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The Secondary Structure of X-Ray Absorption Edges from Elements in Certain Cubic Crystals

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The K x-ray absorption spectra of potassium, chlorine, calcium and sulfur in several different cubic crystals have been photographed. The absorption spectrum was obtained for potassium from filters prepared with KF, KCl, KBr and KI, and the chlorine spectrum from LiCl, NaCl, KCl, RbCl. The calcium and sulfur absorption spectra were obtained from powdered calcium sulfide. A secondary structure was found on the short wave-length side of the K edge of each of these elements. The following results are not in accord with the demands of the Kronig theory for secondary structure:—The absorption spectra of two elements in the same crystal are not similar. The product of the separation of each of the secondary structure components in volts and the square of the lattice space is not a constant for the crystals studied. Some of the structure previously reported for the sulfur edge is shown to be due to the sulfur contained in goldbeater's skin which had been used to cover the slit of the x-ray tube.

A SECONDARY structure[1] has been observed close to the K and L absorption edges of a large number of elements.[1, 2] Kronig,[3] from wave mechanical considerations, suggested that the separation in the secondary structure should be inversely proportional to the square of the lattice constant of the crystal used as absorbing material. This dependence has been confirmed by Coster and Veldkamp[4, 5] for certain metal crystals. Lindsay and Barton[6, 7] find the relations suggested by the theory are not easily satisfied by the observed separations in the K absorption spectrum of several elements in polar crystals. Coster and Klamer[8] have shown that the secondary structures of two elements in the same crystal are not similar.

The alkali halides crystallize in the simple cubic system and it seemed desirable to obtain the secondary structure of the K edges of potassium and chlorine in their various combinations in this crystal system. Calcium sulfide was studied because it is also of the same type.

EXPERIMENTAL PROCEDURE

A Siegbahn vacuum spectrograph of 180.6 mm radius was used to obtain the absorption photographs. The metal x-ray tube was separated from the main chamber of the spectrometer by windows of goldbeater's skin or films of pyroxalin or collodion.[9] The targets of the x-ray tube were made of silver, copper, molybdenum or tungsten and were so chosen that no emission lines appeared in the region of secondary structure. The filament consisted of a flat spiral of chromel wire coated with barium oxide. The tube was run at currents up to 30 milliamperes.

Screens of the alkali halides may easily be prepared by saturating a very thin paper with a water solution of the salt and drying rapidly over a hot plate. A variation of this procedure was necessary in the case of lithium chloride, which is hygroscopic. The paper was placed in position in the path of the x-ray beam and saturated with a water solution of lithium chloride. A dish of phosphorous pentoxide was then placed in the chamber of the spectrometer and the pumps turned on. This was also successfully tried with some of the other water soluble salts. The calcium sulfide was ground in a mortar containing a small quantity of amyl acetate. The finely divided particles remained in suspension long enough to be transferred to an amyl acetate solution of collodion or pyroxalin. This solution was then thoroughly mixed and spread on a glass plate to

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[2] B. J. Kievit and G. A. Lindsay, Phys. Rev. **36**, 648 (1930); P. A. Ross, Phys. Rev. **44**, 977 (1933); A. H. Barnes, Phys. Rev. **44**, 141 (1933).

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

[5] J. Veldkamp, Zeits. f. Physik **77**, 250 (1932).

[6] G. A. Lindsay, Zeits. f. Physik **71**, 735 (1931).

[7] G. A. Lindsay and V. P. Barton, Phys. Rev. **41**, 391 (1932); **46**, 362 (1934).

[8] D. Coster and G. H. Klamer, Physica **1**, 145 (1934).

[9] L. Harris and E. A. Johnson, Rev. Sci. Inst. **4**, 455 (1933).

Table I. *Separation of secondary structure of absorption edges.*

		A	α	B	β	C	γ	D	δ	E	ε
Potassium absorption											
KF	v	1.76	6.12	10.2	17.0	23.0	30.2	36.9			
	x.u.	1.68	5.85	9.2	16.3	22.0	28.9	35.2			
	$v \cdot a^2$	50	176	290	483	653	863	1000			
KCl	v	1.44	3.12	4.73	6.16	8.20	12.8	18.7	23.6	28.7	
	x.u.	1.00	2.98	4.54	5.90	7.85	12.2	17.2	22.6	27.4	
	$v \cdot a^2$	39	123	186	243	324	505	710	893	1080	
KBr	v	1.11	2.90	4.33	6.20	9.54	12.1	16.5	22.0	27.1	
	x.u.	1.06	2.77	4.14	5.92	9.10	11.5	15.8	21.1	25.9	
	$v \cdot a^2$	45	125	187	268	411	522	712	949	1170	
KI	v	1.01	2.27	3.30	5.54	6.67	10.1	14.1	18.3	23.2	29.4
	x.u.	.97	2.17	3.15	5.29	6.38	9.7	13.5	17.6	22.2	28.7
	$v \cdot a^2$	50	112	164	275	332	502	702	910	1152	1490
Chlorine absorption											
LiCl	v	1.51	3.35	5.50	9.94						
	x.u.	2.34	5.21	8.57	15.5						
	$v \cdot a^2$	40	89	145	267						
NaCl	v	1.83	6.07	8.20	10.5	12.8	15.2	16.6			
	x.u.	2.84	9.45	12.8	16.4	19.9	22.6	25.8			
	$v \cdot a^2$	58	193	260	334	405	483	527			
KCl	v	1.84	3.41	5.40	6.59	7.56	9.54	11.6			
	x.u.	2.85	5.32	8.41	10.3	11.8	14.9	18.1			
	$v \cdot a^2$	53	136	213	260	299	376	460			
RbCl	v	.97	2.94	5.02	8.67	10.8	14.6	17.2			
	x.u.	1.52	4.54	7.80	13.5	16.9	22.6	26.7			
	$v \cdot a^2$	42	127	216	537	468	627	740			
Calcium absorption											
CaS	v	3.45	5.62	7.20	13.0	18.7	25.5	37.5	46.6	59.8	
	x.u.	2.35	4.27	5.47	9.9	14.2	19.4	28.5	35.4	45.4	
	$v \cdot a^2$	111	181	232	422	604	824	1210	1502	1930	
Sulfur absorption											
CaS	v	1.67	4.39	6.3	8.8	10.6	12.4	16.8			
	x.u.	3.41	8.94	12.9	17.9	21.9	25.3	34.1			
	$v \cdot a^2$	54	142	210	285	342	402	543			

dry. The films could be stripped off and were ready for use as screens.

The screens were placed between the reflecting crystal and the photographic plate. A very thin pyroxalin film, blackened by holding it over burning camphor was placed in front of the plate. The screen and the blackened film thus assist in reducing the amount of scattered and fluorescent radiation that may be present. Using these precautions, plates have been obtained which show almost no blackening except that due to the reflected beam.

The separations between the *K* absorption edge and the center of each dark line and each absorption line, respectively, on the short wavelength side of the edge were measured and reduced to electron volts and x units and are shown in Table I. The Greek letters refer to the minimum of absorption (black lines on the plate) and the Latin letters to the maximum of absorption. On several of the plates some of the dark lines appeared to contain a further structure but this structure was so faint that it could not be satisfactorily measured. The dispersion was scarcely sufficient to resolve the secondary structure accompanying the *K* edges of rubidium, bromine and iodine.

Discussion of Results

Several theories have been proposed to explain the secondary structure of x-ray absorption edges. A brief review of the several suggestions

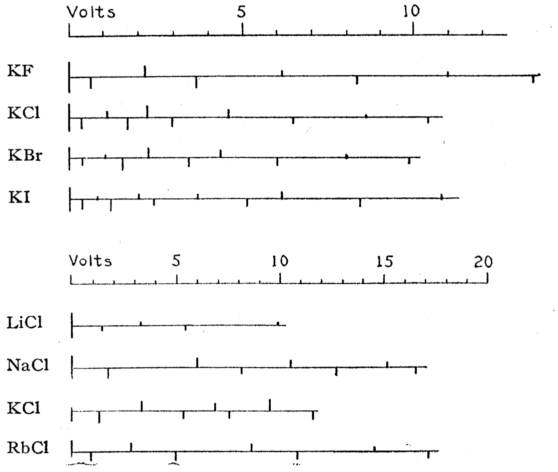

FIG. 1. Structure of potassium and chlorine edges in terms of the electron volt separations of the secondary structure from the absorption edge. The minima of absorption (black lines on the plate) are represented by vertical lines rising above the horizontal. The maxima of absorption (white lines on the plate) are represented by vertical lines extending down from the horizontal.

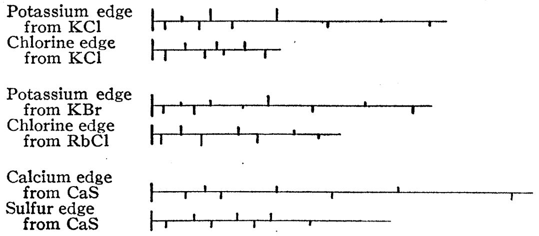

FIG. 2. Comparison of two elements in the same crystal.

has been published by Hanawalt.[1] By means of wave mechanics Kronig has developed a theory of secondary absorption. The absorbing crystal was considered by Kronig as a periodic array of potential walls corresponding to the ions in the lattice. The ejected electron, resulting from the ionization of the K level, can enter into only certain energy bands resulting from the crystal lattice structure. The transition of an electron from a K level of an atom to the lowest of these energy bands accounts for the absorption edge. Absorption lines in the secondary structure of the edge correspond to energies an electron may possess after being ejected from the K shell. The values of these energies are given by

$$W_n = n^2h^2/8ma^2,$$

where $n = 1, 2, 3, \cdots$, m is the mass of the electron, a the lattice constant and h Planck's constant. The correctness of this formula has been experimentally verified by the work of Coster and Veldkamp,[4, 5] who obtained the K absorption spectra of a number of metallic elements of similar crystal structure.

Kronig's formula suggests several tests that may be applied to the data. These are:

a. The secondary structure of the absorption edges of two or more elements in the same crystal should be identical unless very near the edge. A comparison of the x-ray absorption spectrum of potassium and chlorine (Fig. 2) obtained from a KCl screen and the absorption spectrum of calcium and sulfur from CaS, shows that this is not true. Coster and Klamer[8] arrive at the same conclusion. They photographed the potassium and chlorine absorption spectra using a KCl filter with an instrument having a smaller radius than that reported here. The secondary structure reported in this paper is much closer to the absorption edge; however, the two sets of measurements are not inconsistent as the line farthest from the edge measured by the author coincides with the line nearest the edge as reported by Coster and Klamer. Stephenson[10] obtained the absorption spectrum of bromine near the K edge by using a KBr crystal in a double crystal spectrometer. A comparison of the the bromine spectrum with that of potassium shows them to be quite dissimilar.

b. If the structure of the absorption spectrum is determined by the lattice constant of a crystal, the spectra of elements in different crystals having the same lattice constant should be identical. Two of the alkali halides have approximately the same lattice constant; KBr and RbCl. A comparison of the absorption spectra of potassium in the KBr and that of chlorine in the RbCl shows little similarity (Fig. 2).

c. In a series of crystals of the same structure, the product of the separation of the lines in the secondary structure, expressed in volts, and the square of the lattice dimension should be a constant for corresponding lines, since $W\cdot a^2 = n^2h^2/8m = kn^2$. Lindsay[6] reported only an approximate agreement for potassium from KCl, KBr, and KI. This same approximate agreement

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[10] S. T. Stephenson, Phys. Rev. **44**, 349 (1933).

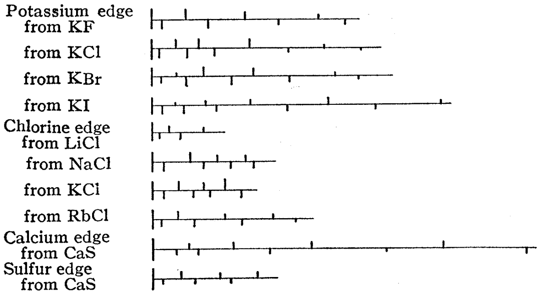

FIG. 3. Comparison of potassium, chlorine, calcium and sulfur edges showing lack of agreement of the data. The scale is in arbitrary units. Volts$\times a^2$.

was found in the present work for potassium but it will be noted that there is no such regularity in the secondary structures of the chlorine edges. When the absorption spectrum of potassium from KF is compared with the potassium from the other potassium halides, one finds an absorption maximum missing close to the potassium edge from KF. It is interesting to note that fluorine is the only halogen that does not show a multiple valence. The lack of agreement of the data may be seen in Fig. 3.

Goldbeater's skin has often been used as a window over the slit of the Siegbahn vacuum spectrometer. During the course of this work the skin was found to contain sulfur which gave an absorption edge at about 4.990A. In previous work with various sulfur compounds,[11] several edges have been reported one of which almost invariably occurred at the above wave-length. It is probable, therefore, that this particular edge was due to the goldbeater's skin, rather than to the compound in the filter. A photometer trace of this absorption will be found in Fig. 4.

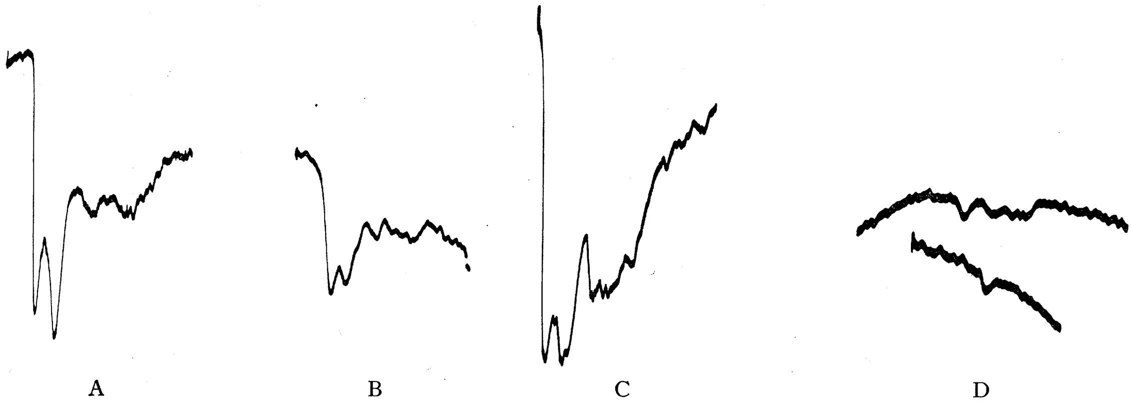

FIG. 4. Representative photometer traces of plates. (A) Potassium absorption edge from KF; (B) chlorine absorption edge from RbCl; (C) chlorine absorption from KCl; (D) sulfur absorption edge from CaS, photographed through goldbeater's skin (upper), sulfur absorption edge in goldbeater's skin (lower).

It would appear, from the data obtained, that Kronig's theory is not, in its present form, capable of explaining completely the secondary structure of x-ray absorption edges of elements existing in crystals with polar binding.

The writer wishes to take this opportunity to express his appreciation to Professor G. A. Lindsay, who suggested the problem and greatly assisted in its completion with many helpful criticisms; also to Professor H. M. Randall for the privilege of working in the laboratory.

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[11] M. Siegbahn, *Spektroskopie der Röntgenstrahlen*, p. 284, 1931.