

## K X-Ray Absorption Spectra of Some Compounds of Bromine, Rubidium and Strontium

S. T. STEPHENSON, *State College of Washington, Pullman, Washington*

(Received August 3, 1936)

The *K* x-ray absorption spectrum of Br in solid AgBr and in each of the vapors CH<sub>3</sub>Br, C<sub>2</sub>H<sub>5</sub>Br and Br<sub>2</sub> is obtained with a double crystal ionization spectrometer. Edge widths and the positions of secondary fine structure are given and discussed. The small widths given were checked by narrow *K* edges obtained for Rb in RbBr and Sr in SrCl<sub>2</sub> and are shown to be in agreement with data on emission line widths. The effect of chemical combination on the wavelength position of the main edge is discussed.

### INTRODUCTION

THE width and secondary structure of x-ray absorption edges are of importance since the former is related to the widths of x-ray energy levels and emission lines<sup>1</sup> and the latter is determined by the different energy zones in the absorber.<sup>2</sup> It was thought that it would be of interest to investigate the Br edge in AgBr, CH<sub>3</sub>Br, and C<sub>2</sub>H<sub>5</sub>Br because of the use of these compounds in photographic or ionization methods of x-ray detection. (This part of the present investigation was suggested by Professor C. D. Cooksey in correspondence concerning some results which have already been reported.) Br<sub>2</sub> and the edges of Rb in RbBr and Sr in SrCl<sub>2</sub> were also studied.

The apparatus was the same as that described previously.<sup>3</sup> The absorbers were placed either between crystals *A* and *B* or immediately in front of the ionization chamber. The AgBr absorber consisted of five dental films. RbBr and SrCl<sub>2</sub> screens were made up of several cigarette papers saturated with a solution of the salt and rapidly dried. CH<sub>3</sub>Br, C<sub>2</sub>H<sub>5</sub>Br and Br<sub>2</sub> vapors were used in glass tubes either with Cellophane or thin glass windows.

### RESULTS AND DISCUSSION

Figs. 1 and 2 show typical results obtained. Ordinates are ionization currents in mm/sec. due to transmitted energy, and abscissae are wavelengths in X. U. starting from an arbitrary zero.

<sup>1</sup> F. K. Richtmyer, S. K. Barnes and E. Ramberg, *Phys. Rev.* **46**, 843 (1934).

<sup>2</sup> R. de L. Kronig, *Zeits. f. Physik* **70**, 317 (1931); **75**, 191 (1932).

<sup>3</sup> S. T. Stephenson, *Phys. Rev.* **49**, 495 (1936).

Table I contains a summary of the experimental results.

The distances (in volts) from the center of the main edge of any secondary structure observed are given in the last three columns of Table I. *A* refers to the first minimum,  $\alpha$  the first maximum, and *B* the second minimum in the trans-

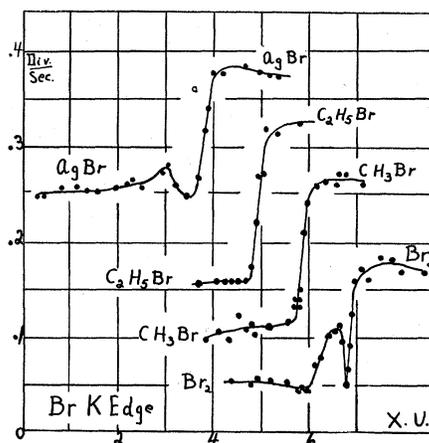


FIG. 1. *K* x-ray absorption spectra of Br in AgBr, C<sub>2</sub>H<sub>5</sub>Br, CH<sub>3</sub>Br and Br<sub>2</sub>.

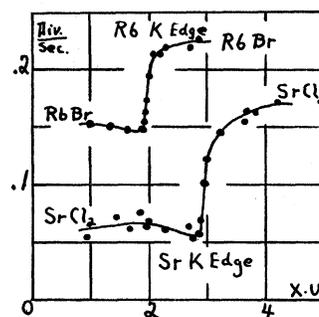


FIG. 2. *K* x-ray absorption edges of Rb in RbBr and Sr in SrCl<sub>2</sub>.

TABLE I. Widths of absorption edges and positions of secondary structure in volts.

Edge	Compound	Width	<i>A</i>	$\alpha$	<i>B</i>
Br	AgBr	9 ± 1.5	6	12	22
Br	C <sub>2</sub> H <sub>5</sub> Br	5 ± 1.5			
Br	CH <sub>3</sub> Br	5 ± 1.5			
Br	Br <sub>2</sub>	3.5 ± 1.5	1.5	4.5	10.5
Rb	RbBr	5 ± 2			
Sr	SrCl <sub>2</sub>	6 ± 2			

mission curve. The secondary structure for AgBr is similar to that for those other bromides of cubic lattice which have previously been studied<sup>3</sup> as would be expected from Kronig's theory. A secondary structure peak about 10 to 13 volts out on the short wave-length side of the edge is apparently quite characteristic of these different compounds. The expected shift of the structure due to the smaller grating space of AgBr (*ca.* 0.8Å less than KBr) is not found and is perhaps within experimental error here so close to the main edge. The presence of this secondary structure for AgBr would make difficult the interpretation of results obtained photographically on the structure of the bromine edge in other bromine compounds. Secondary structure in agreement with that reported here has been obtained by Hanawalt<sup>4</sup> and by Sandström and Carlsson,<sup>5</sup> using a photographic method.

The structure for Br<sub>2</sub> is interesting because of its pronounced character and its closeness to the edge. It may be of the Kronig<sup>2</sup> type and due to a forbidden zone in the Br<sub>2</sub> molecule, or of the Kossel<sup>6</sup> type and due to some outer lying level of the Br atom involved. In either case differences in the positions of *A*,  $\alpha$ , and *B* between Br<sub>2</sub> and a crystalline bromide containing Br ions are to be expected. No definite evidence was obtained for any pronounced structure in or near the edges of the other Br compounds investigated.

Any shifts in the positions of the main edges due to different chemical combinations are very small. As a special test, readings for absorbers of KBr, CH<sub>3</sub>Br, and Br<sub>2</sub> considered typical of cubic crystalline bromides, polyatomic bromides, and molecular bromine, respectively, were obtained during the same run. The transmitted

energy for each absorber in turn was measured at each setting of crystal *B* before moving crystal *B* to a new position. This provides a very delicate test for small shifts. No significant difference was found between the edges of KBr and CH<sub>3</sub>Br. Both of these were shifted about 1.1 ± 0.5 volts to the short wave-length side of Br<sub>2</sub>. The effect of chemical combination on the position of the Br edge would seem to be less than that indicated by Hanawalt's data.<sup>4</sup>

The widths (in volts) of the edges determined by the usual triangle method and not corrected for the effect of the crystals are given in the third column of Table I. The widths of the Br edges differ considerably among themselves. This is not to be attributed to an actual variation due to the element's being in different chemical compounds but rather to a very small shift with time in the verticality or some other adjustment of the crystals caused by slight jarring of the apparatus. The width (9 volts) for Br in AgBr was obtained from runs made shortly after the completion of work previously reported<sup>3</sup> for other bromides and agrees with the results reported then. CH<sub>3</sub>Br and C<sub>2</sub>H<sub>5</sub>Br were run later after a readjustment of the ionization chamber had jarred the apparatus slightly and gave widths of about 5 volts. Still later, after one absorption tube had blown up and sent a blast of air against crystal *B*, the runs for Br<sub>2</sub> were made giving widths of 3.5 volts. To check the fact that the narrower widths were not due to the new compounds tried, KBr and CH<sub>3</sub>Br were run again and gave widths of 3.5–4.5 volts, so any actual effect on the width due to chemical combination is small. The uncorrected width of the Br edge is between 3 and 5 volts as determined in this experiment. As a further check on these values, the edges of Rb<sup>7</sup> in RbBr and Sr in SrCl<sub>2</sub> were run and were found to have about the same angular width as the bromine edge. The voltage width of course is greater. This is considered evidence for the fact that the widths of the *K* absorption edges for Br and for Rb and Sr in the compounds studied are less than those reported in the literature reviewed, due presumably to a fortuitous adjustment of the crystals in this case.

Richtmyer<sup>1</sup> and others have suggested that the

<sup>4</sup> J. D. Hanawalt, Phys. Rev. **37**, 715 (1931).

<sup>5</sup> A. Sandström and E. Carlsson, Zeits. f. Physik **80**, 597 (1933).

<sup>6</sup> W. Kossel, Zeits. f. Physik **1**, 119 (1920).

<sup>7</sup> The 11-volt value previously given for Rb was obtained at the same time that the 9-volt value was found for Br.

width of an x-ray emission line is the sum of the widths of the initial and final states of the radiating atom. The full width at half maximum of either line in the  $K\alpha$  doublet for Ge (32) is about  $3.5^8$  volts and for Sr (38) is about  $5.8^8$  volts, so that the sum of the  $L$  and  $K$  energy level widths for Br, Rb and Sr should lie between 4 and 6

<sup>8</sup> S. K. Allison, *Phys. Rev.* **44**, 63 (1933).

volts and the widths of the  $K$  levels alone must be less than this. The widths of the  $K$  edges of Table I, determined as they are by the triangle method, are approximately  $\pi/2$  times the actual<sup>1</sup> widths of the  $K$  levels involved. It would seem, therefore, that the width values given in this paper are not too low but are in agreement with experimental line width data.

## Geologic Time and Isotopic Constitution of Radiogenic Lead

JOHN L. ROSE AND R. K. STRANATHAN, *Department of Physics, New York University, University Heights, New York City*

(Received August 10, 1936)

The isotopic constitutions of samples of lead from Colorado carnotite, Wilberforce uraninite, and Katanga and Great Bear Lake pitchblendes were found from densitometer measurements of the hyperfine structure of  $\lambda 5372$ . The probable geologic ages of these minerals calculated from the Ac D : Ra G ratios agree very well with the ages from Pb : U ratios with the exception of the Great Bear Lake pitchblende in which case leaching or some other method of alteration may have changed the Pb : U ratio.

ACCURATE knowledge of the relative abundance of the lead isotopes, Th D, Ac D, and Ra G ( $Pb^{208}$ ,  $Pb^{207}$ , and  $Pb^{206}$ ), end products of the thorium, actino-uranium (Ac U), and uranium (U I) families, found in radioactive minerals is very useful in the solutions of certain cosmological problems, especially those of the geologic ages of the minerals<sup>1, 2</sup> and origin of the actinium series.<sup>3-12</sup> Estimates of the isotopic

constitutions of radiogenic leads have been made from chemical atomic weights. Mass spectrograph results<sup>11</sup> are available for only a few samples of lead. Both methods of analysis are long and laborious, the mass spectrograph requiring a new discharge tube for each lead examined.

From the hyperfine structure of the lead spectral line  $\lambda 4245$ , Rose and Granath<sup>12</sup> were able to observe Ac D in lead from Katanga pitchblende and it was suggested by them that densitometer measurements of certain hyperfine structure patterns might be a very simple and effective method of determining the relative abundance of the isotopes of lead. Recently the present authors,<sup>13</sup> using the structure of  $\lambda 5372$  found this method very satisfactory in obtaining the isotopic constitution of ordinary lead from galena.

### ISOTOPIC ANALYSES OF RADIOGENIC LEADS

The spectra of several samples of lead from different uranium bearing minerals have been photographed and variations in the relative

<sup>1</sup> "The Age of the Earth" (National Research Council Bull. 80, 1931).

<sup>2</sup> Annual Report of the National Research Council Committee on the Measurement of Geologic Time (1932, 1933, 1934, 1935).

<sup>3</sup> A. Piccard, *Arch. des Sci.* **44**, 161 (1917); A. Piccard and E. Stahel, *ibid.* (5) **3**, 541 (1921).

<sup>4</sup> T. R. Wilkins, *Nature* **117**, 719 (1926); *Phys. Rev.* **29**, 352 (1928).

<sup>5</sup> O. Hahn, *Zeits. f. anorg. allgem. Chemie* **147**, 16 (1925); *Zeits. f. angew. Chemie* **42**, 927 (1929).

<sup>6</sup> F. Western and A. E. Ruark, *J. Chem. Phys.* **1**, 717 (1933); *Phys. Rev.* **45**, 69 (1934).

<sup>7</sup> A. V. Grosse, *Phys. Rev.* **42**, 565 (1932); *J. Phys. Chem.* **38**, 487 (1934).

<sup>8</sup> F. H. Bruner and H. Schlundt, *J. Phys. Chem.* **38**, 1183 (1934); M. Francis and Tchong Da-Tchang, *Comptes rendus* **198**, 733 (1934), *Phil. Mag.* **20**, 623 (1935); E. Gleditsch and E. Foeyn, *Comptes rendus* **199**, 412 (1934).

<sup>9</sup> F. Western and A. E. Ruark, *Phys. Rev.* **44**, 675 (1933); *ibid.* **45**, 628 (1934).

<sup>10</sup> Lord Rutherford, *Nature* **123**, 313 (1929).

<sup>11</sup> F. W. Aston, *Proc. Roy. Soc.* **A140**, 535 (1933).

<sup>12</sup> J. L. Rose and L. P. Granath, *Phys. Rev.* **39**, 1017 (1932); *ibid.* **40**, 760 (1932).

<sup>13</sup> J. L. Rose and R. K. Stranathan, *Phys. Rev.* **49**, 916 (1936).