K-Absorption Edges of Ni, Cu, Zn and their Compounds

By

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Abstract

Investigating the K-absorption limits and their structures for the elements Ni, Cu, Zn and their compounds, we found the following facts : that the appearance of the structure of the absorption edge for a pure element was very different from that for its compounds and that the structures of the absorption edges seemed to depend upon the crystal forms of the substances.

Experimental Method

The photograms were taken by the absorption screen method with a spectrograph of Seeman's "Loch Kamera" type made in this laboratory. The absorption screens for the pure elements were prepared by rolling the metals, and the absorption screens for the compounds by rubbing them in the form of a fine powder on filter paper and dropping Zapon Enamel on them. Calcite was used as the analyser throughout our experiments. As the source of X-rays, a Shearer metal tube which was evacuated by a Cenco oil pump was used. The tube was excited by a transformer at about 60 kilovolts and the current through it was about 9 milli-amperes.

Results

(1) The main edge.

To calculate the wave-length difference between the main absorption limits of the pure metal and its compounds, several photograms were taken for each sample. The mean values of the edges are shown in Table 1. We also compared the separation between the main

edge of a pure metal and its oxide by taking the two photograms on one plate as shown in Plate Group A. The results are summarized in Table 2. For the main edge, we read the shorter wave-length limit

Table 1.

The wave-lengths of the K-absorption main edges obtained by
taking the mean of a few plates.

(A)　Ni and its compounds.

Substance	Valency	λ(x. u) of the main edge	ν/R	$\Delta\lambda$	$\Delta(\nu/R)$	ΔV
Ni	0	1482.71	614.60	0	0	0
NiO	2	1482.68	614.61	0.03	0.01	0.14
Ni(SO$_4$)$_2$	4	1482.40	614.72	0.31	0.12	1.63

(B)　Cu and its compounds.

Cu	0	1375.77	662.37	0	0	0
Cu$_2$O	1	1375.73	662.39	0.04	0.02	0.27
CuO	2	1375.32	662.58	0.45	0.21	2.84

(C)　Zn and its Compounds.

Zn	0	1279.52	712.19	0	0	0
ZnS (Wurtzite)	2	1279.02	712.48	0.50	0.29	3.39
ZnS (Zinc Blende)	2	1279.27	712.34	0.25	0.15	2.03
ZnO	2	1279.34	712.30	0.18	0.11	1.49

Table 2.

The wave-lengths of the K-absorption main edge obtained from
two photograms on one plate.

(A)

Substance	Valency	λ(x. u) of the main edge	ν/R	$\Delta\lambda$	$\Delta\nu/R$	ΔV	Ref. lines
Ni	0	1482.81	614.56	0	0	0	Cu K α_1
NiO	2	1482.24	614.79	0.57	0.23	3.11	Cu K β_1

(B)

Cu	0	1376.01	662.26	0	0	0	Cu K α_1
Cu$_2$O	1	1375.71	662.40	0.30	0.14	0.90	Cu K β_1

(C)

Cu	0	1375.69	662.41	0	0	0 ·	Zn K α_1
CuO	2	1374.94	662.77	0.75	0.36	4.88	Cu K β_1

(D)

Zn	0	1279.97	711.95	0	0	0	Zn K α_1
ZnO	2	1279.67	712.11	0.30	0.16	2.17	Zn K β_1

of the blackening by a comparator. The wave-lengths of the reference lines were taken from Siegbahn's " The spectroscopy of X-rays ". The dispersions on our plates are about 15 x. u. per mm. Lindh[1] has already reported that the wave-lengths of the K-edge of an element in the state of compounds are a few x. u. shorter than in the case of the pure element and that the difference increases with the valencies of its compounds. From our results we can also see the tendency to shift to the shorter wave-length side in accordance with the valency for an element in the state of compounds. Our result for CuO is a little smaller than that obtained by Owen and Williams.[2]

(2) The structure of the edge.

The structure of the edge which appeared on the shorter wave-length side of the main edge, has been investigated by G. A. Lindsay,[3] R. de L. Kronig,[4] D. Coster,[5] J. D. Hanawalt,[6] and A. E. Lindh,[7] etc. The former two discussed the problem of the origin of this structure. Lindsay explained the fine structure by considering that in one absorption act not only one electron from the K orbit but many electrons transit to the outer orbits simultaneously, and corresponding to the

1. Axel E. Lindh: ZS. f. Phys. **63**, 106. (1930).
   Hand. d. Experimental Physik: 24, (2) Röntgenspektroskopie, Kap. 10, S. 281.
2. Owen and Williams: Pro. Roy. Soc. London. (A) **123**, 282. (1931).
3. G. A. Lindsay and G. Van Dyke: Phys. Rev. **28**, 613. (1926).
   G. A. Lindsay and H. R. Voorhees: Phil. Mag. **6**, 910. (1928).
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   G. A. Lindsay: ZS. f. Phys. **71**, 735. (1931).
4. R. de L. Kronig: ZS. f. Phys. **70**, 317. (1931).
5. D. Coster and J. H. van der Tuuk: ZS. f. Phys, **37**, 367. (1926).
   D. Coster and M. Wolf: Nature, **124**, 652. (1929).
   D. Coster and J. Veldkamp: ZS. f. Phys. **70**, 306. (1931).
6. J. D. Hanawalt: Phys. Rev. **37**, 715. (1931).
   J. D. Hanawalt: ZS. f. Phys. **70**, 293. (1931).
7. Axel E. Lindh: loc. cit. (the former)

Table 3

The Wave-length Difference (Δλ) and the Energy Difference (Δ(ν/R.) ΔV)
of the Fine Structure from the K–Absorption edge.

		a	a′	b	b′	c	c′	d	d′
Ni	Δλ	2.78	6.06	7.71	14.27	17.56	24.12	29.87	34.80
	Δ(ν/R)	1.15	2.52	3.21	5.97	7.37	10.16	12.63	14.77
	ΔV	15.58	34.14	43.49	80.88	99.84	137.64	171.10	200.09
NiO	Δλ	2.81	5.29	6.12	9.43	10.25	16.87	22.67	24.32
	Δ(ν/R)	1.17	2.21	.2.56	3.94	4.29	7.08	9.54	10.25
	ΔV	15.85	29.94	34.68	53.38	58.12	95.91	129.24	138.86
Ni(So₄)₂	Δλ	2.48	7.71	12.93	18.16	29.92	36.46		
	Δ(ν/R)	1.03	3.22	5.42	7.63	12.67	15.51		
	ΔV	13.95	43.62	73.42	103.36	171.64	210.11		
Cu	Δλ	1.48	4.79	5.62	10.57	13.05	19.67	22.15	27.10
	Δ(ν/R)	0.71	2.31	2.72	5.13	6.34	9.61	10.84	13.31
	ΔV	9.62	31.29	36.85	69.50	85.89	130.19	146.85	180.31
Cu₂O	Δλ	1.82	8.46	13.45	18.43	25.07	31.72		
	Δ(ν/R)	0.88	4.09	6.54	8.99	12.29	15.63		
	ΔV	11.92	55.41	88.60	121.79	166.49	211.74		
CuO	Δλ	2.33	3.67	4.33	7.66	10.16	13.50	15.99	20.99
	Δ(ν/R)	1.12	1.77	2.09	3.71	4.93	6.56	7.79	10.26
	ΔV	15.17	23.98	28.31	50.26	66.79	88.87	105.53	138.99
Zn	Δλ	1.37	3.62	5.13	8.13	9.64	14.15	17.16	21.67
	Δ(ν/R)	0.76	2.02	2.87	4.56	5.41	7.97	9.70	12.28
	ΔV	10.30	27.36	38.88	61.77	73.29	107.97	131.41	166.36
ZnO	Δλ	1.64	5.98	10.48	14.22	17.97	26.96	31.45	40.44
	Δ(ν/R)	0.91	3.35	5.88	8.00	10.14	15.33	17.94	23.24
	ΔV	12.33	45.38	79.66	108.38	137.37	207.68	243.03	314.83
ZnS Zinc Blende	Δλ	1.21	7.05	8.51	14.35	15.81	21.65	28.95	34.79
	Δ(ν/R)	0.67	3.95	4.77	8.07	8.91	12.26	16.49	19.91
	ΔV	9.08	53.51	64.62	109.32	120.70	166.09	223.39	269.72
ZnS Wurtzite	Δλ	1.05	5.51	6.99	14.42	16.64	24.07	30.01	35.95
	Δ(ν/R)	0.58	3.09	3.91	8.12	9.38	13.66	17.11	20.60
	ΔV	7.86	41.86	52.97	110.00	127.07	185.05	231.79	279.07

e	e'	f	f'	g	g'	h	h'	i	i'
37.26	38.90	43.83	53.68	60.25	71.74				
15.84	16.56	18.72	23.08	26.04	31.24				
214.58	224.34	253.60	312.66	352.76	423.21				
30.94	35.91	46.66	48.32	50.80	52.46	58.25	64.87	68.18	81.42
13.10	15.25	19.97	20.70	21.80	22.54	25.13	28.11	29.61	35.70
177.47	206.59	270.53	280.42	295.32	305.35	340.44	380.81	401.13	483.63
29.58	31.24	35.37	41.98	46.94	56.86				
14.56	15.40	17.49	20.86	23.41	28.57				
197.24	208.62	236.94	282.59	317.14	387.04				
24.32	32.65	34.32	40.98	42.65	47.65				
11.92	16.10	16.95	20.34	21.20	23.77				
161.48	218.11	229.62	275.55	287.20	322.01				
26.93	32.87								
15.33	18.80								
207.68	254.68								
46.43	55.42								
26.81	32.24								
363.20	436.76								

energies of these electron transitions the discontinuities of the absorption on the shorter wave-length side of the main edge result. So the fine absorption structures are pure atomic. Kronig proposed the following theory : Owing to the interaction between the atoms which are distributed regularly in the substance, the range to which an electron is able to transit appears periodically in the outer field of the atom and the transitions of an electron to these ranges are the cause of the fine structures. According to this theory, therefore, the structure must depend upon the crystal form of the absorber. To test these two ideas, we investigated the appearance of the structures of two different elements which have the same crystal form and that of the structures of an element which has a different crystal form. The photograms are shown in Plate Group B. On the photographic plates we can see many black lines, and the energy differences and wave-length differences from the main edge are measured. The results are summarized in Table 3, and graphically represented in the annexed figure. In the Table, a, b, c,...mean the points where the blackening begins, i. e. the absorption ends, and a′, b′, c′,......the points where the blackening ends, i. e. the absorption begins. The black lines near the principal edge are in general sharper than those farther from the edge as Hanawalt[1] pointed out. Owing to the diffuseness of the structure, the errors in wave-length reading were about 1 x. u. From the results obtained, we can get the following conclusions :—

(1) So far as Ni, Cu and Zn are concerned, in the structures of the pure metal and its compounds, there are no black lines which correspond to each other, i. e. the structures are not alike in appearance. This is contrary to the result of Lindsay's early investigation on metallic Fe and its compounds[2].

(2) The appearance of the structure of metallic Ni is very like that of metallic Cu. We can easily point out the black lines and white lines which correspond to each other. The crystal forms of these metals are both face centred cubic lattice. Taking the grating constants of metallic Ni and Cu, 3.51 Å and 3.628 Å respectively, we calculated the product of the energy separation in volts from the main edge and the square of the grating constant for Ni and Cu. The results are tabulated in Table 4.

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1. J. D. Hanawalt : loc. cit. (the former)
2. G. A. Lindsay and H. R. Voorhees : loc. cit.

Table 4

(Energy Separation in Volts) × (Grating Constant)^2

	Ni	Cu
a	191.95	126.62
a'	420.61	411.85
b	531.80	485.03
b'	996.45	914.79
c	1230.04	1130.52
c'	1695.74	1713.61
d	2107.97	1932.90
d'	2465.13	2373.31
e	2643.65	2596.15
e'	2763.89	2745.94
f	3124.38	3118.70
f'	3852.00	3719.56
g	4346.04	4174.32
g'	5213.99	5094.37

In this table we see that the products are nearly of the same order in Ni and Cu for corresponding lines, but not so good as the data Lindsay[1] obtained for K compounds. Moreover we can not fail to see that the energy separations of each corresponding black line are generally larger for Ni than for Cu.

(3) We can not point out corresponding lines in metallic Cu or Ni and metallic Zn.

(4) While the structures of metallic Ni and Cu are very similar in appearance, those of their oxides NiO, CuO are quite different, so we can not point out any corresponding lines in them. The appearance of the ZnO edge is also different from those of CuO and NiO. Here we must call attention to the fact that the crystal forms of NiO, CuO and ZnO are all different.

(5) Comparing the structures of the Zn edge for zincite and zinc blende, we can not point out corresponding lines in them. The appearance of the Zn edge for wurtzite seems to be like that of zincite in some respects and to zinc blende in other respects. The crystal forms of zincite and wurtzite are both hexagonal and that of zinc

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1. G. A. Lindsay: loc. cit.

blende is cubic.   In this connection we must note that wurtzite crystals are always mixed with more or less zinc blende crystals.   At any rate, we can conclude that metallic zinc, zincite and zinc blende are different in appearance.

These facts seem to support Kronig's idea rather than the idea of simultaneous transitions of many electrons.   But the problem " What is the origin of these structures ? " can only be solved by farther investigation.

In conclusion, we wish to express our thanks to Prof. Matsubara of the Mineralogical Institute for his kindness of giving us the sample of wurtzite crystal.

Figure

Graphical Representation of the Energy Separations (in volts) of the Fine Structures from the Main Edge.
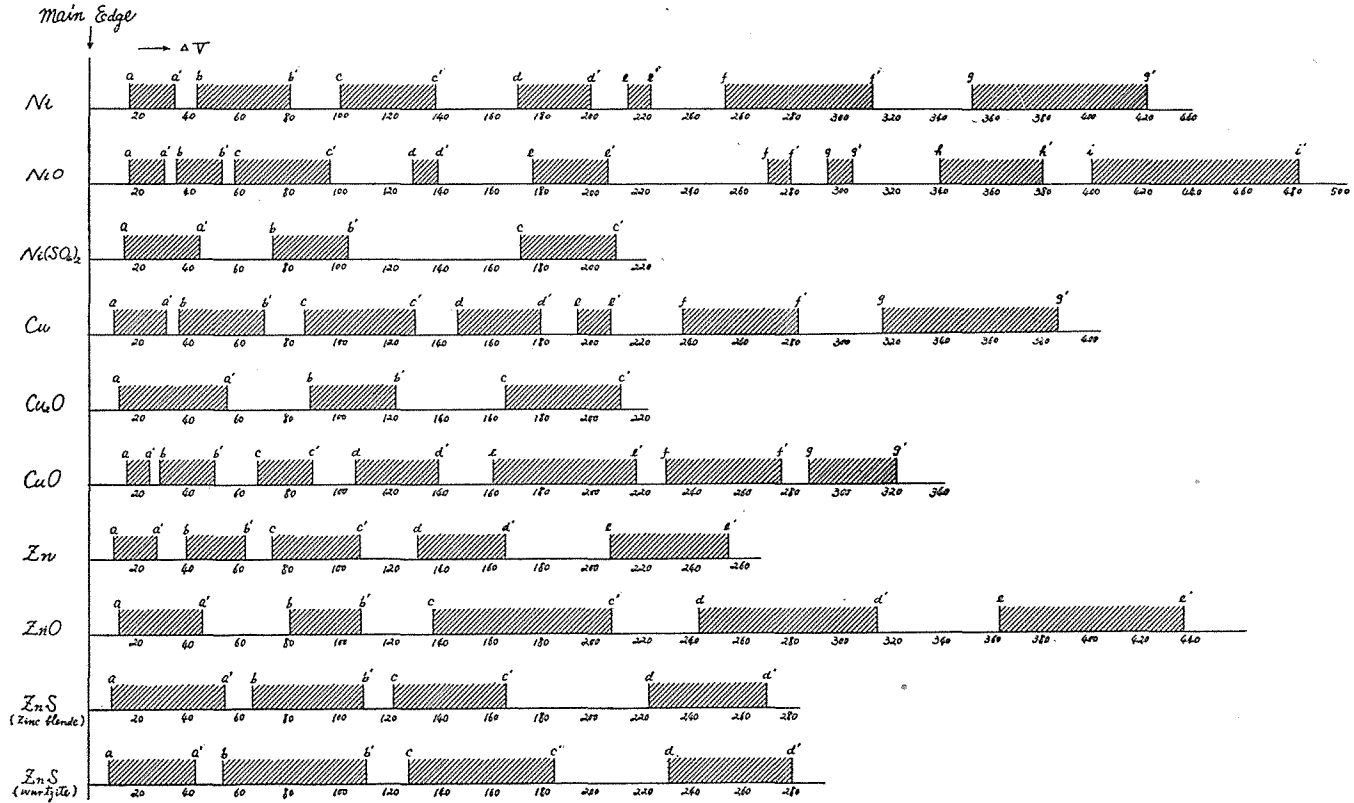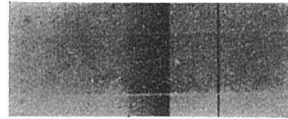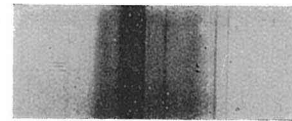
Group A

Ni / NiO / Ni

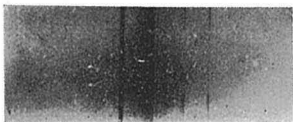Cu / CuO / Cu
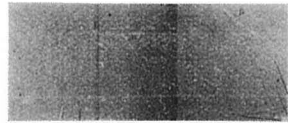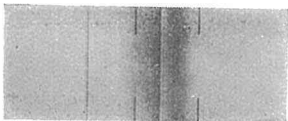
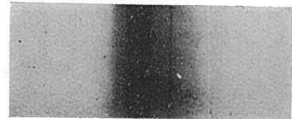Cu / Cu₂O / Cu
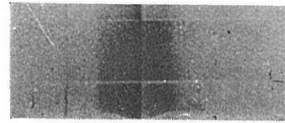
Zn / ZnO / Zn

Group B
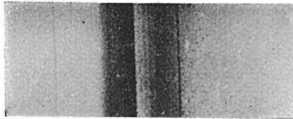
Ni
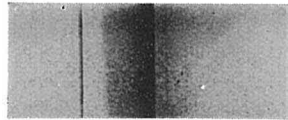
Cu
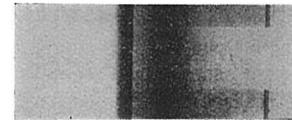
Zn

NiO
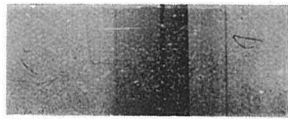
Cu₂O

ZnS (Zinc Blende)

Ni(SO₄)₂

CuO

ZnS (Wurtzite)

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Plate