SEPTEMBER 1, 1933 PHYSICAL REVIEW VOLUME 44

Fine Structure in the *K* X-Ray Absorption Spectrum of Bromine*

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(Received June 26, 1933)

The existence of an extended Kronig type fine structure in the *K* absorption edge of bromine is established by the double crystal ionization spectrometer method. This fine structure as obtained with partially polarized x-rays and a single crystal absorber is very pronounced and some evidence has been found of a smoothing out and shifting of the structure for orientations of the crystal absorber in which the most probable direction of ejection of electrons is not perpendicular to an important plane in the crystal. There is some indication that the structure is less pronounced for unpolarized x-rays. The results follow from Kronig's theory of extended fine structure and quantitative agreement with the theory is obtained when comparison is made with results obtained (photographically) by others. A value for the side of a unit cube of KBr is given.

INTRODUCTION

A MORE or less complicated fine structure has often been observed on the short wavelength side of x-ray absorption edges. This structure has been found to extend only a few volts from the main edge in the case of monatomic gases and vapors. Polyatomic gases and solids exhibit, in addition to this close in structure, a fine structure extending several hundred volts from the main edge. The fine structure in and close to the edge has been explained by Kossel.[1] Recently Kronig[2, 3, 4] has given a theoretical explanation of the extended fine structure and much evidence has been accumulated in favor of the theory.

In a preliminary report[5] some experimental work on fine structure was presented. It is desired to give a brief description of the work and to give some additional results. The purpose of the present investigation is twofold. All the experiments on extended fine structure appearing in the literature reviewed were performed by the photographic method. The ionization method has been used with the double crystal spectrometer in investigations on the width and structure of the main absorption edges and some fine structure in the edge itself has been observed. The first part of the present problem, then, is to obtain the extended fine structure by the ionization method and to compare these ionization results with the photographic results of others in checking some aspects of Kronig's theory.

It occurred to Professor C. D. Cooksey that, by the use of polarized x-rays and a single crystal acting both as absorber and grating, one should obtain very pronounced fine structure. In addition one would expect from Kronig's[3] theory a variation in intensity and a shift in position for each discontinuity, with change of orientation of the electric vector with respect to the crystal axes of the absorber. The second part of the present problem is to look for such effects. The variations and shifts observed will be small because of (1) the large number of planes concerned, (2) incomplete polarization and the fact that all the electrons are not ejected in the direction of the electric vector and (3) the finite resolving power of the crystal grating.

APPARATUS

A double crystal spectrometer of the precision type designed by Compton[6] and made by the *Societe Genevoise* was used. The first crystal, C_1, acted both as polarizer and grating. A calcite crystal was used having its reflecting face ground

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* Part of a dissertation presented for the degree of Doctor of Philosophy in Yale University.

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

[2] R. de L. Kronig, Zeits. f. Physik **70**, 317 (1931).

[3] R. de L. Kronig, Zeits. f. Physik **75**, 191 (1932).

[4] R. de L. Kronig, Zeits. f. Physik **75**, 468 (1932).

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

[6] A. H. Compton, R.S.I. **2**, 365 (1931).

parallel to a set of (110) planes, thus giving a high degree of polarization. (In the third order, for this face, the Bragg angle for the wavelength of the bromine K edge is 46°.) The second crystal, C_2, contained the absorbing element. A large crystal of artificial KBr kindly sent to us by Professor G. A. Lindsay of the University of Michigan was used, with reflection taking place from a cleavage (100) face. By rotating C_2 about an axis normal to its reflecting face, the angle between the normal to a set of (100) planes and the principal direction of ejection of electrons could be altered. Very pronounced extended fine structure should be observed when this angle is zero. For other angles it should be shifted and somewhat smoothed out.

A sensitive quadrant electrometer measured the ionization currents in a small copper ionization chamber. About every two minutes small kicks of 1 or 2 divisions due to α-particles were noted and these formed the most serious source of error.

RESULTS

Because of the low intensity with C_1 reflecting in the third order, no satisfactory curves could be obtained for this position most closely approximating complete polarization. (Work is now in progress in the third order with a metal x-ray tube capable of giving greater intensity.) C_1 was set for the second order reflection of a small region near and including the Br K edge. The total deviation produced by C_1 was about 57°30″, giving about 75 percent polarization of the rays incident on C_2. Therefore, the fine structure was expected to be less pronounced and the variations with the change of orientation of C_2 less noticeable than for the case of completely polarized x-rays but the effects, though smaller, were easier to detect because the intensity in the second order was some three or four times that in the third order.

The figure in the preliminary report[5] showed a pronounced extended fine structure obtained by the double crystal ionization method. After the completion of runs for this curve, work was started on the effects of polarization and crystal orientation. C_2 was set with a cube edge accurately parallel to its axis of rotation. Most of the electrons, with C_2 in this position, were ejected normal to the (100) planes of the crystal. The curve shown at the top of Fig. 1 was taken with C_2 in this position at an electrometer sensitivity of 2500 divisions per volt using the Mo target tube at 50 kv and 25 m.a. The fine structure A in the edge itself is of the Kossel type. The peaks B, C, E, and F represent extended fine structure caused by forbidden zones in the KBr crystal lattice. The minima, of which D is the most pronounced, correspond to the permitted zones.

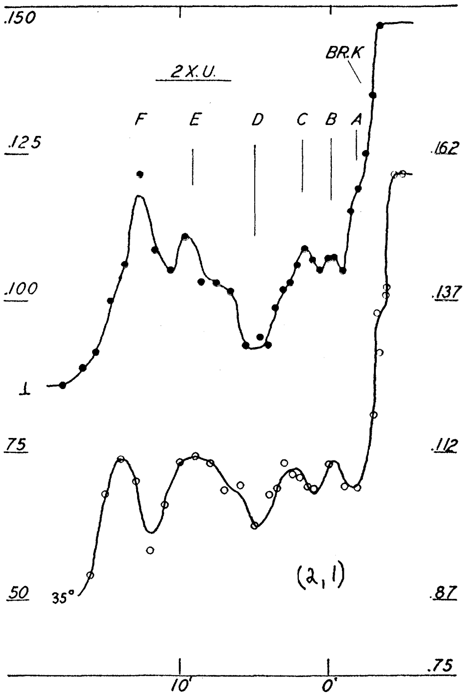

FIG. 1. Fine structure observed when the most probable direction of ejection of electrons is perpendicular (⊥) and at an angle of 35° with the normal to a set of (100) planes. Mo target.

The curve just described is to be compared with the curve appearing below it in Fig. 1. This curve (marked 35°) was taken with C_2 rotated about an axis normal to its reflecting cleavage face some 35°. The main direction of ejection of electrons for this orientation was perpendicular to no very important plane in the crystal. The main features of the structure A, B, C, D, E and F repeat in their general shape and appearance in the lower curve. This proves the fine structure to be independent of any imperfections in C_2. The valley D is more pronounced in the top curve than in the lower curve and the peaks E and F

appear more pronounced. It should be noted, however, that peaks *B* and *C* do not smooth out in the lower curve as do *E* and *F*. It may be that *B* and *C* being closer to the main edge are in a region where Kronig's approximations do not hold so well as they do for higher energy values.

The fact that *E* and *F* are two peaks on a broader fine structure peak lends some weight to Kronig's assumption that the structure usually observed is an aggregate of the discontinuities due to individual planes. Apparently *E* and *F* are due to two important individual planes. *E* and *F* are slightly more separated in the lower curve than in the upper. This shift is small but is as large as one might expect. The shift according to the theory should be towards the main edge for some planes and away from it for others which would account for the broadening observed.

In order to obtain more intensity, a W target tube was used at 50 kv and 25 m.a. Fig. 2 shows the results for normal (⊥) ejection (top curve) and 35° ejection (lower curve). The electrometer sensitivity was 1900 divisions per volt. The main edge is less pronounced than in Fig. 1 because of a more curved distribution of background intensity. No attempt was made to run over the structure *A* accurately.

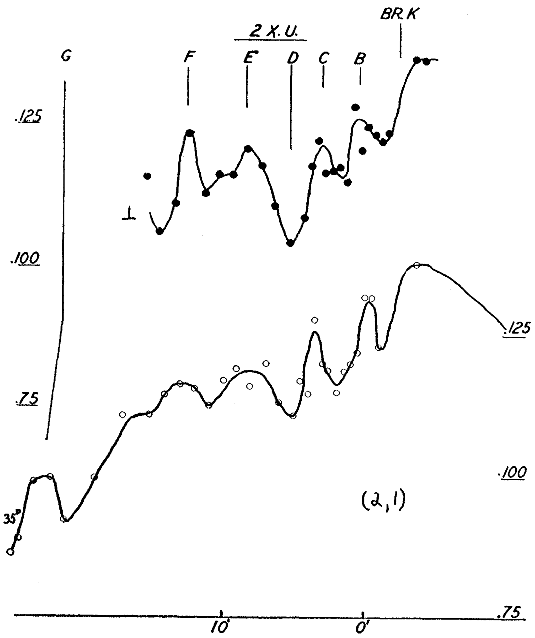

FIG. 2. Fine structure as in Fig. 1. W target.

C_1 was not in exactly the same position for these curves as for the previous curves, also a broader focal spot gave a different distribution of intensity on C_1. The fact that these curves are so nearly identical with those of Fig. 1 proves that the fine structure observed is not due to imperfections in C_1 or to the structure of the focal spot.

In Fig. 2 as in Fig. 1, we notice a more pronounced minimum *D* in the upper curve than in the lower and the structure *E* and *F* appears slightly smoothed over and broadened in the lower curve. Again *B* and *C* do not show such effects.

Thus, we have obtained with the ionization method very pronounced fine structure with partially polarized x-rays and a single crystal absorber. The top curves in Figs. 1 and 2 and the previously reported curve[5] show a more pronounced fine structure compared to the main edge than any structure appearing in the literature reviewed. It is interesting to note that the most pronounced fine structure referred to in the journals is that obtained with a single crystal as absorber and no appreciable polarization, polycrystalline absorbing screens giving a much less pronounced structure. There is some evidence of a smoothing over and shifting of the structure as one changes the orientation of C_2. It is well to mention here three objections to this evidence on the smoothing and shifting of the structure. (1) The scattering of the points (necessarily present because of the weak intensity), the effects observed being within a possible scattering of the points. (2) Crystal imperfections, which may cause slight variations in the structure for different positions, although the structure in general has been shown to be independent of such imperfections. (3) Peaks *B* and *C* do not behave as do peaks *E* and *F* but the strictest application of the theory may not be permissible so close to the edge.

In a search for further fine structure discontinuities the peak *G* was found. Its presence was later verified with C_1 reflecting in the first order.

Runs in the (1, 1) position (no appreciable polarization and lower dispersion) gave the fine structure again. Here it is still quite pronounced since the absorption is in a single crystal but possibly not quite so pronounced as for the (2, 1) position where the polarization is appreciable. However, the change due to polarization is small.

TABLE I. *Fine structure positions relative to the main edge. (2, 1)*

Units	A	B	C	D	E	F	G
Minutes	0.8	2.6	5.2	7.8	11.8	16.1	24.7
X. U.	0.3	1.0	2.0	3.0	4.5	6.2	9.7
Volts	4.4	14.9	28.9	43.7	65.8	90	140

Table I shows the positions of the fine structure peaks relative to the center of the main edge, the values being averages of the values obtained from all the (2, 1) curves.

TABLE II. *Fine structure positions relative to the main edge. (X.U.)*

Position	A	B	C	D	E	G
(2, 1)	0.3	1.0	2.0	3.0	4.5	9.7
(1, 1)	0.3	1.0	1.85	3.0	4.7	10.2

Table II shows a comparison of the positions of the fine structure distances relative to the main edge with C_1 in second and first orders. (Because of low dispersion in first order F was not separated from E.) It is obvious from this table that the fine structure is independent of crystal imperfections, line-up and source of x-rays.

TABLE III. *Distances from center of main edge in volts.*

Author		B	C	$\frac{1}{2}(E-D)$
Lindsay[7]	(K in KBr)	14.2	24.9	
Nuttall[8]	(K in KCl)	14.2	24.9	62
Hanawalt[9]	(Br in NaBr)	5.5–13	28.0	54
Present	(Br in KBr)	14.9	28.9	55

Table III shows a comparison of the present results with those obtained photographically by other authors. The values given by Lindsay[7] are for the K edge of potassium in a KBr crystal. On Kronig's theory bromine and potassium should show the same fine structure absorption in KBr. The agreement shown is well within experimental error. Following Kronig's theory Nuttall's[8] values for the absorption of potassium in KCl were corrected for the difference in grating space between KBr and KCl and the values thus obtained agree well with those obtained here for bromine. Finally Hanawalt's[9] results for bromine in NaBr are shown corrected and the agreement is excellent although Hanawalt's data for the first peak leaves the exact position of the maximum in doubt. (In this table the values given by the other authors were with respect to the bottom of the main edge. The values here given have been corrected for half the width of the edge as estimated from the curves which were published. The first two columns give the positions of maxima. The third column shows the beginning of the secondary structure hump E and represents a point about half way between D and E in the present work, i.e., 55 volts. Nuttall's and Lindsay's B and C are given as the same because Lindsay remeasured Nuttall's plates and remarks that the values are the same within experimental error.)

The results are in striking agreement with Kronig's fundamental postulate that the extended fine structure depends on the crystal structure and not on the elements in the crystal.

The side of a unit cube of KBr has been given by various observers as 6.59,[10] 6.57,[11] and 6.5904A.[12] There is some discrepancy in these results. Taking the value of the wave-length of the Br edge to be 918.1 X.U.,[13] runs in the (2, 1), (2, −1), (1, 2) and (1, −2) positions gave for $2d$ the value 6.574 ± 0.006A. Though not a precision measurement, it is felt that this value is more accurate than those previously obtained.

In conclusion, the author wishes to express his thanks to Professor C. D. Cooksey for suggesting the problem and for his help and advice while directing the experimental work and to Dr. Donald Cooksey for the loan of precision instruments and for suggestions. The author is indebted to Professor L. W. McKeehan for making the necessary apparatus available.

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