

Two-Crystal Study of the Structure and Width of K X-Ray Absorption Limits

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The double-crystal spectrometer has been used to examine the K absorption limits of the elements Se, Rb, Zr, Mo and compounds of these elements. All of the substances examined show structure either on the short wavelength side of the main absorption limit or in the limit itself. The intensity and location are discussed with

reference to the theory of secondary structure given by Kronig. The widths of the absorption limits have been measured and it is shown that the widths are approximately constant for elements of atomic number less than 32 and that from there on they increase as the fourth power of the atomic number.

THE purpose of this investigation is to obtain data on the structure, width and the effect of chemical combination on the structure and width of the K absorption limits of elements of atomic number greater than 34. Barnes¹ has used the double-crystal ionization method to examine the fine structure² of the K limits for the elements manganese to zinc. All other investigations of K limits of the elements of atomic number less than 34 have been made with the single crystal spectrograph. Bergen Davis and Harris Purks³ have demonstrated that the two-crystal spectrometer is suitable for measurements of the widths of limits of elements of higher atomic number, while recently P. A. Ross⁴ has used this instrument to measure secondary structure as well.

APPARATUS

The double-crystal x-ray spectrometer has been described by Bergen Davis and Harris Purks.⁵ A water-cooled tungsten target x-ray tube with a thin glass window provided the continuous spectrum. The beam was limited by slits 0.4 cm wide and 0.8 cm high. The cylindrical ionization chamber, of length 7 cm and diameter 2.5 cm, was filled with methyl bromide gas. The ionization current was amplified by an FP-54 plicotron and read on a Leeds and Northrup type R galvanometer. Rates of deflection of the galvanometer were observed. Sensitivities of

10,000 mm/volt to 30,000 mm/volt were found convenient, the corresponding currents being of the order of 3 to 1×10^{-15} ampere.

The absorbing screens were prepared in various ways. Substances in powder form were ground as fine as possible and then sifted onto cigarette paper coated with a thin layer of castor oil, several sheets being used as the absorbing screen. The selenium compounds were pressed between two very thin sheets of mica by a pair of brass grids. As these compounds appeared to react with the paper and glue this method was necessary. The rubidium was distilled into a small Pyrex tube with very thin glass windows and then a small amount was melted on one of the windows to form the absorbing layer.

The absorbing screens were placed either between the crystals and the x-ray tube, or, between the second crystal and ionization chamber. With the exception of rubidium, the screens were oscillated back and forth several times a second in order that spurious effects due to non-uniformities in the thickness of the screens would be avoided.

To make certain that the transmission curves represented changes in the x-ray intensity due to the absorbing substances and not fluctuations in the primary radiation, the following procedure was adopted. For a particular setting of the second crystal three rates of deflection readings were made with the absorbing screen in position and then three readings with the screen replaced by an aluminum sheet. The rates of deflection with the aluminum in the beam were approximately the same as those for the absorbing substance in the region of secondary structure. A comparison of a plot of the aluminum readings and the transmission curve makes it possible to

¹ Barnes, *Phys. Rev.* **44**, 141 (1933).

² See Hull, *Phys. Rev.* **40**, 676 (1932) for the distinction between fine and secondary structure.

³ Bergen Davis and Harris Purks, *Phys. Rev.* **32**, 336 (1928).

⁴ Ross, *Phys. Rev.* **44**, 977 (1933).

⁵ Bergen Davis and Harris Purks, *Proc. Nat. Acad. Sci.* **13**, 419 (1927).

definitely distinguish structure from errors in measurement. When it was desired to measure the shift in position of the absorption limit due to chemical combination, rates of deflection for each setting of the crystal were recorded for the element, for the compound, and for the unfiltered radiation.

EXPERIMENTAL RESULTS

In Figs. 1 to 4 typical experimental curves are shown. The abscissae are wave-lengths in x-units obtained from the second crystal angle readings. Since no attempt was made to measure the wave-length position of the absorption limit, the center or half maximum of the edge was fixed on the wave-length scale at the best value given in Siegbahn's *Spektroskopie der Roentgenstrahlen*.

The ordinates are the I/I_0 values for the free metal (lowest) curve where I is the x-ray energy transmitted through the absorber and I_0 is the incident energy. For comparison the transmission curves of the compounds, plotted to the same scale as the metal, are shown displaced an arbitrary amount above the free metal curve so that their secondary structures do not overlap. The I/I_0 values for the compounds are nearly the same as those for the metal. At the top of the figure is shown a plot of the radiation transmitted by the aluminum sheet and for which the I/I_0 value is the same as the I/I_0 values in the region of secondary absorption. Each curve is the result of a single run and each point is the average of the three rate of deflection readings. Five or more exactly similar curves were obtained for each substance.

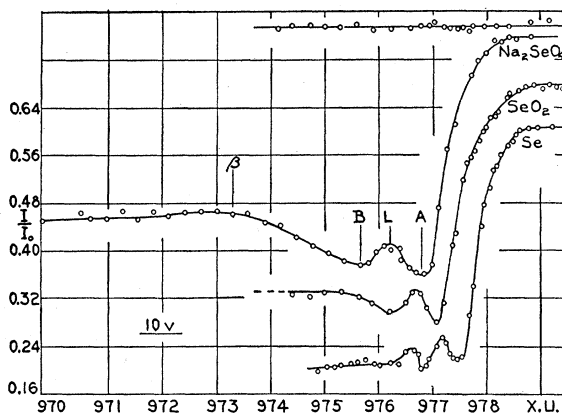


FIG. 1. The absorption limits of Se, SeO_2 and Na_2SeO_4 .

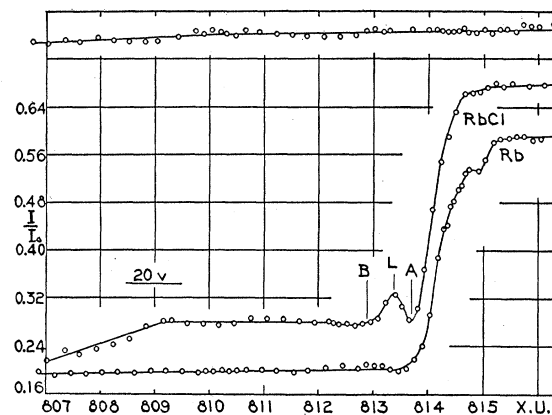


FIG. 2. The absorption limits of Rb and RbCl.

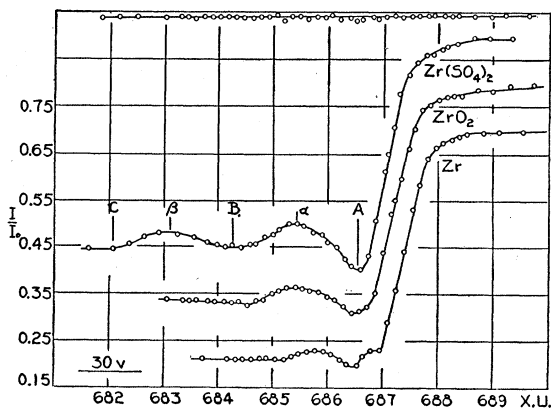


FIG. 3. The absorption limits of Zr, ZrO_2 and $\text{Zr}(\text{SO}_4)_2$.

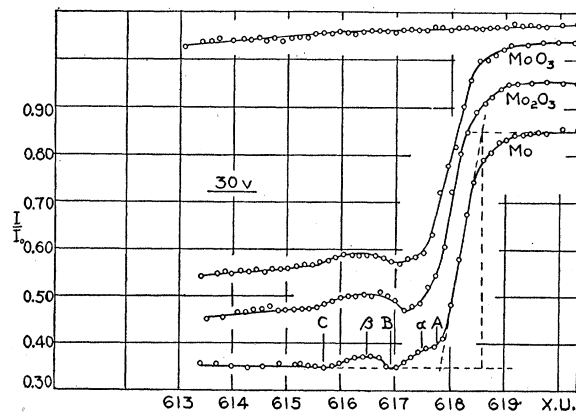


FIG. 4. The absorption limits of Mo, Mo_2O_3 and MoO_3 .

DISCUSSION OF RESULTS

Table I gives the separation in volts of the secondary structure from the center of the

TABLE I. *Position (in volts) of secondary structure.*

	<i>A</i>	α	<i>B</i>	β	<i>C</i>
Se	4.5	8.3	13.0	15.6	20.5
SeO ₂	5.6	10.7	17.5		
Na ₂ SeO ₄	6.2	13.5	20.6	50.0	
Rb					
RbCl	9.3	12.5	23		
Zr	11.5	17.2	23	43	53
ZrO ₂	18.5	47	70		
Zr(SO ₄) ₂	13.7	43	72	107	128
Mo	14	24	41	56	79
Mo ₂ O ₃	25	51	80		
MoO ₃	28	51	80		

absorption edge. The convention of Coster and Veldkamp⁶ of labelling the minima of the transmission curves by *A*, *B*, *C* and the maxima by α , β , γ is followed.

All of the substances show some structure. Rubidium is the only one which shows fine structure of the kind found by Barnes.¹ No structure is found farther from the principal edge than 110 volts. From a comparison of the various curves for the same substance it is concluded that the position of the structure can be specified to within 10 seconds of angle on the second crystal. This is less than 2 volts for selenium and 5 volts for molybdenum.

Hanawalt⁷ has examined Se and SeO₂ by the single crystal photographic method. Within the errors of measurement the curves of Fig. 1 are in agreement with his results. Idei⁸ photographed Se and Na₂SeO₄ as well. For Se he gives a single absorption line at 102 volts which probably is second order silver absorption. For Na₂SeO₄ he gives a minimum at 16.0 volts, the next maximum at 48 volts and the minimum at 104 volts. This would be similar to the Na₂SeO₄ curve of Fig. 1 if the first small maximum were not resolved. From this comparison it is clear that the two-crystal spectrometer is suitable for secondary structure measurements and that, due to its great resolving power, it should reveal structure which could be detected only with

great difficulty by the single crystal spectrograph.

Ross⁴ has examined zirconium and molybdenum with the double-crystal spectrometer. For the maxima α and β he obtains 21 and 52 volts for zirconium, 25.9 and 53.5 volts for molybdenum. For molybdenum these values and the ones of Table I are in agreement within the experimental error. The discrepancy of approximately 10 volts in the position of the zirconium structure hardly can be ascribed to experimental error. Perhaps the disagreement may be explained by the fact that Ross employed foils for both elements while in this case the zirconium was in powder form.

According to the theory of the secondary structure given by Kronig,⁹ the structure depends on the type of crystal lattice in which the absorbing atom finds itself. It follows from this that elements which crystallize with the same type of lattice should have similar secondary structures. Kronig also has shown that the separation of the structure from some zero level, which can be taken as the main edge, is proportional to $1/a^2$ where *a* is the crystal lattice constant. Therefore, the structures of two elements of the same lattice type should be identical if one of them is multiplied by the square of the ratio of the lattice constants. Coster and Veldkamp¹⁰ compared the structures of Pt, Cu and Au in this way and found that the theory is verified. Fe and Mo belong to the body-centered cubic system. Although Fe shows a much richer structure than Mo such a comparison can be made for the first few maxima.

The long lines of Fig. 5 represent the distances of the maxima and the short lines the distances of the minima of the transmission curves from the principal edge. The distances for Mo have all been multiplied by $(a_{\text{Mo}}/a_{\text{Fe}})^2$. The heavy line on the right is the principal edge and it is seen that arbitrarily displacing the Mo edge about 5 volts brings the secondary structures approximately together. A shift of 5 volts is permissible because of the experimental error in measuring the position and because in the photographic work no definite point in the edge is chosen from which to measure the structure.

⁶ D. Coster and J. Veldkamp, *Zeits. f. Physik* **70**, 306 (1931).

⁷ J. D. Hanawalt, *Phys. Rev.* **37**, 718 (1931).

⁸ Idei, *Sci. Rep. Tokoku Imp. Univ.* **19**, 653 (1930).

⁹ R. de L. Kronig, *Zeits. f. Physik* **70**, 317 (1931); **75**, 191 (1932); **75**, 468 (1932).

¹⁰ D. Coster and J. Veldkamp, *Zeits. f. Physik* **74**, 191 (1932).

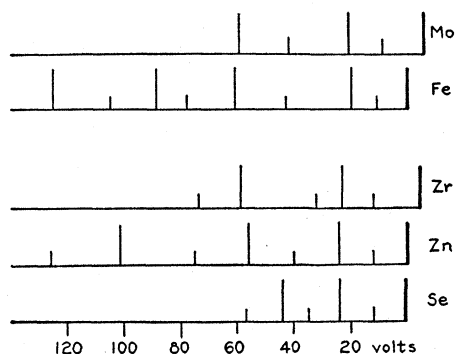


FIG. 5. Comparison of secondary structure for elements of the same crystal type.

Zr, Se and Zn have lattices of the hexagonal type. Fig. 5 also shows the structures of Zr and Se expanded for comparison with the Zn structure. The agreement for Zn and Zr is very good but for Se there is none. The data for Fe and Zn are from Coster and Veldkamp.¹⁰

Secondary structure is characterized by magnitude as well as by location. The intensity of the structure is defined as the ratio of the largest change in absorption coefficient in going from a maximum to a minimum to the average absorption coefficient. Coster and Veldkamp¹⁰ have proposed the general rule that the higher the melting point of a substance the greater will be the changes in the absorption coefficient in the region of secondary structure. That is, the intensity depends on the melting point. This would be expected from Kronig's theory.

As evidence, Coster and Veldkamp point out that the intensities of 19 percent for Fe, 13 percent for Cu and 7 percent for Zn, measured at room temperature, are in the same relative order as the respective melting points 1550°, 1083° and 419°C. The values of the maximum intensity and the melting points for the elements examined here are shown in Table II.

TABLE II. Maximum intensity of secondary structure and melting points.

	Melting Points	Intensity
Se	220°C	13 %
Rb	38	0
Zr	1700	6.5
Mo	2620	5.5

Since rubidium was within 15°C of its melting point it would not be expected to show any secondary structure. Hg¹¹ and Ga¹² with low melting points also show no structure. The intensities for Zr and Mo, however, are approximately one-third as great as for Fe and yet their melting points are higher. Great care was used in selecting, by trial, screens of thickness which gave most pronounced structure. It is surprising that Se with a relatively low melting point has a greater intensity than either Mo or Zr. These results are not in agreement with the rule stated above.

The small intensity for Mo and Zr perhaps explains why not more structure was found for these elements, although they were examined over a region of 300 volts on the short wavelength side of the main absorption edge. It is estimated that structure with an intensity as small as 4 percent could have been observed with little difficulty.

As would be expected, the secondary structures of an element and its compound are not similar either in position or in intensity. The change in intensity in going from the element to the compound is sometimes considerable. For example, the intensity for Zr is 6.5 percent while for the compound Zr(SO₄)₂ it is 13 percent.

TABLE III. Displacement of the K limits in compounds.

Com- pound	Volts	Com- pound	Volts
SeO ₂	4.5±0.4	Zr(SO ₄) ₂	8.0±0.8
Na ₂ SeO ₄	7.0±0.4	Mo ₂ O ₃	5.1±1.0
RbCl	1.5±0.5	MoO ₃	5.1±1.0
ZrO ₂	4.6±0.8		

Table III gives the displacement of the absorption edges of the compounds with respect to the absorption edges of the elements. The displacements are measured from the center of the element edge to the center of the compound edge. All of the shifts are to the short wavelength side of the absorption limit of the element.

Table IV lists the widths of the absorption edges measured as the base of the triangle shown on the Mo curve of Fig. 4. The values given are uncorrected averages of measurements

¹¹ Hanawalt, Phys. Rev. **37**, 715 (1931).

¹² Kievit and Lindsay, Phys. Rev. **36**, 648 (1930).

TABLE IV. Width of K absorption limits.

Sub- stance	Seconds	Volts	Sub- stance	Seconds	Volts
34 Se	42±3	7.9±0.6	40 Zr	53±3	20.2±1.2
SeO ₂	40±3	7.5±0.6	ZrO ₂	46±3	17.6±1.2
Na ₂ SeO ₄	43±3	8.1±0.6	Zr(SO ₄) ₂	46±3	17.6±1.2
35 KBr	49±3	10.4±0.6	42 Mo	47±3	22.0±1.4
37 Rb	47±3	12.8±0.8	Mo ₂ O ₃	45±3	21.2±1.4
RbCl	42±3	11.4±0.8	MoO ₃	65±3	30.5±1.4

from curves obtained with the same screen. Richtmyer and Barnes¹³ have stated that an unambiguous value of the width is obtained only if it is measured from a plot of μ/ρ against λ rather than from a plot of I/I_0 against λ . Accordingly, $\log(I_0/I)$ was plotted and the widths were again measured. The two sets of values were the same within the errors of measurement.

Various corrections for the "crystal width" have been proposed. The formula calculated by Schwarzschild¹⁴ would give a negligible correction for the crystals used in this work. Ross,⁴ however, subtracts twice the half maximum width of the (1, -1) rocking curve from the observed absorption limit width. This would mean a subtraction of 15 seconds from each of the widths of Table IV since the crystals had a half maximum rocking curve width of 7.5 seconds. There is, as yet, no good proof that one correction is better than another.

Chemical combination has practically no effect on the width of the absorption limit. In only one case, molybdenum and its trioxide, is the difference in widths greater than the experimental error. It was, therefore, considered permissible to use the width of the bromine limit measured in the compound KBr for plotting widths and atomic number. The KBr curve is not shown in this paper.

In Fig. 6 the volt widths of the elements which have been measured by Barnes,¹ by Ross,⁴ as well as those of this investigation are plotted against the atomic number. The points of the upper curve are the uncorrected values. Those of the lower curve are the upper curve values corrected in the Ross manner. Since it is not probable that a correction greater than the Ross

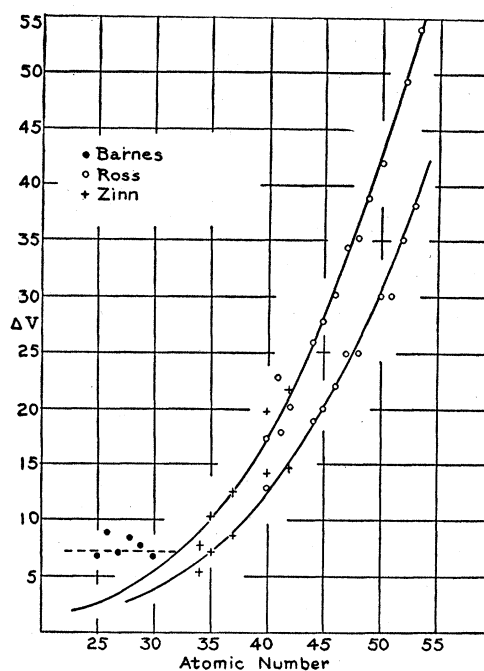


FIG. 6. Plot of the volt widths of the K absorption limits against the atomic number.

correction should be used, the points of Fig. 6 represent the extreme values for the widths. When the absorption limit itself exhibits considerable fine structure there is more than one way of drawing the triangle whose base is used as the width of the limit. For the elements manganese to zinc, studied by Barnes, the construction for measuring the width was made on that part of the curve which would give the smallest value. In this connection it should be noted that the method of determining the width is an artificial and arbitrary one.

The solid lines are plots of the equation $\Delta V = KZ^4$ with two different values for the constant K . For the atomic numbers 34 to 53 the experimental points fit the curves very well. Richtmyer and Barnes¹⁵ have measured the widths of the K limits of W and Au. The upper curve gives values 20 percent too large for the uncorrected widths and the lower curve gives values 50 percent too large for the corrected widths of these elements.

It is clear that in the neighborhood of atomic number 32 the widths reach a constant value,

¹³ Richtmyer and Barnes, Phys. Rev. **45**, 754A (1934).¹⁴ Schwarzschild, Phys. Rev. **32**, 162 (1928).¹⁵ Richtmyer and Barnes, Science **77**, 459 (1933).

and that for lower atomic numbers they may even increase. The break in the curve occurs just when the width becomes of the same order of magnitude as the ionization potential. This would be expected as an absorption limit could not have a width less than the ionization potential if it represents a removal of the K electron to the outside of the atom. Since the wave-length position of the absorption edges varies as $1/Z^2$ (Moseley law), it follows from the Z^4 law for the volt width of the absorption edges that the wave-length width is constant and

independent of Z . This becomes obvious when it is noted that the "seconds" widths of the elements of Table IV are very nearly constant. It would appear then that the diffuseness of the K level is due to something like a classical damping which for lines gives a constant value for $\Delta\lambda$.

In conclusion, the author wishes to express his thanks to Professor Bergen Davis for suggesting this investigation and for his interest and advice throughout the course of the experiment.

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On the Near Infrared Absorption Spectrum of Mono-Deutero-Acetylene

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The absorption spectrum of mono-deutero-acetylene has been photographed over the region 6000–10,500A in the first order of a 21-foot grating using absorbing columns up to 20 feet in length at atmospheric pressure. One band was found with origin at 10,302A. It is attributed to the molecule C_2HD . From the rotational constants of the band and similar data from the C_2H_2 bands, the interatomic distances in acetylene are computed as $r_{CD} = (1.247 \pm 0.008) \times 10^{-8}$ cm and $r_{CH} = r_{CD} = (0.940 \pm 0.036) \times 10^{-8}$ cm.

FROM a study of the bands of the "heavy" acetylenes considerable interesting information concerning physical properties of the acetylene molecule can be obtained. This possibility was mentioned by Randall and Barker¹ in their preliminary report of experimental results obtained on the far infrared bands of C_2D_2 and C_2HD . From the expected intensity alternation ratio in the C_2D_2 bands a check can be obtained on the nuclear mechanical moment of the deuterium atom and from the moments of inertia of any two of the acetylene molecules C_2H_2 , C_2HD or C_2D_2 , the internuclear distances can be directly calculated.

Consideration of previous work²⁻⁹ on the infra-

red absorption spectrum of acetylene indicates that two of the valence vibrational frequencies of C_2D_2 associated with the C-D motions should have magnitudes of about 2400 and 2500 cm^{-1} . Employing the notation of Sutherland⁹ these are the vibrations ν_3 and ν_2 , respectively. Therefore the band of C_2D_2 corresponding to the strong $\lambda 7887$ band of C_2H_2 should lie at about 10,300A. The $\lambda 7887$ band, from which Childs and Mecke determined the nuclear spin of the proton, is believed assignable to the combination $\nu_3 + 3\nu_2$. While the present paper was being written there appeared a *Letter to the Editor of Nature* by Herzberg, Patat and Spinks¹⁰ on the near infrared bands of "heavy" acetylene. Reference will be made to this later.

In our work the "heavy" acetylene was prepared by allowing water consisting of certainly more than 95 percent D_2O (sp. gr. 1.1054, indicating >99 percent D_2O) to drop slowly on finely ground calcium carbide. The gas generated

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¹ Randall and Barker, *Phys. Rev.* **45**, 124 (1934).

² Levin and Meyer, *J.O.S.A.* **16**, 137 (1928).

³ Hedfeld and Mecke, *Zeits. f. Physik* **64**, 151 (1930).

⁴ Childs and Mecke, *Zeits. f. Physik* **64**, 162 (1930).

⁵ Mecke, *Zeits. f. Physik* **64**, 173 (1930).

⁶ Hedfeld and Lueg, *Zeits. f. Physik* **77**, 446 (1932).

⁷ Lochte-Holtgreven and Eastwood, *Zeits. f. Physik* **79**, 450 (1932).

⁸ Mecke, *Zeits. f. physik. Chemie* **B17**, 1 (1932).

⁹ Sutherland, *Phys. Rev.* **43**, 883 (1933).

¹⁰ Herzberg, Patat and Spinks, *Nature* **133**, 951 (1934).