wave-length of any point on the absorption edge can be determined by using these lines as standards of reference.

The ionization chamber was 4 cm in diameter and 9 cm long, and was filled with methyl bromide. The ionization current was amplified by an F.P. 54 Pliotron feeding into a Leeds and Northrup type R galvanometer of sensitivity 10,000 megohms.

Water-cooled tungsten-target x-ray tubes were used throughout the investigation. The x-ray beam passed out of the tube through a thin glass window 3μ thick. To reduce air absorption the crystals and the entire path of the x-ray beam were enclosed by a flexible tube system filled with hydrogen at atmospheric pressure.

It is of importance that the absorbing screen be of uniform thickness throughout. Otherwise the slight shift of the x-ray beam across the screen may cause it to pass through regions of varying thickness and thus introduce a variation in the energy of the transmitted beam. The effect of a possible nonuniformity was overcome by oscillating the absorption screen at right angles to the x-ray beam. The screen was mounted on horizontal guide rods and the motion produced by an electrically driven cam. The screen was thus oscillated several times per second, and since the ionization current readings each extended over a period of 10 seconds or longer, the effect of any irregularities in the screen was completely smoothed out.

Absorption screens were made by coating thin paper with castor oil upon which the absorbing substance was sifted until optimum thickness

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[1] Lindh, Zeits. f. Physik **31**, 210 (1925); **63**, 106 (1930).

[2] Coster and Veldkamp, Zeits. f. Physik **74**, 191 (1932); **70**, 306 (1931).

[3] Lindsey and Vorhees, Phil. Mag. **6**, 910 (1928); Lindsey and Kievit, Phys. Rev. **36**, 648 (1930).

[4] Hanawalt, Zeits. f. Physik **70**, 293 (1931).

[5] Davis and Purks, Phys. Rev. **36**, 336 (1928).

[6] Hull, Phys. Rev. **40**, 676 (1932).

[7] Spencer, Phys. Rev. **38**, 618 (1931).

was reached. All the oxides and the free elements Mn, and Co, were used in fine powdered form. The free elements Fe, Ni, Cu, and Zn, were used in thin foils. The possibility of any chemical change in the samples produced by x-radiation was reduced to a minimum by placing the absorber behind the second crystal where the intensity was small.

The slit limiting the beam of x-rays was placed at the ionization chamber. This slit was 1 cm wide and 0.8 cm high. The maximum deviation due to vertical divergence was 0.03 x.u. The effect of the crystals likewise was negligible.

In obtaining the curves the procedure was to make three determinations at each point: one with the free element as absorber, one with the oxide, and one without either absorber, each determination consisting of three or more individual readings. Correction could then be made for variation in the intensity of the spectrum obtained without the absorber, as well as obviating any error which might have been introduced by slight displacements of the apparatus, had the curves been run separately. The curves so obtained were repeated a number of times.

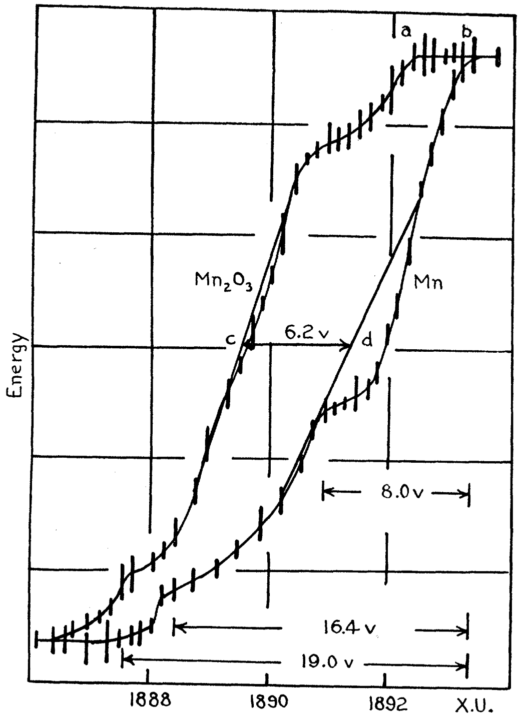

FIG. 1. Absorption edges of Mn and Mn_2O_3.

EXPERIMENTAL RESULTS

Figs. 1 to 6 show the absorption curves obtained for the free elements Mn, Fe, Co, Ni, Cu, and Zn, and the oxides Mn_2O_3, Fe_2O_3, Co_2O_3, Ni_2O_3, CuO, and ZnO. All the curves except those of Zn and ZnO show a definite structure.

The graphs are so plotted that the weight to be attached to the variations in slope is readily apparent. The position of the midpoint of the vertical lines is the mean of the ionization current readings taken at a given setting of the second crystal of the spectrometer. The length of the line has the following significance. Its extension on either side of the midpoint, bears the same relation to the interval from maximum to minimum absorption on the graph, as the average deviation of the ionization current readings from the mean (a. d.), bears to the total change in ionization current corresponding to maximum and minimum absorption. The curves thus plotted are the results of individual runs. They are to be taken as typical of the three or more sets of observations made on each of the sub-

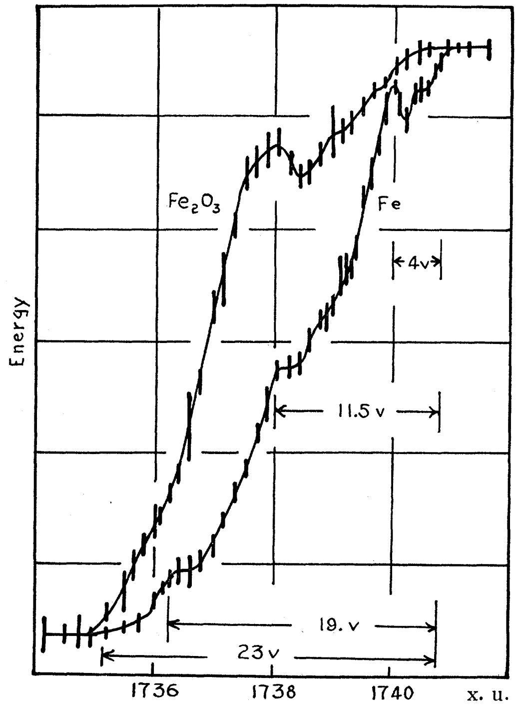

FIG. 2. Absorption edges of Fe and Fe_2O_3.

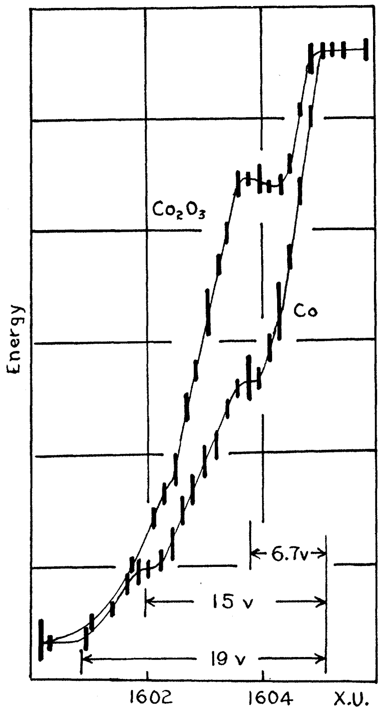

FIG. 3. Absorption edges of Co and Co_2O_3.

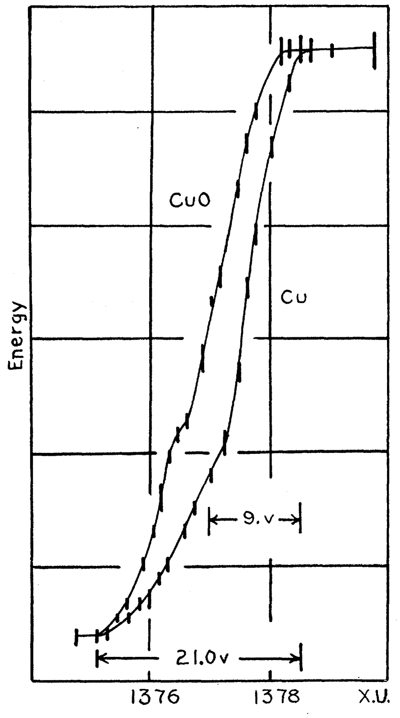

FIG. 5. Absorption edges of Cu and CuO.

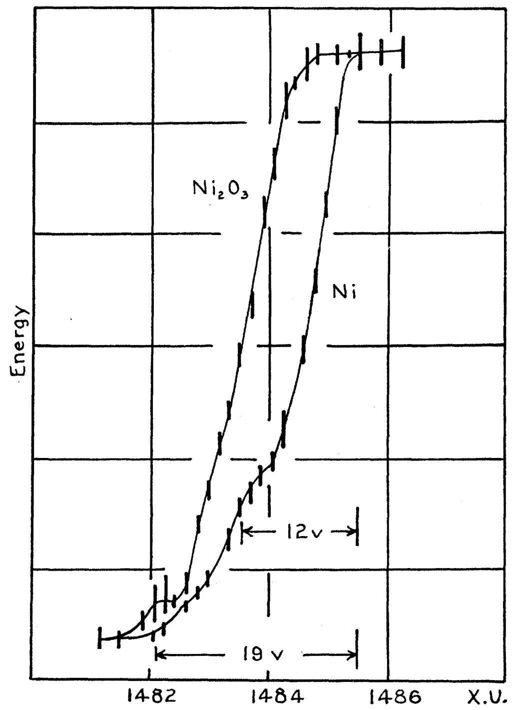

FIG. 4. Absorption edges of Ni and Ni_2O_3.

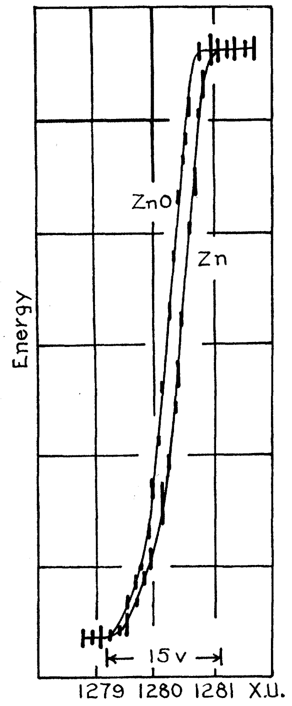

FIG. 6. Absorption edges of Zn and ZnO.

stances investigated. The deviation of the readings taken at any given spectrometer setting varied of course for different runs. The average probable error for all cases varied from 2 percent in the case of Cu to 4 percent for Fe_2O_3.

The wave-lengths in the region of the edges were determined by locating the position of the tungsten L lines and by using them as standards of reference. The lines used were $W_L\beta_1$ at 1279.17 x.u. and $W_L\alpha_2$ at 1484.38 x.u. It was possible to check the precision of the instrument by checking these lines against each other. The measured $d\lambda$ between the two lines agreed with the tabulated value to within a few hundredths of an x.u. The curves have accordingly been plotted with abscissae expressed in x.u.

The displacement of the oxides has been measured in two ways. In the first, the displacement of the position of initial observable increase in absorption has been determined. Values thus obtained are listed in Table I. The estimated precision is also indicated.

TABLE I. *Displacement of oxide edges with position of initial increase in absorption* $(a-b)$.

	x.u.	volts
Mn_2O_3	0.9±0.3	3.3±0.9
Fe_2O_3	0.6±0.3	2.3±1.0
Co_2O_3	0.2±0.2	1.0±1.0
Ni_2O_3	0.7±0.4	4.0±1.5
CuO	0.5±0.3	3.0±1.8
ZnO	0.3±0.2	2.0±1.5

To determine the displacement of the oxide edge as a whole the following construction was made. On each curve lines were drawn through points whose ordinates were $\frac{1}{4}$ and $\frac{3}{4}$ of the value of the maximum ordinate (see Fig. 1). The interval between the midpoints of these lines was then taken as a measure of the displacement of the oxide edge. Values obtained in this manner are listed in Table II. Displacements thus measured should more nearly compare to single crystal photographic determinations.

TABLE II. *Displacement of oxide edges with projected position* $(c-d)$.

	x.u.	volts
Mn_2O_3	1.8	6.2
Fe_2O_3	1.6	6.3
Co_2O_3	0.8	3.7
Ni_2O_3	0.9	4.7
CuO	0.6	3.7
ZnO	0.2	1.6

Table III lists the overall width of the observed edges in x.u. and in volts. The interval taken in each case was from the termination of the region of continuous absorption on the long wave-length side of the curve to the beginning of the region of continuous absorption on the short wave-length side. The oxides have approximately the same width as the free elements and exhibit similar discontinuities.

TABLE III. *Width of edges.*

Element	x.u.	volts
Mn	5.5±0.5	19±1.7
Fe	5.7±0.5	23±2.0
Co	3.9±0.5	19±2.4
Ni	3.2±0.5	19±2.8
Cu	3.4±0.5	21±3.2
Zn	2.1±0.4	15±2.8

This investigation, in agreement with work previously done by others, indicates that the absorption edges are of considerable width. The difficulty arises of deciding which point on the curve is to be taken in specifying the wave-length of the absorption edge. Previously, when the edges appeared to be symmetrical, some arbitrary point either at half or three-quarters of the interval from maximum to minimum absorption, has been used. A point so chosen, however, has no significance as far as electron transitions are concerned.

By referring to a table of wave-lengths of x-ray emission lines it will be seen that the wave-lengths of the $K\beta_2$ [8] lines of the elements Mn to Zn are very nearly the same (within limits of experimental error) as the wave-lengths at which the initial increase in absorption occurs.

The generally accepted theory of the K absorption edge[9, 10, 11, 12, 13] is that it corresponds to the ejection of a K electron to the various un-

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[8] In notation used by Siegbahn, *Spektroskopie der Roentgenstrahlen*, this would be $K\beta_5$ for elements Mn to Cu.

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

[10] Stoner, Phil. Mag. **2**, 97 (1926).

[11] Coster and Wolff, Nature **124**, 652 (1929).

[12] Sandstrom, Zeits. f. Physik **66**, 784 (1930).

[13] Kawata, Kyoto Coll. Sci. Mem. **14**, 55 (1931).

occupied levels of the atom. In the usual scheme of arrangement of electrons the outer *M* level of the atoms Mn, Fe, Co, Ni (and probably Cu in the solid state)[11] is not completely filled. Inspection of the curves reveals that Mn, Fe, Co, Ni, and Cu, show irregularities in the edge, while the curve for Zn is smooth and without observable structure. This might be considered an indication that the uncompleted *M* shell is responsible for the structure observed.

In conclusion the writer wishes to thank Professor Bergen Davis for suggesting this problem, and for his interest throughout the course of the experiment.