

X-Ray Absorption Edges of Transition Metal Salts

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A series of K -edges of transition elements in ionic compounds are presented. It is found that absorption in the $3d$ region is most prominent in cases where the bonding is least ionic and the symmetry is lowest. As the $3d$ levels become progressively filled, this low-lying absorption disappears.

THE fine structure of the K absorption edges in the 1 and 2 angstrom region has been studied by several investigators.¹ The reason for this interest lies in the fact that (1) the energy region represented by these edges is readily accessible to investigation and (2) the nature of the electronic configuration of the elements involved, which includes the first transition series, makes them of particular interest. A definitive study of the K -edges of the pure elements from Fe thru Ge was made by Beeman and Friedman.² The edges for the compounds of this general range of elements, however, have found their way into the literature on a piecemeal basis. The edges have been presented by many experimenters using varying techniques and different instruments; this has hindered interpretation and analysis. In this paper we present a coherent series of measurements on the simple salts of the elements, Mn thru Zn, somewhat in a survey fashion in which we can observe trends and irregularities.

In particular, we wish to emphasize the long-wavelength, low-absorption structures of the K -edge curves. Hanson and Beeman³ pointed out that even in such ionic compounds as MnCO_3 and $\text{Mn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$ the simple $1s-np$ transitions do not account for all features. There is a faint low-energy absorption into the $3d$ region which probably becomes permitted as a result of hybridization. This effect was verified by Coster and Kiestra,⁴ and they showed that this absorption occurred even in salts having highly electro-negative anions such as $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ or $\text{MnSO}_4 \cdot \text{H}_2\text{O}$. In this paper we present the results of our examination of this effect for the salts of the elements manganese through zinc.

MEASUREMENT AND DATA

This series of measurements was made with a two crystal spectrometer using Geiger counter recording. A conventional stabilized high-voltage power supply

was used. The x-ray tube was a continuously pumped, all metal, demountable unit with a tungsten target.

Although it is somewhat misleading, we have followed the customary procedure of normalizing the data so that the absorption maximum for the elements in each of its chemical states is represented by the same height. The absorption in argon⁵ indicates the jump ratio for the free atom at the $1s-4p$ line is about twice as high as the absorption from the $1s$ level to the continuum. For the metallic ions, which reveal a structure much like argon, unpublished studies indicate that the absolute absorption coefficient of the $1s-4p$ transition is much larger than the equivalent transition in the metal.

In the curves 2, 3, 4, and 5, little care was taken with getting precise data in the region of high absorption. In the low-absorption portion of the edge, the measurements were repeated as many as ten times. In this instance, the single-crystal photographic method would enjoy an advantage. The mechanical smoothing involved in making densitometric studies of the film avoids the difficulty in the point-by-point Geiger counter measurement that neighboring points are independent. The numerous runs we took should insure that the purely statistical error would be less than the width of the line. The mathematics notwithstanding, the data are not nearly as good as this, but we are confident that the curves give a quite accurate indication of the amount of low-energy absorption.

SIGNIFICANCE OF THE CURVES

As many experimenters have pointed out, the edge structure in the region close to the edge is a function of the atom and not of the crystal lattice as a whole. With this as a premise, the edge structure has been interpreted in many papers on the basis of transitions from the K -level into electronic states of the K excited atom. If one could deal in general with isolated ions or atoms of atomic number Z , transitions of the K -electron to weakly bound states would be known in the same sense as are excited optical states of complex atoms. However, since one does not have information about such states, one makes the reasonable assumption that the energy configuration for the K excited state would

⁵ L. G. Parratt, Phys. Rev. **56**, 295 (1939).

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¹ V. H. Sanner, thesis, Uppsala, Sweden, 1941 (unpublished); S. Yoshida, Sci. Papers Inst. Phys. Chem. Research (Tokyo) **38**, 277 (1939).

² W. W. Beeman and H. Friedman, Phys. Rev. **56**, 392 (1939).

³ H. P. Hanson and W. W. Beeman, Phys. Rev. **76**, 118 (1949).

⁴ S. Kiestra, "Applications of X-ray Spectroscopy to Solid State Problems," (WARF and Office of Naval Research, 1950) (unpublished), p. 26.

duplicate the optical states of the atom or ion of the element $Z+1$. On the basis of this concept, Parratt⁵ has given a very convincing explanation of the edge structure for the argon atom.

The atoms in solids, however, are not isolated, and the bound states associated with these atoms must be influenced by the environment. Thus the edge structure should be dependent on the character of the binding, which involves the number and nature of the nearest neighbors as well as the interatomic distances. Since the transitions from the $1s$ level to the empty levels leave the absorbing atoms in a nonequilibrium condition, it is difficult to say to what extent the edge structure is indicative of the original bonding in the solid and to what extent it is uniquely characteristic of the excited atom. The success of the exciton concept in explaining the electro-optical behavior of nonconducting solids has led some physicists into attempting to explain the x-ray edge on the same basis. While this approach may be valid in the x-ray situation, it would seem to be an unnecessary complication at best. It does not seem probable that the exciton point of view can invalidate the idea that the structure reasonably close to the edge is primarily concerned with essentially atomic states. Figure 1 shows a curve for the Ni^{++} edge in solution which is taken from a paper by Beeman and Bearden⁶ and our measured curves for $NiSO_4 \cdot 7H_2O$ and NiF_2 . The great similarity is apparent.

Because of the hydrated nature of $NiSO_4 \cdot 7H_2O$ one would probably not expect any significant difference between its edge and that of aqueous Ni^{++} . However, the curve shown for NiF_2 is an almost exact prototype for the aqueous Ni^{++} . Thus even in ionic salts which are not hydrated the same basic pattern occurs. The essential point is this: the exciton concept is based on the idea of the production of solid state levels which have a relation to the valence and conduction bands in a solid. In solution, one does not have the repeating steric organization involved in band formation, yet the edge structure is the same as in solid ionic salts. In this study we shall, therefore, maintain the viewpoint that the structure close to the edge is primarily determined by transitions into bound states of the K excited ions. These levels and the transition probabilities involved are, of course modified by the number, the nature, and the symmetry of the nearest neighbors.

In recent years, crystal field theory has come into prominence as a means of accounting for the optical absorption of ions surrounded by various ligands. Bethe⁷ has shown the effect of fields of different symmetry on the orbits of an atom. Hartmann and Ilse⁸ accounted quantitatively for the spectra of the Ti^{+++}

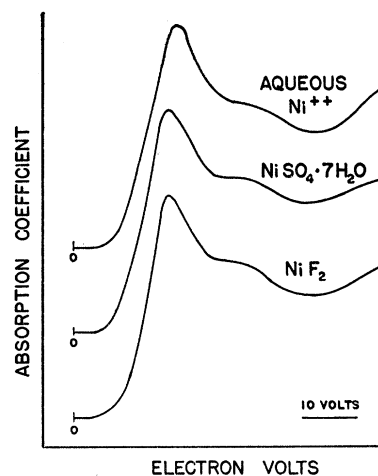


Fig. 1. K -edge structure for Ni^{++} in aqueous solution and in the solid ionic salts.

ion by application of this theory. Orgel⁹ and Ballhausen¹⁰ have generalized this approach to include the effect of crystal fields of various symmetries.

In x-ray absorption spectroscopy, Beeman¹¹ has laid considerable stress on the symmetry of the field in producing a broadening and splitting of states. If the symmetry is high enough and if the approximation that one has an ion in the field of its neighbors is satisfactory, then one does not expect any more distortion of the ionic energy levels than a general broadening due to ligand motion. If a lower symmetry obtains, the degeneracy may be removed and the levels may undergo splitting of the order of volts.

The edge structure cannot always be accounted for by ordinary splitting, however, since in some cases it is apparent that other states than p states are involved. One does not expect violation of the x-ray selection rules from the crystal fields regardless of the symmetry. Rather one may regard the symmetry as being indicative of the state mixing and homopolar character of the bond. In any event, comment will be made about the crystal symmetry in those cases where it is known and where it seems appropriate.

The absorption edges shown in Figs. 2-5 are designed to show the amount of low-energy absorption as a function of Z . Consequently, these curves are displayed in a somewhat different fashion from that customarily employed in absorption edge studies. The curves are organized so that a group is made of a given combined form of each metal considered. This method has the advantage that inspection of fine structure features for a series of compounds of the same type is facilitated. The principle disadvantage is that a comparison of different compounds of a given element is difficult. To offset this in part, vertical lines are drawn along the

⁶ W. W. Beeman and J. A. Bearden, *Phys. Rev.* **61**, 455 (1942).

⁷ H. Bethe, *Ann. Physik* **3**, 133 (1929).

⁸ F. E. Ilse and H. Z. Hartmann, *Z. physik. Chem.* **197**, 239 (1951).

⁹ L. E. Orgel, *J. Chem. Phys.* **23**, 1004 (1955).

¹⁰ Bjerrum, Ballhausen, and Jorgenson, *Acta Chem. Scand.* **8**, 1275 (1954).

¹¹ Beeman, Forss, and Humphrey, *Phys. Rev.* **67**, 217 (1945).

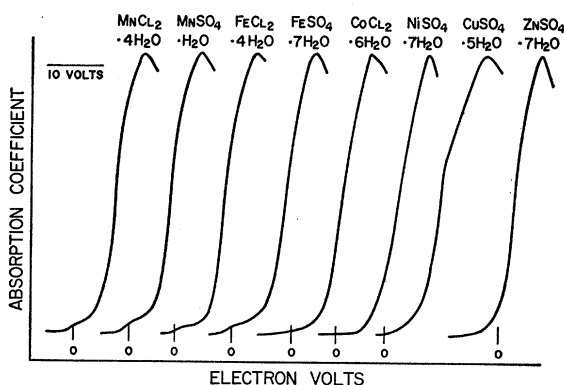


FIG. 2. *K*-edge structures in ionic salts of transition metals.

abscissa to indicate the top of the Fermi band in the corresponding metal.

To establish the position of the Fermi level, measurements were taken on all of the metals of this series. The edge structure for the metals were essentially the same as those first reported by Beeman and Friedman.² The viewpoint developed by Beeman and Friedman involves band theory which is appropriate to the interpretation of the metal edge, but which does not seem to contribute a great deal to the case of compounds.

(a) Ionic Salts

In the case of the edge structures of the metallic ions in solution, a fairly substantial case can be built up for regarding the main features of the curves as being due to transitions into the various p states of the *K* excited ion. That is, the ion absorbs much as it would in a vacuum with some broadening due to the solvation layer. The analysis is much the same as Parratt's for the case of argon gas.⁵

Since the edge structure for the ion in solution is so similar to that of solid ionic salts, we ascribe the structure to the same phenomena. The first strong peak (see Fig. 2) is a $1s \rightarrow 4p$ transition, the second hump is an unresolved conglomeration of $1s \rightarrow np$ with $n \geq 5$. The similarity between a metallic ion in a compound and an isolated atom of argon shows that the ion has a high degree of symmetry in the positions of its neighboring atoms and is relatively distant from these neighbors.

In previous work,³ it was pointed out that in the case where the difference in electronegativity between the anion and cation was not large, a low-energy absorption was observed. While our present results indicate that strongly ionic salts also show the effect,⁴ we find that it is definitely smaller in this latter instance. Curves for MnCO_3 (not shown) have a low absorption that is considerably more prominent than in the sulfates and chlorides. The MnCO_3 probably offers a situation of more complicated symmetry than the other two. This compound has the NaNO_3 structure which is like rock

salt in a sense, but which is distorted by the spatial requirement of the carbonate radical.

The low-energy absorption is also present in $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$. However, the sulfates and chlorides of the elements of higher Z than iron do not show any measurable low-energy absorption in our studies. A photographic study with thick samples might indicate that this low-lying structure exists for $Z > 26$ in these compounds, but it would certainly show that the structure gets smaller. The electronegativities of the transition elements have about the same value for all members of the series. From this standpoint, one would not expect any great difference in the type of bonding for ionic compounds of the series although the number of unoccupied $3d$ levels can influence the nature of the binding. Presumably, the low-energy absorption in the Mn^{++} and Fe^{++} ionic salts indicate some state mixing. The lack of this structure at higher Z is probably due to the decreasing number of $3d$ vacancies rather than a change in bond type. The transition probability is, of course, small.

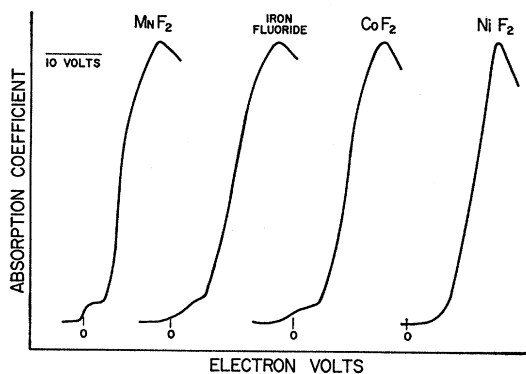


FIG. 3. *K*-edge structures for fluorides of transition metals.

The fluorides (Fig. 3) were obtained from Dr. R. A. Erickson, who was at the Oak Ridge National Laboratories at that time. The iron fluoride is somewhat suspect in that the position of the maximum absorption indicates that the iron is in the ferric rather than the ferrous state in which it was originally formed. It was anticipated that the fluorides would have a fairly strong low energy absorption and this was born out by experiment. The effects of covalent bonding in fluorine compounds are well known. This is interpreted as being due to the small size of the fluorine and its great electronegativity. In most of the ionic salts the symmetry is very nearly octahedral. All of the fluorides shown have the SnO_2 structure in which the metals are found at the center of a slightly distorted octahedral structure.

(b) Oxides

Many of the oxides have been presented by Sanner.¹ The low-energy absorption is certainly present in all

of the oxides we studied (see Fig. 4) with the possible exception of Cu_2O and ZnO .¹² The curves of these two as shown have very slight variations from the smooth curves expected. We could not make an unambiguous decision even with repeated measurements and the curves may well exaggerate whatever effect there is. The virtual absence of low lying absorption in these compounds is to be expected on the basis of the fact that they have no $3d$ vacancies. Some state mixing could account for whatever low-energy absorption exists. This is to be expected since all the other metallic ions have $3d$ vacancies. It should be noted that ZnO also shows fairly prominently this characteristic absorption. Although zinc is not a transition element, it apparently forms a transition-like atom when exhibiting a valence of four.

The electronegativity of oxygen is somewhat greater than that of chlorine. On this basis, one might expect oxygen to form quite ionic compounds. However, the large electronegativity applies mainly to the attraction of the first electron. The divalent character of oxygen

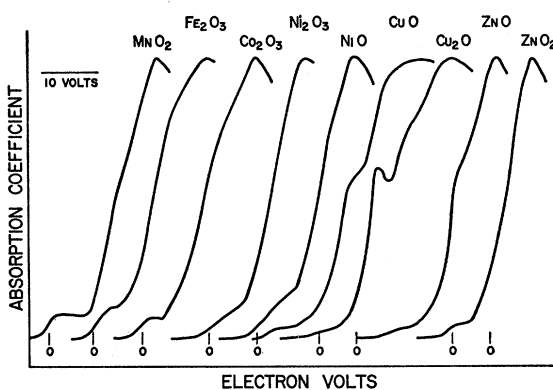


FIG. 4. K -edge structures for oxides of transition metals.

causes the oxides to reveal a certain degree of state mixing so that low-energy absorption is to be expected.

The symmetries of the oxides range from the simple cubic structure of NiO to the more complicated arrangements in Cu_2O and MnO_2 . The low-lying absorption seems to be independent of the symmetry and occurs when the $3d$ levels have a vacancy. Within the effect of sample uniformity, it shows a decreasing prominence with increasing Z . The structure beyond the first peak is more symmetry sensitive. NiO shows an edge structure not greatly different from that of ionic nickel salts; and CuO , which has a plane configuration of O^{2-} ions about the Cu , has a corresponding edge which bears

¹² Recent measurements on various oxides of nickel show some unexpected results in terms of valence, etc. This will be discussed elsewhere.

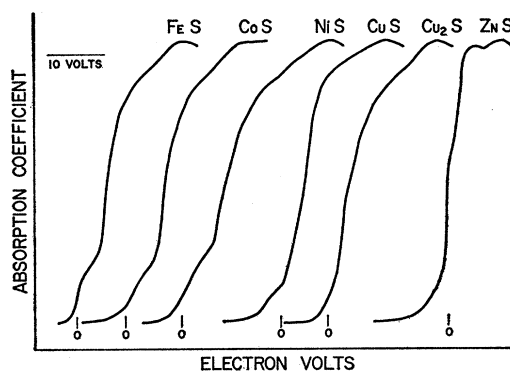


FIG. 5. K -edge structures for sulfides of transition metals.

no resemblance to ionic cupric salts. These NiO and CuO edges are not shown.

(c) Sulfides

Figure 5 shows that the general pattern followed by the sulfides of the transition element out to about 30–40 volts is a small low-energy absorption at the $3d$ range, a very significant absorption in the $4s$ range, and, after a small but fairly distinct bump in the $4p$ range, an undetailed structure that is nearly flat. The absorption in the $4s$ range is quite large, being more prominent than even that observed in the metals.

These curves are characterized by broad rather flat absorption peaks. The lack of definition in these compounds is not unexpected when one considers the structure of these sulfides. Many of these structures have not been analyzed in detail, but one can say that the metal ion is usually dispersed through a fairly close packed structure of sulfide ions. There is good evidence in some cases¹³ that the metal ions occupy two different kinds of sites. Neither of these are sites of highest symmetry, one having tetrahedral symmetry and the other being located at the center of the sulfide triangle.

Only two compounds show any deviation from the general pattern. These are the cuprous and zinc sulfides. We found no low-lying absorption in these cases, but they were not examined quite as carefully as the corresponding oxides. The decrease of the absorption with atomic number in going from $Z=25$ to $Z=30$ is not so marked as in other compound classes, but the CuS does show considerably less $3d$ absorption than the others.

ACKNOWLEDGMENTS

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¹³ R. W. G. Wyckoff, *Crystal Structures* (Interscience Publishers, Inc., New York, 1948).