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The Cu K Absorption Edges of the Cuprous Halides

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The x-ray K absorption edges of copper in crystalline CuCl, CuBr, and CuI have been measured with a double crystal spectrometer. Near the edge the experimental curves have been analyzed into component absorption lines. The most intense absorption maximum is due to excitation of the K electron into the $4p$ level of the absorbing ion. However, the line structure is too complex to be completely explained by the unperturbed optical levels of Zn^+ or by any perturbation of these levels arising from crystalline fields. It is suggested that the excited electron is shared with neighboring ions even in the lowest states.

INTRODUCTION

THE fine structure within 30 or 40 ev of the Cu K edge has already been studied under high resolution in the metal,[1] certain alloys,[2] and in aqueous solutions[3] of Cu^{++}, $Cu(NH_3)_4^{++}$, and $Cu_2(CN)_4^{--}$. In most cases interpretation of the experimental results is very difficult because of the complexity of the electronic energy levels of crystals and molecules. However, for the pure metal there were available Krutter's[4] electronic band calculations and good agreement was found between theory and experiment. It was found also that the edge of hydrated Cu^{++} could be understood quite simply. It consisted of two absorption maxima which were identified as a $1s \rightarrow 4p$ transition and an unresolved mixture of $1s \rightarrow 5p$, $6p$, etc., transitions. The positions of the maxima were not altered by the water of hydration although there was considerable broadening of the absorption lines.

In extending the work to the compounds of copper it was decided to measure first the cuprous halides because the completed $3d$ shell of Cu^+ should simplify the interpretation of the absorption edge structure. The interaction between the np series electron and the unfilled $3d$ shell broadens the absorption lines of the cupric ion and makes it difficult to say just what edge structure is characteristic of the free ion and what is caused by the fields of surrounding ions or molecules. With the cuprous salts any deviation of the absorption edge from a series of sharp lines, the $1s \rightarrow np$ transitions, may be ascribed to the effects of the surroundings. The doublet separation is not large enough to be detected.

The halides have, in addition, the advantage of a known and relatively simple crystal structure. They crystallize in the zinc sulphide arrangement which is a diamond lattice with half the sites occupied by one type of ion, half by the other. The $Cu^+ - Cu^+$ separation is 3.82A in CuCl, 4.01A in CuBr, and 4.27A in CuI.

EXPERIMENTAL

The double crystal spectrometer used in this investigation was designed especially for absorption work in the 1 to 5A region and was built in the departmental machine shop. The spectrometer, x-ray tube, power supply, and counting equipment will be described at another time.

Geiger counters similar to those described by Shaw[5] were used to record x-ray intensities. The incident intensity, I_0, was constant over the frequency range concerned and also, because of the use of a tungsten filament and target, remained constant despite filament evaporation. This saved a great deal of time as it was necessary to measure I_0 but once.

The crystals were split from a specimen of calcite kindly loaned to us by Professor G. A. Lindsay. After grinding, and etching in HCl, the $(1, -1)$ half-maximum width was 11 seconds. The crystals were used with this half-width.

The absorption samples were prepared by

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[1] W. W. Beeman and H. Friedman, Phys. Rev. **56**, 392 (1939).
[2] H. Friedman and W. W. Beeman, Phys. Rev. **58**, 400 (1940).
[3] W. W. Beeman and J. A. Bearden, Phys. Rev. **61**, 455 (1942).
[4] H. Krutter, Phys. Rev. **48**, 664 (1935).
[5] C. H. Shaw, Phys. Rev. **57**, 877 (1940).

mixing the finely powdered salts with a few drops of melted paraffin on a thin sheet of mica. After the paraffin had solidified, the mica was placed on a glass plate over a 15 watt lamp and the paraffin-powder mixture rolled flat. A small test tube makes an excellent rolling pin. The lamp served a double purpose. It kept the paraffin soft enough to roll easily and in addition made possible an easy control of uniformity of thickness. At the best thickness for x-ray measurements the specimens were still slightly translucent and quite small variations in thickness could be detected and eliminated. The samples were left on the mica backing which was too thin to absorb the x-rays appreciably.

The three cuprous halides were precipitated from solutions of $CuSO_4$ and the potassium halide by the addition of SO_2. As a check, alternative methods were also used. For CuCl, the cupric chloride in hydrochloric acid was reduced by boiling with copper turnings. CuBr was prepared by heating the cupric bromide to a dull red heat and CuI by adding KI to a solution of $CuSO_4$ (without addition of SO_2). The precipitates were washed with absolute alcohol and dried in vacuum. All these methods are described in Mellor's[6] treatise. In every case salts prepared by different methods gave identical absorption edges.

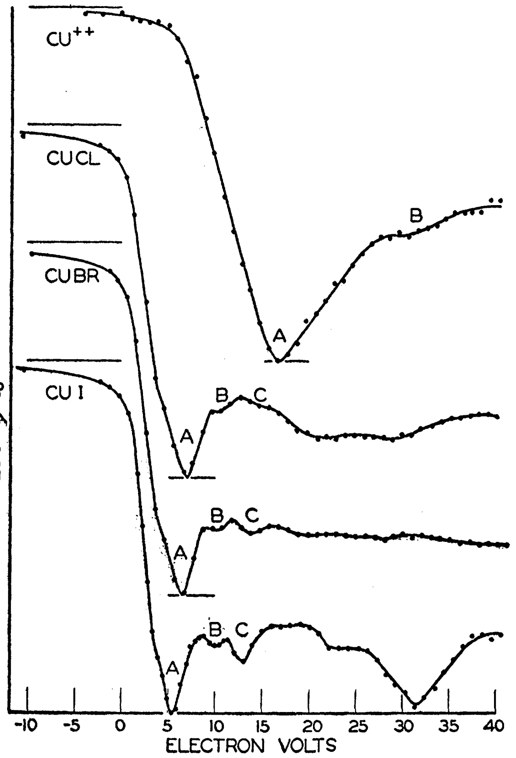

FIG. 1. Some K absorption edges of copper. Cu^{++} is redrawn from reference 3. The experimental points are averages of several runs.

TABLE I. Positions of absorption maxima (Fig. 1).

	A	B	C
Cu^{++}	16.7 ev	30.5–32.5 ev	
CuCl	7.1	11.2	14.6 ev
CuBr	6.4	10.5	14.2
CuI	5.6	10.3	13.0

The chloride and bromide hydrolyze in contact with moist air but not quickly enough to interfere with the measurements. Apparently the hydrolysis is accompanied by some oxidation as rough measurements on Merck reagent CuCl which had hydrolyzed to a pale green color (CuCl is white) showed a pronounced absorption at the position of the $1s \rightarrow 4p$ transition of Cu^{++} which is not present if the salt is freshly prepared.

In Fig. 1 are presented the three cuprous halide absorption edges and that of hydrated Cu^{++} from reference 3. The zero of the abscissa is at the energy of the first absorption line of the metal edge, i.e., the energy necessary to excite a K electron into the lowest empty level of the Fermi distribution. All the curves have been plotted to this same abscissa so that shifts of structure from one curve to the next are accurately portrayed.

The experimental points are averages over several independent runs. The statistical probable error per point is about 1 percent of the total change in $\log I/I_0$, from minimum to maximum absorption, at the K jump. This estimate is based on the total number of counts recorded at a given setting for all runs. Numerous checks have shown that at a particular spectrometer setting, with a particular absorber in place, a set of readings will vary by no more than the statistical amount. However a portion of the curve extending over several points may be in error by 3 or 4 percent of the top to bottom jump

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[6] J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry* (Longmans, Green and Company, London, 1928), Vol. III.

because of the movement of the beam over inhomogeneities in the absorber.

Angular settings of the crystal are reproducible to about 1 second of arc or roughly 0.1 ev at these wave-lengths. The accuracy with which the relative positions of absorption minima can be determined is limited mainly by their sharpness, about ±0.5 ev for the $1s\rightarrow4p$ of Cu^{++} and ±0.2 ev for $1s\rightarrow4p$ of Cu^{+}. None of the uncertainties is large enough to affect any of the conclusions drawn from the data.

We have listed in Table I the positions of the principal absorption maxima of the four curves.

DISCUSSION

The first absorption maximum ($1s\rightarrow4p$) of hydrated Cu^{++} lies at 16.7 ev. It is labeled *A* in Fig. 1. In reference 3 the separation of the metal edge and the $1s\rightarrow4p$ line of the cupric ion was calculated on the assumption that the ion absorbs as if in vacuum. Good agreement was obtained with the above experimental value. The calculation made use of a simple energy cycle which is easily adapted to the problem of the $Cu^{+}-Cu^{++}$ edge separation. When carried through the cycle gives 9.4±0.6 ev for the energy difference of the $1s\rightarrow4p$ transition in Cu^{+} and Cu^{++} assuming, again, that the optical levels are not influenced by neighboring ions. The uncertainty in the calculated result is due largely to the splitting of the $3d^94p$ configuration of Zn^{++}. Experimentally (Table I) the separations are 9.6 ev for CuCl; 10.3 ev for CuBr and 11.1 ev for CuI if one identifies point *A* of each curve with the $1s\rightarrow4p$ transition. The agreement with the calculation is close enough to give confidence in the identification.

The differences in the positions of absorption maximum *A* of the three cuprous halides are greater than the experimental uncertainty and must be real. Thus while the principal factor determining edge position is the valence of the absorbing ion, easily measurable shifts are produced by a change in the neighboring negative ions or in the lattice constants even when the crystal type is unaltered.

The broad maximum *B* of Cu^{++} was shown[3] to arise from unresolved $1s\rightarrow np$ absorption, $n=5, 6, 7$, etc. If such transitions also contribute to the cuprous halide curves they should produce a maximum about 7.7 ev above the $1s\rightarrow4p$ maximum. This figure was reached by taking an average of the positions of the $5p$, $6p$, and $7p$ terms of Zn^{+} giving them the relative weights 4:2:1 as determined by Parratt[7] for the absorption of argon gas. The observed separations of maxima *A* are *C* are 7.5 ev in CuCl; 7.8 ev in CuBr; and 7.4 ev in CuI, in excellent agreement with the optical terms.

However, not too much significance should be attached to this very close agreement because the unperturbed levels of Zn^{+} cannot explain at all certain other features of the experimental curves such as the absorption maximum *B*, the inflection point 2 or 3 ev below *A* in each curve, and the previously mentioned variation in the position of the $1s\rightarrow4p$ absorption line. In addition, when the edge is analyzed into component absorption lines, it is found that apparently single absorption maxima may be composed of several lines.

Such an analysis is much more feasible for the cuprous edges than for the cupric because of the smaller number of component lines in the former. As has been previously pointed out, this simplification comes about because of the full $3d$ shell of Cu^{+}. Its effect on the experimental curves may be seen at once in the greater sharpness of the initial absorption break in the cuprous edges of Fig. 1.

The individual absorption lines are of the form[8]

$$y=A/(x^2+B^2)$$

where y is proportional to the *K* absorption coefficient (positive y plotted down in Figs. 1 and 2), B is the half-width at half-maximum, A/B^2 the maximum ordinate, and x the distance from the center of the line. B is inversely proportional to the lifetime of the *K* excited state and should be the same for all Cu *K* absorption lines since the most probable transitions filling the *K* shell involve only the inner electrons.

It is not easy to determine the correct value of *B* when the edge contains no single isolated absorption lines. In the work on copper metal[1] *B* was estimated to be about 1.0 ev (including the contribution of the calcite crystals). The

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[7] L. G. Parratt, Phys. Rev. **56**, 295 (1939).

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

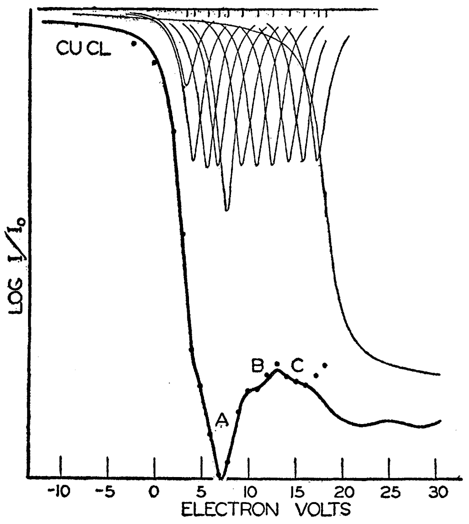

FIG. 2. The component absorption lines of the CuCl edge. The edge is redrawn from Fig. 1. The points are not the experimental points of Fig. 1, but are obtained by adding the ordinates of the component lines drawn at the top of this figure and listed in Table II.

estimate was made by matching the initial absorption of the experimental edge with a family of theoretical curves drawn for different values of B and on the assumption of a uniform distribution of absorption lines. Similar comparisons were made using the present data but assuming a single strong line to be responsible for the initial absorption. Again B was approximately 1.0 ev.

The drawing and matching of curves is laborious and always somewhat uncertain when only limited portions of the curves are compared since different combinations of horizontal and vertical scales may produce quite similar curvatures. The following semianalytic method furnishes an upper bound to B which is the more accurate the further separated are the absorption lines in the edge and which is independent of the vertical scale to which the data are plotted.

The ratio $|y'/y| = |2x/(x^2+B^2)|$ evaluated for a single absorption line has its maximum value at $x=B$, at which point $|y'/y| = 1/B$. On the initial steep part of an experimental absorption curve one can easily determine the observed maximum $|y'/y|$ and thus the maximum $B=|y/y'|$ of the component absorption lines making up the edge.

Of course at the point of maximum $|y'/y|$ on the experimental absorption curve the observed absorption coefficient will generally contain contributions from several component lines. Not all these lines will be evaluated at the abscissa for which $|y'/y|$ is a maximum. The method therefore may considerably overestimate B but cannot underestimate it. The estimate is the more accurate the smaller the overlapping of successive absorption lines.

From the cuprous halides we obtain by this method the following upper limits to B, CuCl -1.4 ev; CuBr-1.3 ev; CuI-1.1 ev. Applied to Cu^{++} this method gives $B \leq 2.4$ ev showing that at the point of maximum $|y'/y|$ several different component lines are contributing appreciably to the absorption.

In analyzing the present experimental data, absorption lines with a half width at half maximum of 1.22 ev were used. The choice was a convenient one in terms of the arbitrary abscissa on which the data were originally plotted and in terms of which the absorption lines were calculated. In view of the several experimental values around 1.0 ev, it is very doubtful that the true half width of the line can be greater than 1.22 ev. It is important not to use too narrow a line in the analysis since the mistake will not betray itself in a failure to reproduce the absorption edge, and the number of transitions making up the edge may be greatly overestimated. Any absorption edge can be analyzed into very narrow absorption lines by using a sufficient number of them. The converse, of course, is not true. No combination of broad lines can be added together to give a narrow line although one might successfully analyze an edge using too broad a component line if the edge were composed of a large number of overlapping lines. In this case $|y'/y|$ for the edge would everywhere be less than the maximum for a single absorption line.

The results of the analysis are collected in Fig. 2 and Table II. No attempt was made to analyze the edges in the region more than 12 or 15 ev beyond the initial absorption. However, the contributions made by higher energy transitions to the initial absorption were taken account of in an arctangent curve[8] with its inflection point located as indicated in Table II under "continuum." The line strength is proportional to the height of the line since the half-width is constant. In terms of the same arbitrary unit of line strength used in Table II the maximum difference of ordinates (base line to absorption maximum A) of each edge is 31. The calculated points for just the CuCl curve are shown in Fig. 2. The other two analyses show a similar agreement with the observed curve.

Eleven lines were used for each edge and the question naturally arises whether or not as good agreement might be reached with fewer lines. Some time was spent attempting to match the CuBr edge with nine lines, but without success. When nine lines are used, the positions of maxima and minima can be reproduced, but because of the necessarily greater separation of the lines, the magnitude of the structure is exaggerated, i.e. the change in $\log I/I_0$ from maximum to minimum is too great.

The region of greatest interest is that near absorption maximum A. Careful checks on both CuCl and CuBr have shown that the observed structure cannot be reproduced with fewer than five lines (the first five lines in each edge). This is probably too low an estimate since the actual line width is almost certainly less than 1.22 ev. There is evidence to this effect in Fig. 2. The second and third calculated points (between -5 and 0 ev) fall below the experimental curve. A similar result obtained with CuBr and even more noticeably with CuI. The absorption at the beginning of the curve is not determined predominantly by any one line, but is rather made up of roughly equal contributions from the first four or five lines and the continuum. Thus no permissible reshuffling of the lines could change these two points. They could be brought onto the experimental curve only by a narrowing of all the lines and, of course, an increase in their number.

TABLE II. Component lines of the cuprous halide edges.

CuCl		CuBr		CuI	
Line position	Line strength	Line position	Line strength	Line position	Line strength
3.12 ev	5	2.83 ev	5.0	2.95	5.0
3.94	10	3.65	10.0	3.76	10.0
5.37	10.5	5.07	10.0	4.99	10.0
6.59	10.3	6.13	10.0	5.80	10.0
7.61	13.3	6.91	10.0	6.82	10.0
9.24	10.3	8.28	10.3	8.56	10.0
10.77	10.3	9.97	10.0	10.09	10.0
12.36	10.3	11.36	10.0	11.62	10.0
14.14	10.0	13.03	10.0	13.15	11.0
15.56	10.0	14.37	10.0	14.57	10.0
17.13	10.0	15.89	10.0	16.00	10.0
continuum 18.01	25.00	continuum 16.90	25.00	continuum 18.25	25.00

Thus the $1s \rightarrow 4p$ absorption which should be a single relatively isolated line (the $4p-5p$ separation in Zn^+ is 6.5 ev) if the ion were in vacuum is split in the crystal into at least five components with a total separation of about 4 ev. The splitting of 4 ev could easily be produced by the fields of the surrounding ions, but the number of components is not so easily understood. The surrounding ions have closed shells and will not remove the spin degeneracy. Therefore the level should be split into at most three components (ignoring the very small doublet separations), no matter how low the symmetry of the crystalline field. The additional lines observed must be an indication of sharing of the $4p$ electron with the neighboring Cu^+ ions.

Such a sharing is entirely plausible on the basis of Krutter's[4] work on the copper bands. He published a curve showing the energy of the lower limit of the $4p$ band as a function of interatomic distance. His curve was not meant to be taken quantitatively, but it indicates strongly that at the positive ion separations of about 4.0A existing in the halides, the $4p$ band should be at least 2 or 3 ev wide. The smaller size of Zn^{++} compared to Cu^+ will reduce the interaction somewhat, but there should still be an appreciable sharing of the $4p$ electron.

It will be noticed in all three edges that the ratio of the total intensity of the two lines making up the first inflection point to the three lines in the main $4p$ absorption is about 1 to 2. This suggests that the three $4p$ wave functions may have been split into a non-degenerate and a doubly degenerate level by the crystalline field and then each level further split up into a number of lines by mixing with the $4p$ functions of neighboring positive ions.

It is probably not worth while to discuss in greater detail the structure beyond the absorption maximum A. Certainly a great many more lines are present than indicated by the present analysis and probably no unique breakdown into component absorption lines is possible. This does not mean that the more distant absorption maxima may not have a simple interpretation. In all the ions and ionic compounds investigated thus far there has been an absorption maximum at the center of gravity of the $1s \rightarrow 5p$, $6p$, etc., transitions, a result which could hardly be accidental. However, these maxima are generally not very pronounced and for this reason the analysis into component absorption lines is not unique and therefore not of any great interest. One might just as well take such maxima as they are measured and attempt to correlate them with possible transitions.

The work is being extended to other crystals. If, as appears likely, the symmetry of the crystalline field, by determining the splitting of the excited levels, has an important effect on the shape of the absorption edge, then x-ray absorption measurements should find interesting applications in structural chemistry.

In conclusion, we wish to thank the Machlett Laboratories for kindly supplying the beryllium sheet used on the x-ray tube window and to express our particular appreciation of the many suggestions offered by Mr. J. P. Foerst, department mechanician, during the design of the spectrometer and of his excellent workmanship in its construction.

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A Simple Counting System for Alpha-Ray Spectra and the Energy Distribution of Po Alpha-Particles

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An alpha-ray counting system, consisting of parallel wire electrical counters and amplifying circuits, etc., is described. The conditions of reliable operation have been carefully examined and well defined. The mechanism of the counters as to why they answer only to alpha-particles but not to even strong beta- or gamma-rays is generally discussed. The distribution form of the Po-alpha particles determined by these counters in conjunction with an alpha-ray magnetic spectrograph agrees well with that obtained from a photographic line. The resolving power for the alpha-ray lines is very high, owing to the small active region of the counters.

1. INTRODUCTION

To count alpha-particles a parallel plate ionization chamber, a ball counter, or a tube counter is generally used. However, in the first case, the chamber is usually operating with such a small total charge that the change of potential is only of the order of a few micro-volts. Such a small change of potential is ordinarily made recordable only by means of a well-built linear amplifier of four or five stages. In the second and third cases the proportionality of counting depends on an appropriate working potential applied to the counters and the characteristics of the counters.[1] They also need an amplifier of several stages to magnify the initial electrical pulses in order to actuate a mechanical device. All of them are very liable to either mechanical or electrical disturbances.

When the counting method is employed in the case of an alpha-ray magnetic spectrograph, a great saving in time as well as other advantages can evidently be secured, if several counters are operating at the same time. These counters must be closely spaced, and each of them must be sensitive along a line of considerable length and coupled to an amplifier, preferably one which is easily built and inexpensive. These conditions are not easily fulfilled by counters of the above types. However, in the following, we shall describe a system of counters which is very simple in construction and economical in cost and has been shown to be satisfactory for determination of alpha-ray spectra. A spark counter of similar principle has been very generally described by Greinacher.[2]

2. THE COUNTER

If a thin wire is stretched in front of, and insulated from a smooth brass plate, it is found to

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[1] S. A. Korff, Rev. Mod. Phys. **14**, 1 (1942).

[2] H. Greinacher, Zeits. f. tech. Physik **16**, 165 (1935).