

The Mn K Absorption Edge in Manganese Metal and Manganese Compounds*

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The Mn K edge has been measured in twelve different states of chemical combination with a high resolution double crystal spectrometer. The "white line" at low energies in KMnO_4 is shown to be characteristic of the compound and not of impurities. Less intense low energy absorption is observed in several other compounds. It is believed due to the mixing of states of different angular momentum accompanying homopolar bonding, which thus makes available p -type function at lower energies than would be the case in a purely ionic compound.

INTRODUCTION

THE K edges of the elements of the first transition series lie in a relatively accessible region of the spectrum and, in addition, the elements enter into a wide variety of chemical combinations from simple ionic salts to complexes where the binding is largely homopolar. For these reasons their K absorption edges have been measured by several investigators¹⁻⁴ interested in the problem of chemical influences on absorption edge structure. However, no accurate, comprehensive measurements have been available for the manganese edge. It is the purpose of this paper to present such measurements and to attempt an explanation of the more prominent features of the curves.

EXPERIMENTAL

A double crystal spectrometer with an Allison type mounting was employed. The crystals were of ground and etched calcite. Their 1, -1 width at half-maximum was 15 seconds at the Mn K edge. This is equivalent to 0.73 ev.

The data were taken with thin glass end window Geiger counters operated in conjunction with a scale of 128 recording unit. Two counters were used in the course of obtaining the data. They were filled with 40-50 cm of argon, 2 cm of alcohol, and a trace of methylene bromide. Both counters had plateaus of about 200 volts with no more than a 1 percent slope.

The absorbing foil of manganese metal was obtained by vacuum evaporation. The samples of the compounds were prepared in two ways. By the first method the finely powdered sample was mixed with melted paraffin which was then allowed to solidify on a sheet of cellophane. The second technique was merely to spread a thin uniform layer of the powdered sample between two pieces of adhesive cellulose tape. No significant differences were found between curves taken with the two different types of specimens.

Under the action of the x-ray beam the salts become somewhat discolored. If the discoloration is due to decomposition, calculations show that in the time of a complete run, less than 0.001 percent of the molecules are decomposed, and this should have no detectable effect. Checks were made which verified that the edge structure was not affected by long exposures to the beam.

The samples of ferromanganese, which is a crude alloy of manganese and iron, were made in the same manner as the salt samples.

In preparing a sample of Mn^{++} ion in solution, the absorption in the cell windows and in the water must be kept at a minimum. The cells were made by cutting a hole through a sheet of lead, 0.25 mm thick, and using two pieces of beryllium, 0.4 mm thick, as windows. A 2*N* solution was admitted through a slit in the lead spacer before the cell was sealed. The solution run was made with only one anion, that being NO_3^- . However, it was found by Beeman and Bearden³ that results independent of the anion were obtained on solution samples of the ionic compounds of Ni^{++} , Cu^{++} , and Zn^{++} .

The original data for the present measurements were taken in the form of seconds per given number of counts. Since one is interested in the variation of the absorption coefficient, μ , one plots $\log I/I_0$ against the energy of the x-ray photon being absorbed, where I_0 and I are the intensities of the incident and transmitted beams. With a constant I_0 , it is sufficient to plot the log of the time required for the given number of counts.

Ordinarily, one must correct for the following things: (1) the background, (2) the second-order component of the beam, and (3) the deadtime of the counter. The effects of the latter two were negligible in the data taken. Careful measurements showed that the second order was certainly less than 1 percent and probably less than $\frac{1}{2}$ percent of the total x-ray flux measured, and consequently, no attempt was made to correct for it. As for the deadtime of the counter, a linear response was obtained up to the maximum counting speed employed, which was 128 pulses/second. The background corrections were never more than 2 percent of the maximum height of the curve, and were made by a nomographic method.

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¹ V. Hugo Sanner, Thesis, Uppsala University, Sweden (1941).

² S. Yoshida, Sci. Papers Inst. Phys. Chem. Res., Tokyo 38, 272 (1941).

³ W. W. Beeman and J. A. Bearden, Phys. Rev. 61, 455 (1942).

⁴ D. Coster and S. Kiestra, Physica 14, 175 (1948).

DISCUSSION OF CURVES

Figures 1 and 2 show the Mn K edge for manganese in twelve different states of chemical combination. The relative positions of the curves should be accurate to ± 0.2 ev. The individual points are taken with a statistical error of 1 percent or less, except for K_2MnO_4 and $KMnO_4$. The curves for these two compounds are the composites of several runs, although the points plotted are the values obtained in a single series of measurements.

1. Manganese and Ferromanganese

The quantum-mechanical radiation theory of Weisskopf and Wigner has been adapted to the specific problem of x-ray absorption by Richtmeyer, Barnes, and Ramberg.⁵ They have shown that the absorption coefficient as a function of frequency at an absorption edge of a metal is given by

$$\mu(\nu) = C \left\{ \frac{1}{2} - \frac{1}{\pi} \tan^{-1} \left(\frac{\nu_0 - \nu}{\Gamma/2} \right) \right\} \quad (a)$$

where Γ is the width of the K excited state.

This equation is strictly true only for a uniform distribution of absorption levels, but the initial part of the the absorption curve is relatively unchanged by a more complex distribution of levels on the high frequency side of ν_0 .

By adjusting the parameters Γ and C , one can match curves of type (a) with the experimental curves up to the inflection point, which is the position of the first empty level in the Fermi distribution. Although the method does not yield a very accurate value of Γ , one finds that the width of the K level is somewhat more than 1 ev when correction is made for the 1, -1 width of the crystals. This is in good agreement with the values obtained by Beeman and Friedman⁶ for Fe, Co, and Ni.

The edge obtained for manganese by Coster and Kiestra⁴ agrees very well with that presented here. As was also found by Coster and Kiestra, the percentage of the maximum absorption jump accounted for by absorption into the first empty levels is larger in manganese than in iron. Using the definition suggested by Beeman and Friedman,⁶ the percentage is found to be 34 percent, while in iron it is only 23 percent. This increase is a reversal of the trend observed in going from Zn to Fe where the initial absorption grows smaller with decreasing atomic number.

According to Wyckoff,⁷ iron and manganese are supposed to form a series of solid solutions. For the composition which the ferromanganese sample had, namely 81 percent manganese, the crystal structure should correspond to pure manganese. From the curves, the absorption into the first empty levels in ferromanganese

is about 28 percent, which is intermediate between that for pure iron and pure manganese. Calculations show that no reasonable assumptions about possible inhomogeneities in the powdered sample used can account for the differences between the manganese and the ferromanganese curves.

2. The Mn^{++} Ion in Solution

It was found previously by Beeman and Bearden⁸ that the ions Cu^{++} , Zn^{++} , and Ni^{++} in solution absorbed about the same as they would in vacuum. They were able to demonstrate that the first absorption peak is due to the $1s-4p$ transition and the second peak to unresolved $1s-np$ transitions ($n \geq 5$). The K edge of Mn^{++} in solution has many characteristics in common with those of Cu^{++} , Ni^{++} , and Zn^{++} , and it is reasonable to expect that the structure is due to the same transitions.

After an absorption in Mn^{++} , the excited $1s$ electron moves in a field similar to that of a doubly ionized iron atom. Using the data of Edlen and Swings⁸ for the term values of Fe^{++} , one finds that the energy difference one might expect between the $3d^54p$ configuration and unresolved $3d^5np$ configuration ($n \geq 5$) is about 10 ev, which corresponds to the energy difference between the first and second absorption peaks at about 13.5 ev and 23.5 ev in Fig. 2. Also, through the use of the energy

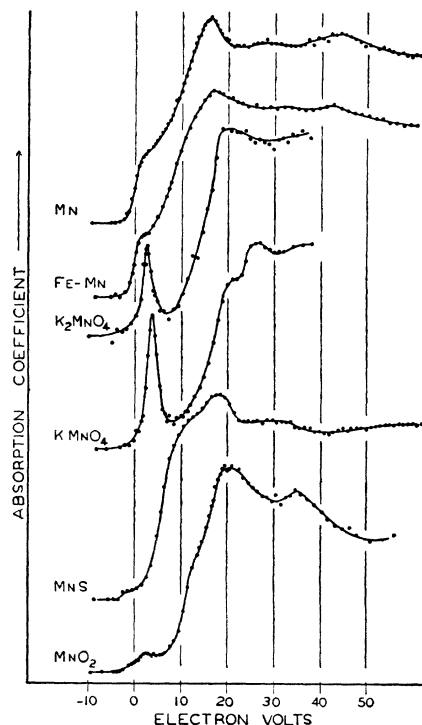


FIG. 1. The Mn K x-ray absorption edges of six manganese compounds. The curves are plotted to a common abscissa whose zero is the energy of the first empty level above the Fermi distribution in Mn metal.

⁵ Richtmeyer, Barnes, and Ramberg, *Phys. Rev.* **46**, 843 (1934).

⁶ W. W. Beeman and H. Friedman, *Phys. Rev.* **56**, 392 (1939).

⁷ R. Wyckoff, *The Structure of Crystals* (The Chemical Catalog Company, Inc., New York, 1924), first edition, p. 258.

⁸ B. Edlen and P. Swings, *Astrophys. J.* **95**, 532 (1942)

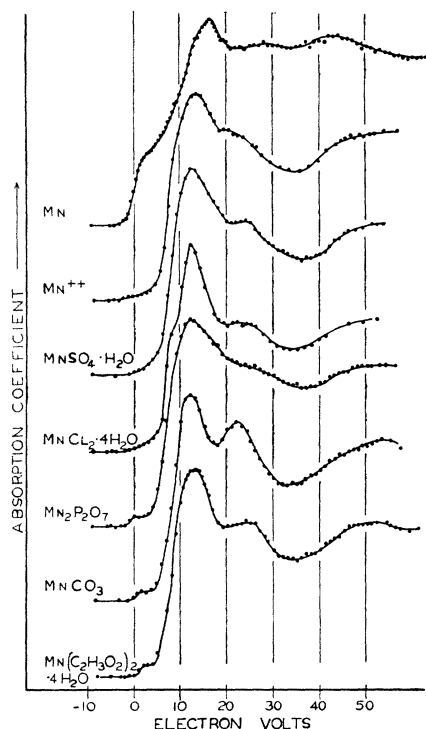


FIG. 2. The Mn K x-ray absorption edges of seven manganese compounds plotted as in Fig. 1.

cycle described in reference 3, one can calculate the energy difference between absorption into the lowest empty levels in the metal and the $1s-4p$ absorption in the ion. The experimentally determined energy difference of 13.5 eV lies within the 12.6 eV calculated upon the assumption that only the lowest P states are available and the 15.8 eV which assumes that all P states are equally available.

3. The Ionic Compounds of Manganese

The curves for the ionic compounds, shown in Fig. 2, are quite similar in their main features. Within at most 0.5 eV, these compounds all have their main absorption peak at 12.5 eV. All show a second absorption peak in the neighborhood of 24 eV. The resemblance of these curves to the curve obtained for the solution sample makes it quite probable that the structure is due to the same electronic transitions.

One notes, however, that in each instance the peaks for these ionic compounds occur at an energy value which is about 1 eV less than for the peak of the Mn^{++} ion in solution. A reasonable qualitative explanation for the shift is that there is a certain amount of sharing of the $4p$ electron or band formation in these crystals. The center of gravity of the band will be lower than the original levels, and this will give an effect in the same direction as the observed shifts.

Another feature deserving comment is the low energy absorption at 0-5 eV of some of the ionic compounds. This is the region where absorption into $3d$ levels would

be expected. It has been assumed that in such compounds the selection rules would forbid any transition on the long wave-length side of the $1s-4p$ transition. However, the anomalous absorption indicated in the curves was very well verified by using quite thick absorbing samples so that differences in intensity of 25 percent between top and bottom values of the $3d$ absorption were obtained. One might suspect that free manganese was responsible for this absorption, but this can be definitely ruled out. The manganese acetate sample is a pink crystalline solid. It is readily soluble and upon solution no evidence of free manganese can be seen, although the curves would require that there be nearly 20 percent free manganese in the sample. This point will be discussed again in connection with MnO_2 .

It is probably significant that this absorption into low lying levels occurs only when manganese is compounded with a radical which is rather weakly electronegative. $MnCl_2 \cdot 4H_2O$ and $MnSO_4 \cdot H_2O$ show no indication of the absorption on this scale. Even with thick samples the data gave no definite sign of structure. A qualitative explanation can be offered which might account for the observed behavior. The chemical binding of metallic salts is accomplished through a combination of ionic attraction and homopolar bonding. The wave function representing the state of the crystal is a linear combination of the wave function representing only the ionic bonds and the wave function representing the homopolar attraction. Covalent bonding involves the sharing of electrons between the anion and cation. When the transition elements participate in such homopolar binding, Pauling⁹ has shown that hybrid orbitals are formed which are made up of linear combinations of the s , p , and d orbitals. Because of this mixing of states it is not surprising, in compounds where the covalent part of the binding becomes important, that transitions to low lying hybrid states containing some p function are observed.

4. $KMnO_4$ and K_2MnO_4

As long ago as 1924, Coster¹⁰ observed the absorption edge of Mn in $KMnO_4$ and found a "white line" on the long wave-length side of the main edge. The white line is photographic terminology and denotes a narrow region of strong absorption. It was pointed out by Lindh¹¹ and Chamberlain¹² that the white line occurred very close to the position where the manganese metal edge began. Since Miss Chamberlain was able to show that x-rays will reduce $KMnO_4$, she suggested with Lindh, that the white line which Coster observed was due to the free manganese produced by the action of the x-rays on $KMnO_4$. Coster's data were actually quite good, but he apparently accepted this explanation. Sanner¹ measured the $KMnO_4$ edge, among others, and

⁹ L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York), second edition, p. 93.

¹⁰ D. Coster, *Zeits. f. Physik* 25, 83 (1924).

¹¹ A. Lindh, *Zeits. f. Physik* 31, 210 (1925).

¹² K. Chamberlain, *Phys. Rev.* 26, 525 (1925).

expressed doubt that the line was due to free manganese. It is clear from the present data, of course, that free manganese cannot be responsible since the Mn curve shows no line absorption at low energies. In addition, only a negligible reduction of KMnO_4 could occur during a single run in our experiments.

A single absorption line has the form⁵

$$\mu(\nu) = \frac{A}{(\nu - \nu_0)^2 + (\Gamma/2)^2},$$

where Γ is the width at half-maximum, and $(\nu - \nu_0)$ is the distance from the center of the line. The entire long wave-length side of the peak can be matched almost perfectly with a curve which sets $\Gamma = 2.2$ eV with no correction for the 1, -1 rocking curve width. When the correction is made, one finds that the width agrees reasonably well with that obtained from the manganese metal edge.

It is difficult to see why this strong, narrow level should occur where it does. Two possible explanations can be discussed.

First, since the bonding in the complex is homopolar in nature, one might suspect that, through the hybridization of orbitals, a low lying level is formed to which the 1s electron is permitted to go. The bonding⁹ in the MnO_4 tetrahedron has been suggested as a combination of sp^3 and sd^3 orbitals. This would leave a certain amount of empty $4p$ orbital which, if the Mn is neutral or near neutral in the complex, would give an absorption near the observed white line. On this explanation one can account for the less intense white line absorption in K_2MnO_4 than in KMnO_4 since the extra electron of K_2MnO_4 probably fills up some of the levels causing the line absorption.

A second, less convincing, explanation is that the white line is due to constructive interference between a directly emitted electron wave and the wave scattered from neighboring atoms. This point of view, first

proposed by Kronig,¹³ correctly predicts the positions of several sharp absorption lines which have been observed¹⁴ in the Ge K edge in GeCl_4 vapor, and the As edge in AsCl_3 . However, it seems quite incorrect to apply Kronig's theory to the lowest energy absorption in an edge since in such an excited state the electron probably remains bound to the absorbing molecule.

The Mn in KMnO_4 may be formally considered to have a valence of 7, and one observes that the main edge is found at considerably higher energies than the $4p$ peak in the ionic compounds. The main edge in K_2MnO_4 , where the formal valence is 6, is found at somewhat lower values than in KMnO_4 . These shifts probably have nothing to do with the formal valence as was formerly considered to be the case, and the explanation lies in the influence that the homopolar bonding has on the energy levels.

5. MnO_2 and MnS

Absorption into low lying levels is also observed in MnO_2 and MnS . The absorption due to free manganese suggests itself as an explanation of the effect, but it can be discounted, at least in MnO_2 , for the reason discussed under KMnO_4 , namely, there exists a region of negative slope in the MnO_2 curve near 2 or 3 eV which is not present in the Mn curve. The explanation must lie in the partial homopolar nature of the bond.

The MnS edge is quite similar in general appearance to the edges observed by Yoshida² for the sulfides of iron. Since the shape of the edge is so unlike those obtained for the ordinary ionic compounds of manganese, it seems quite certain that the binding in MnS is predominantly homopolar in nature. This is in keeping with the relatively low position of sulfur on the electro-negativity scale.

The results may be summarized by the general statement that the amount of absorption into levels in the $3d$ range increases with the amount of electron sharing.

¹³ R. de L. Kronig, *Zeits. f. Physik* **75**, 468 (1932).

¹⁴ S. T. Stephenson, *Phys. Rev.* **71**, 84 (1947).

Pressure Broadening in the Inversion Spectrum of Ammonia

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A formula is developed to explain the low pressure line widths observed in the inversion spectrum of NH_3 by Bleaney and Penrose. The assumptions made are those characteristic of the *statistical* theory of pressure broadening. The result, which is entirely devoid of adjustable parameters, agrees with the data about as well as do the impact theories with their unreasonable collision radius.

THE development of high precision techniques in microwave spectroscopy offers new and attractive

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opportunities for solving the old problem of the broadening of spectral lines. This problem had never received a complete and wholly satisfactory treatment, and the excitement over new events in the realm of the nucleus