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

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The *K* x-ray absorption spectrum of Br in KBr, RbBr, $CdBr_2$, and $NaBrO_3$ and of Rb in RbBr is obtained by using powder absorbing screens with a double crystal ionization spectrometer. Methyl iodide is used in the ionization chamber to eliminate the effect of Br in methyl bromide. The width of the Br edge is about 9 volts and of the Rb edge about 11 volts. The positions of secondary fine structure discontinuities are given and discussed. No discontinuity due to a possible simultaneous ejection of *K* and *L* electrons is observed.

INTRODUCTION

THE fine structure and width of x-ray absorption edges and the secondary fine structure often found on the short wave-length side of these edges have been investigated recently by several observers. According to Kronig[1] the observed secondary fine structure is dependent upon the crystal lattice of the absorber. It was thought that it would be of interest to investigate the *K* x-ray absorption spectrum of bromine in a few bromine compounds and of both bromine and rubidium in RbBr for two reasons. First: The universal use of AgBr photographic plates when the photographic method is employed or the almost universal use of methyl bromide in ionization chambers when the ionization method is employed raises some question as to whether observed effects in the bromine absorption spectrum are due to bromine in the absorber or to bromine in the detecting plate or chamber. Second: In certain cases[2, 3, 4] two elements in the same compound do not exhibit the same secondary fine structure, making a study of both the Rb and Br absorption spectra in RbBr of importance since both edges are comparatively close together and, therefore, easy to investigate and compare.

APPARATUS AND METHOD

The double crystal ionization spectrometer is of the type described by Ross,[5] constructed from a good Societé Génevoise optical spectroscope Crystals *A* and *B* were split from the same piece of optical quality calcite and were mounted with faces parallel to each other by the optical telescope method using a Gauss eyepiece. Crystal *B*, mounted on the prism table, is moved by a rigid lever arm run by Brown and Sharpe micrometer calipers, and the angular motions are further checked by viewing with a good telescope a millimeter scale as reflected from a mirror waxed to the top of the crystal. The angular readings can be relied upon to within 3 seconds of arc or about 0.05 X.U. in the region investigated. The ways supporting crystal *A* were taken from a micrometer microscope and fastened rigidly to the spectrometer in place of the collimator. A quadrant electrometer working at 3000 mm/volt sensitivity on a scale $1\frac{1}{2}$ meters distant measures the ionization currents in a small steel ionization chamber. It should be emphasized that here, as well as in a previous investigation of KBr,[6, 7] methyl iodide is used in the ionization chamber. Fig. 2 shows the Mo $K\alpha_1\alpha_2$ doublet in the (1,1) position, run to insure that the apparatus was working properly.

The metal x-ray tube[8] with Mo or W target was run on the pumps at about 40,000 volts peak and 30 to 40 milliamperes tube current. In view of Bearden's[9] experience with oil diffusion pumps and of their increasing popularity, it may be of interest to state that a regular General Electric X-Ray Universal broad focus filament has been used in the tube for over

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[1] R. de L. Kronig, Zeits. f. Physik **70**, 317 (1931); **75**, 191 (1932).

[2] V. P. Barton and G. A. Lindsay, Phys. Rev. **46**, 362 (1934).

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

[4] G. P. Brewington, Phys. Rev. **46**, 861 (1934).

[5] P. A. Ross, Rev. Sci. Inst. **3**, 253 (1932).

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

[7] C. D. Cooksey and S. T. Stephenson, Phys. Rev. **43**, 670 (1933).

[8] Constructed, with some minor changes, following the design of N. S. Gingrich, Rev. Sci. Inst. **1**, 691 (1930).

[9] J. A. Bearden, Rev. Sci. Inst. **6**, 276 (1935).

200 hours and shows no signs of failure. The tube is pumped with one single stage metal diffusion pump[10] backed by a Megavac with one charcoal trap between fore pump and diffusion pump, no traps of any kind being used between diffusion pump and tube. Apiezon oil B is used and all wax joints are of Apiezon wax. Doubtless a CO_2 or liquid-air trap would make the vacuum conditions still better but no trouble has been experienced and faster pumping is obtained without such traps.

The absorbing screens were made by saturating cigarette papers with a solution of the salt and drying over a hot plate.[4] Seven or more papers were used in each screen to secure uniformity. Various precautions were taken to eliminate any apparent structure due to (1) nonuniform screens or (2) to crystal imperfections or (3) to variations in primary intensity by (1) moving the screens between runs, (2) taking blank runs without the absorber present; also sliding the crystals so that the same portions were not always used, and (3) removing the absorber after each reading to check the intensity without absorber on at least one run for every substance except $CdBr_2$. All readings were made with the crystals in the (1,1) position, the absorbing screens being placed between crystals *A* and *B*. Six readings were usually taken to obtain each point in a given run.

RESULTS AND DISCUSSION

The curves presented in Figs. 1 and 2 show the results obtained. The ionization currents in mm/sec. due to energy transmitted through the absorber are plotted as ordinates and X.U. are plotted as abscissae starting from an arbitrary zero, no attempt having been made to measure the actual wave-length position of the edge itself or any shift of the edge due to chemical combination, though this latter could not have exceeded 3 volts between the compounds studied. In Fig. 1 each of the curves following KBr is displaced an arbitrary amount downward and approximately 1 X.U. to the right of the one preceding it. A summary of the quantitative results obtained is presented in Table I, the average values from several runs being given.

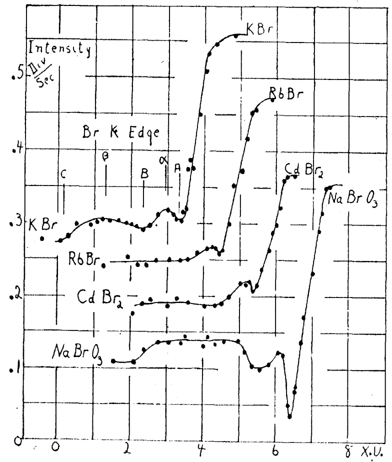

FIG. 1. The *K* absorption spectrum of Br in KBr, RbBr, $CdBr_2$ and $NaBrO_3$.

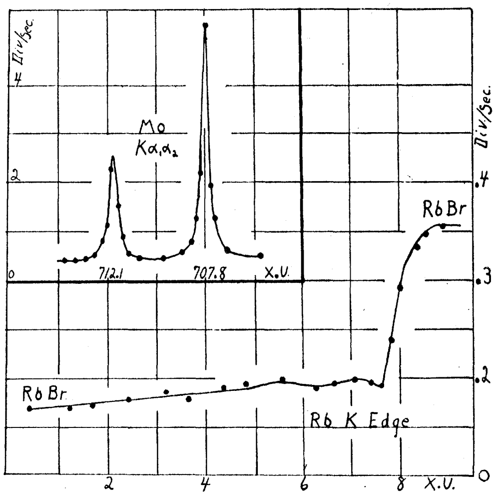

FIG. 2. The *K* absorption spectrum of Rb in RbBr. Mo $K\alpha_1\alpha_2$ doublet in inset.

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

EDGE	COMPOUND	WIDTH	*A*	α	*B*	β	*C*
Br	KBr	9±1.5	6.3	12	22	33	52
Br	RbBr	9±1.5	6.3	10.5	17		
Br	$CdBr_2$	9±1.5	6.3	11	22		
Br	$NaBrO_3$	9.5±1.5	6.5	11	19	48	77
Rb	RbBr	11±1.5	5.8	13(?)	27(?)		

The widths of the Br and Rb edges in the compounds investigated, given in volts in column 3 of Table I, were obtained from the experimental

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[10] The pump is of the type described in detail on page 80, D. H. Sloan, R. L. Thornton and F. A. Jenkins, Rev. Sci. Inst. **6**, 75 (1935).

TABLE II. *Physical constants of compounds used.*

COMPOUND	CRYSTAL STRUCTURE	GRATING SPACE (*A*)	MELTING POINT °C
KBr	Cubic	6.57	730
RbBr	Cubic	6.86	683
$CdBr_2$	Hexagonal	6.63	568
$NaBrO_3$	Cubic	6.71	381

curves by the triangle method[11, 12] and are not corrected for the effect of the crystals. This is not the true width of the edge[13] but serves as a convenient means of recording and comparing results. The widths obtained, though slightly narrower, agree within experimental error with those quoted by Zinn.[12] No pronounced fine structure in the edges themselves of the type found by Barnes[14] for elements of lower atomic number was recorded.

The last five columns in Table I give the displacements of the secondary fine structure from the center of the main edge in volts, A being the first minimum in the transmission curve, α the first maximum, etc. Table II gives the physical characteristics of the substances used which are pertinent to the discussion.

The most pronounced structure is shown by $NaBrO_3$, the substance of lowest melting point, in violation of the general rule that more pronounced structure is obtained for higher melting point substances. Others[12] have noted such violations. RbBr with a comparatively high melting point showed the least pronounced structure though several different screen thicknesses were tried.

The structure for KBr checks satisfactorily with the first two maxima found in a previous investigation of a KBr single crystal.[6,7] RbBr should yield a similar structure slightly closer to the main edge, because of its larger grating space according to Kronig's theory. Because of the unaccountably low intensity of the secondary structure for RbBr only the first maximum was obtained. The points α and B for RbBr are closer to the edge by an amount in accord with the theory. The fact that $CdBr_2$ though hexagonal shows a close-in structure almost identical with that of KBr and RbBr is interesting and perhaps explainable on the same basis as that used by Coster[15] to account for similar structures exhibited by close-packed cubic and hexagonal lattices. $NaBrO_3$ is cubic and of about the same grating space as RbBr and KBr; but as 3 O atoms are associated with each Br atom in the lattice the close-in fine structure should not be similar to that of KBr and RbBr. Comparing we see that β and C differ for KBr and $NaBrO_3$ but A, α, and B are quite closely the same. Hanawalt[16] has obtained photographically pronounced secondary fine structure for $NaBrO_3$. A, α, and B obtained here agree with his data. β and C do not agree although it is possible that the large peak β is complex, being made up of two discontinuities close together as was evidenced by some of the runs, in which case the data are in better agreement. In an ionic crystal the outer electronic shells of Br are complete and after the ejected K electron reaches the outer shells the Br nucleus and incomplete K shell will act on the electron much as the element of atomic number one greater, namely, krypton. Now krypton has a large ionization potential of about 14 volts and it is probable that structure within 15 volts or so of the Br edge should be governed more by the atom[17] than by the crystal lattice, particularly since Kronig's assumptions do not hold accurately close to the edge. This may be the main factor resulting in the similarity of A, α, and B in the cases studied.

The comparison of the secondary fine structure of Br and Rb in RbBr is inconclusive because of the meager structure found for Br and the almost complete lack of structure for Rb, α and B here being doubtful. The structures might be expected to differ at least close to the edge.[18] The two here are similar in that both exhibit comparatively weak structure. α and B are not the same. No very extended structure was found which would prove whether the two are in better agreement 100 or more volts from the edge.

It is of interest that a discontinuity due to the simultaneous ejection of a K and an L electron from a Br atom would have appeared at about 815 X.U. whereas the wave-length of

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[11] P. A. Ross, Phys. Rev. **44**, 977 (1933).

[12] W. H. Zinn, Phys. Rev. **46**, 659 (1934).

[13] F. K. Richtmyer, S. K. Barnes and E. Ramberg, Phys. Rev. **46**, 843 (1934).

[14] A. H. Barnes, Phys. Rev. **44**, 141 (1933).

[15] D. Coster, Physica **2**, 606 (1935).

[16] J. D. Hanawalt, Phys. Rev. **37**, 715 (1931).

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

[18] D. Coster and R. Smoluchowski, Physica **2**, 1 (1935).

the Rb edge is 814 X.U. It was necessary to search for such a discontinuity due to Br to make sure that it did not affect the runs on the Rb edge in RbBr. Two runs over the region 810–820 X.U. with $NaBrO_3$ as absorber failed to show any pronounced evidence for simultaneous *K* and *L* ejection large enough to affect the results for the Rb edge.

The secondary fine structure obtained by others[11, 12] using polycrystalline absorbers of atomic number greater than 34 and the double crystal spectrometer is not very pronounced and is obtained only comparatively close to the main edge as in this investigation. More secondary fine structure of the Kronig type further from the edge than that obtained here undoubtedly exists for all the compounds but does not appear prominently enough to be recorded above experimental errors. It would be more pronounced if the absorption took place in a single crystal, the case of KBr[6, 7] being one example. A study of Rb and Br in a single crystal of RbBr would prove interesting if a perfect enough crystal could be prepared.

APRIL 1, 1936 PHYSICAL REVIEW VOLUME 49

A Simple Method for Demonstrating and Measuring Approximately the Index of Refraction of Crystalline Substances for X-Rays

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An x-ray spectrum line may be formed by reflection at the surface of a crystal even if that surface is not parallel to the atomic planes concerned in the reflection. If two faces are good very close to the line of their intersection, then, using a slit that is not too narrow, the same line may be reflected simultaneously from these two faces of a stationary crystal by turning it so that for the proper reflecting angle the rays must fall at the intersection. If the wave-length of the line is such that the reflected beam from the beveled face almost grazes the surface, then that portion will be refracted much more than the portion of the line reflected from the other face, and the two parts of the line are plainly separated. A very simple calculation gives the index of refraction from the width included between the two portions of the line. In this way δ/λ^2 for a cerussite crystal has been found to agree fairly well with the calculated value.

IN 1922 Davis and Terrill[1, 2] suggested a method of increasing the refraction of a beam of x-rays by grinding a crystal surface at an angle with the atomic planes so that the incident or emergent beam might make a very small angle with the reflecting surface.

The present investigation retains the principle of the Davis method of unsymmetrical reflection, but introduces two important modifications. Firstly, two natural faces were used instead of a natural face and a ground surface; secondly, the same spectrum line was reflected simultaneously from two faces of the crystal by turning the crystal so that for the proper reflecting angle the rays fell at the intersection of the two faces. The crystal was stationary during the exposure. The wave-length of the line was such that the rays reflected from the beveled face, almost grazed the surface, and were therefore refracted much more than the portion of the line reflected from the Bragg face, so that the two parts of the line were plainly separated. No reference line is needed but the two reflecting surfaces selected must be good very close to their line of intersection.

The Crystal Structure of $PbCO_3$

The crystal specimens chosen were cerussite ($PbCO_3$) which is orthorhombic in form and resembles aragonite in its structure and symmetry.[3] The density is 6.5 g/cc. Sharp x-ray emission lines were obtained by reflection from the faces used. In a number of investigations

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[1] Davis and Terrill, Proc. Nat. Acad. Sci. **8**, 537 (1922).

[2] Nardoff, Phys. Rev. **24**, 143 (1924).

[3] W. L. Bragg, Proc. Roy. Soc. **A105**, 16 (1924).