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# ELECTRON SPIN RESONANCE STUDIES ON $\gamma$-IRRADIATED $KMnO_4$

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**Abstract**—Electron spin resonance (ESR) studies have been carried out on the radicals produced by the $\gamma$-irradiation of single crystals of $KMnO_4$.

Analysis of the data yields at least two paramagnetic species. The first radical is produced by room temperature irradiation and gives a single line for each of two inequivalent magnetic sites. There is no resolvable hyperfine structure and the $g$ tensor for the species is given by, $g_b = g_{y'} = 2{\cdot}0176$, $g_{x'} = 2{\cdot}0020$, $g_{z'} = 2{\cdot}0112$. The spectrum is tentatively assigned to the $O_3^-$ radical although $MnO_2$ and $MnO_4$ are also possibilities.

The second radical is produced by irradiation at 77°K and the spectrum disappears irreversibly at slightly higher temperatures. Analysis of the very complicated spectra yields, $g_b = 1{\cdot}9617$, $g_x = 1{\cdot}9452$, $g_y = 1{\cdot}9940$, $A_b = 386$ MHz, $A_2 = 87$ MHz, $A_3 = 20$ MHz. This spectrum is assigned to the $MnO_4^{-2}$ radical. The relationship of the radicals observed to the effect of high energy radiation on the decomposition of $KMnO_4$ in the light of current solid state theory is discussed.

## 1. INTRODUCTION

In recent years much effort has gone into the study of the detailed mechanisms of the decomposition and explosion of energetic compounds. This interest has been generated by a lack of basic understanding of the initiation of these reactions.

In addition, the effects of high energy radiation on the performance of these compounds are not completely understood[1–4]. It is known that radiation can radically alter their decomposition but the mechanisms proposed are not universally accepted. By the same token, if these compounds can be altered by radiation then the question remains as to whether an understanding of these effects will lead to a clarification of the decomposition processes. The subject of thermal decomposition has been studied by numerous authors, among them Prout[5] and Boldyrev[1]. One experimental result that is common to both subjects is the effect of impurities on both reactions. These impurities can be introduced either chemically or radiolytically. Prout[6] and Boldyrev[1] have proposed explanations of these effects. However the details of the chemical changes caused by radiation on these compounds have not been completely characterized.

We have chosen $KMnO_4$ as the initial compound for study. It was our hope that using the technique of electron spin resonance (ESR) we would be able to identify some of the radicals produced by high energy radiation such as X and $\gamma$ rays. This compound is one of the most extensively studied with regard to radiation effects on decomposition and is, at present, the one that offers the best chance of pinpointing the effect of radiation on the decomposition mechanism. Prout in his initial work in 1958[7] on irradiated $KMnO_4$ postulated the interstitial defect mechanism for explaining the shortening of induction times. Basically this involves the liberation of energy when the interstitial defect returns to a vacancy as the compound is heated. Boldyrev[8, 9], on the other hand, believes that it is the catalytic effect of the radiolysis products that is important in affecting the decomposition rates.

A further reason for choosing this compound is that the detailed crystallographic structure has recently been completed[10] and that large crystals necessary for the study were readily available. Both conditions are necessary for an adequate ESR analysis.

Another motivation for this study comes from the fact that the electronic structure of the permanganate and hypomanganate ions have been the subject of considerable controversy and study over the last few years [11, 12], and it was thought that radicals produced here might shed some light on the subject. The ESR technique is an excellent method for detecting the low concentration of radicals produced in the solid state by radiation which at the same time offers some hope of identification and structural study.

## 2. EXPERIMENTAL PROCEDURE

Single crystals of $KMnO_4$ were obtained directly from off-the-shelf bottles of Fisher Reagent Grade $KMnO_4$. Single crystals were also supplied by the Carus Chemical Co. of LaSalle, Illinois. An attempt was made to grow single crystals from aqueous solution but the ones obtained in this way were not large enough for the ESR work. In all, approximately forty crystals were used and the results were identical in every case.

The crystals were irradiated in a $^{60}Co$ $\gamma$-cell which delivers a dosage of about $6 \times 10^5$ r/hr.

Samples were irradiated at 300 and 77K for periods of from 1 to 80 hr. In the instance where crystals were held at 77K, eighty hours (50 Mrad) of irradiation were required in order to produce a sufficient number of radicals for detection by ESR.

Crystals were also subjected to 50 kV X-rays. The identified radicals were identical to those generated by the $\gamma$-rays.

As will be seen later, the hyperfine splitting observed from the paramagnetic defect was quite large and hence very sensitive to the orientation of the crystal in the laboratory magnetic field. As a result the main source of error in the measurements was in the determination of the orientation. This was particularly true for the crystals that were irradiated at 77K since all ESR work had to be carried out at that temperature. All measurements were carried out on a Varian V-4500 EPR system with a model V-4560 100 kHz lock-in amplifier and the V-4531 multipurpose cavity operating at 9100 MHz. Second derivative detection of the abosrption signal was employed. The magnetic field measurements were made with an Alpha Al 675 NMR spectrometer using a water sample. A Bell Telephone Laboratory marker ($g = 1{\cdot}99875$)[13] or a DPPH ($g = 2{\cdot}0035$) was used as a reference standard. The sample was held in the V-4546 liquid nitrogen accessory and a crystal holder was designed to fit into this Dewar. The design of this holder is described elsewhere[14].

## 3. RESULTS

The most recent work done on the crystallographic structure of $KMnO_4$ was carried out by Palenik[10]. The compound forms orthorhombic crystals with $a = 9{\cdot}105$, $b = 5{\cdot}720$, and $c = 7{\cdot}45$ A. The space group is Pnma and there are four molecules per unit cell. It was found by Singhal[15] that the angle between pairs of permanganate ions did not change from room temperature down to liquid oxygen temperature (− 183°C). Our experiments were run at − 196°C and also at − 186°C. No substantial change in the spectrum was noted hence it is safe to assume that the orthorhombic phase remains at liquid nitrogen temperature. Although there are four molecules per unit cell only two of them are magnetically inequivalent and can be observed by ESR. Two of the molecules are related to the other two by 180° rotation and cannot be distinguished by ESR.

The spectrum of $KMnO_4$ irradiated at 310K and recorded at 77K is given in Fig. 1. Henceforth this paramagnetic center will be known as '*A*'. The line widths of the two lines are functions of the angle with high field component of the doublet always being broader. The angular variation of the spectrum as the magnetic field scans the a.c. plane is given in Fig. 2. As the field scans the b.c. and b.a. planes the spectrum consists of a single line.

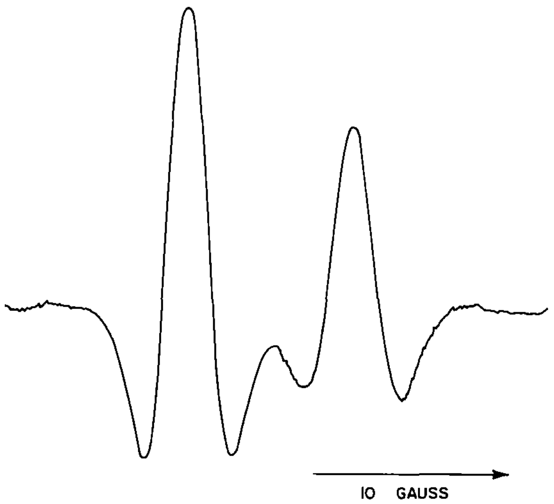

Fig. 1. ESR spectrum of $KMnO_4$, irradiated at 310K and recorded at 77K. This spectrum was taken with the magnetic field in the a.c. plane at an angle of 35° from *c* axis.

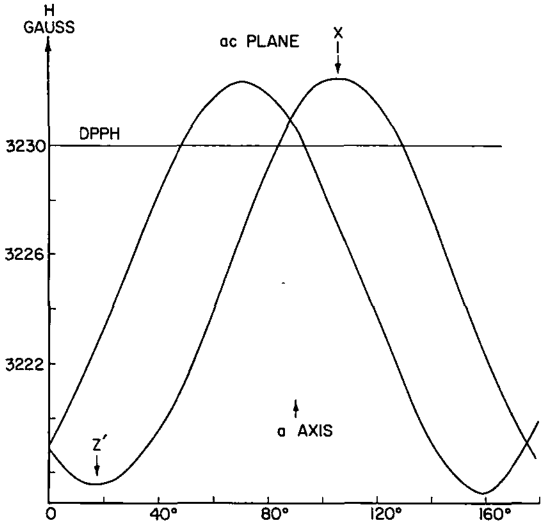

Fig. 2. Angular variation of the ESR spectrum of $KMnO_4$ irradiated at 310K and recorded at 77K. The spectrum was recorded at 77K. The spectrum was recorded with the magnetic field scanning the a.c. plane. Axes $x'$ and $z'$ are indicated. 0° coincides with the *c* axis. The DPPH marker is shown at 3230 G.

It may be noted that only one line shows up in the b.c. and b.a. planes but two lines appear in the a.c. plane. It was noted from saturation studies that the lines were inhomogeneously broadened indicating the existence of unresolved hyperfine splitting[16]. The principal $g$ values of this center are given in Table 1. Axes $x'$ and $z'$ make angles of about 18° with the *a* and *c* axes respectively and are shown in Fig. 2. $g_b$ is the $g$ value along the crystallographic *b* axis. This paramagnetic species was stable over a period of several months.

*Table* 1. *Principal g values of paramagnetic center formed in* $KMnO_4$ *by* $\gamma$*-irradiation at* $310\,K$

$g_{x'} = 2{\cdot}0020$
$g_{z'} = 2{\cdot}0112$
$g_b = g_{y'} = 2{\cdot}0176$

The ESR spectrum of $KMnO_4$ irradiated and recorded at 77K is given in Fig. 3. This paramagnetic species, which we call '*B*', gave a six line spectrum with each line further split into six lines. This would indicate a strong coupling to a nucleus of spin 5/2 and a weak coupling to another nucleus of spin 5/2. The spectrum for the large splitting shows a great deal of anisotropy while the secondary or "superhyperfine" splitting is largely

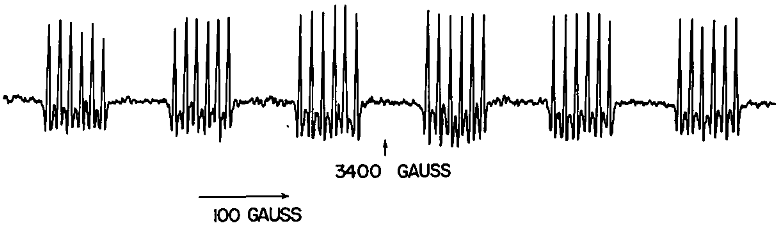

Fig. 3. ESR spectrum of $KMnO_4$ irradiated and recorded at 77K. Spectrum was observed with the magnetic field parallel to the *b* axis of the crystal.

isotropic. The angular dependence of the "center of mass" of the six main groups is given in Fig. 4 where the laboratory field lies along the intersection of the $g$ and $A$ tensors of the two magnetically inequivalent sites, and hence only the spectrum due to one radical is seen. When the magnetic field is not in the b.c. and b.a. planes the two inequivalent magnetic sites are observed.

The solid curves in Fig. 4 were generated from equation (10.1) in Ref. [17].

An iterative procedure was carried out on the BRLESC digital computer and plotted on a Cal Comp Plotter.

The spectrum disappeared irreversibly when the temperature was raised beyond 100K and no spectrum of any kind was left in its place. The spectrum could also be photolyzed with visible light, so care had to be taken so as not to expose the crystal to too much room light.

The spectrum was complicated by several factors. For one the splitting was very sensitive to orientation and accurate evaluation of the constants was difficult. Secondly, as the magnetic field approached the a.c. plane numerous 'forbidden' transitions were induced. As a result many lines appeared in the spectrum in addition to the fundamental 36 line spectrum, which also showed extensive intensity variation. Thus data taken with $H$ scanning the a.c. plane were hopelessly complex and could not be used in the analysis. These 'forbidden' transitions were caused either by direct nuclear Zeeman effect or by the quadrupole effect of the manganese nucleus [17], both of which introduce higher order terms in the transition probability and break down ordinary selection rules.

Since the $a$ and $c$ axes were not principal axes of either the hyperfine or $g$ tensors the off diagonal elements in these tensors must be evaluated. As was mentioned earlier the a.c. plane data could not be used consequently more data were taken with the magnetic field scanning the b.d. plane which was perpendicular to the a.c. plane and made an angle of 25° 10′ with the b.a. plane. $g$ and $A$ values

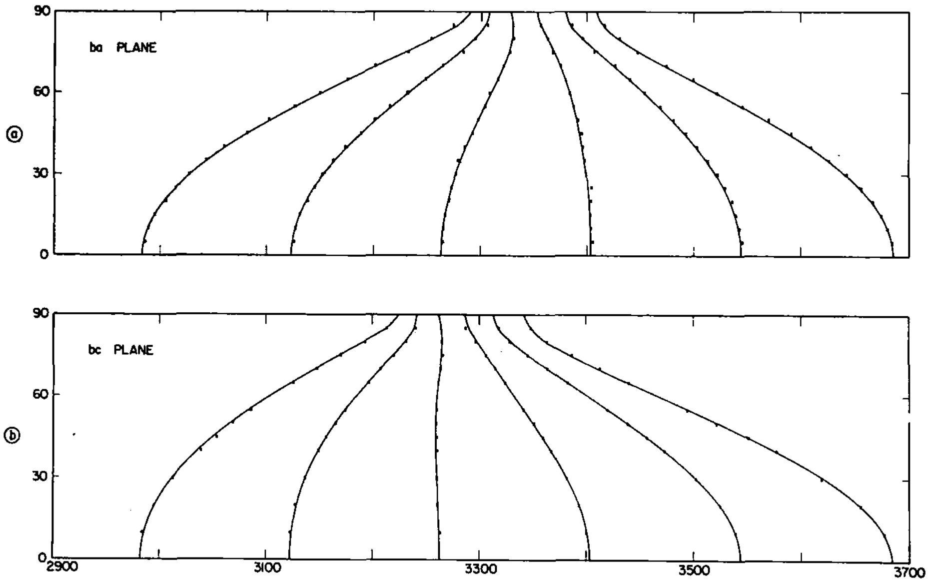

Fig. 4. Angular variation of $\gamma$-irradiated $KMnO_4$. The data were recorded with the magnetic field (a) scanning the b.a. plane and (b) the b.c. plane. 0° coincides with the $b$ axis.

were determined for all of these axes (for the b.d. plane two values can be found for $H$ parallel to the $d$ axis because of the two inequivalent sites). The resulting tensors were then diagonalized and the values are given in Table 2.

*Table 2. g and A tensor elements for diagonal axis system*

| | |
|---|---|
| $g_b = g_z = 1{\cdot}9617$ | $A_b = A_1 = 386$ MHz |
| $g_x = 1{\cdot}9452$ | $A_2 = 87$ |
| $g_y = 1{\cdot}9940$ | $A_3 = 20$ |
| $Q' = 4$ MHz (quadrupole coupling constant) | |

The principal axes of the $g$ and $A$ tensor for the a.c. plane are shown in Fig. 5. The $b$ axis is perpendicular to the diagram.

The main source of error in the measurements was in the determination of the orientation of the crystal. Another source of error was in the measurement of the splitting, especially as the field approached the $a$ or $c$ axis. In the former instance it was found that if the crystal was rotated out of the b.c. or b.a. planes by 1°, an error of 2 G would be introduced in the hyperfine splitting when the laboratory field was at 45° to the $b$ axis. As is seen from Fig. 4 the error is certainly no more than this. Experimentally it was found that a rotation of the magnetic field out of the b.c. or b.a. plane by 1° could be detected by the splitting of the spectrum due to the two inequivalent sites.

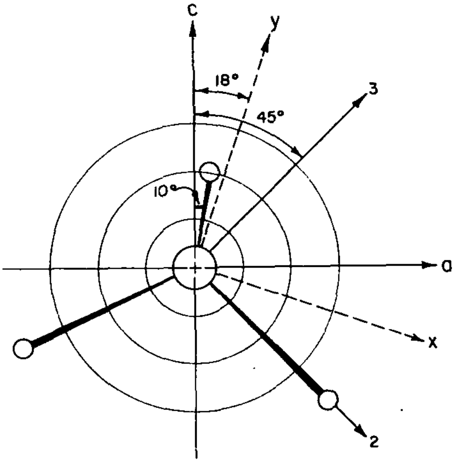

Fig. 5. The $MnO_4^-$ and the principal axes of the $g$ and $A$ tensors sketched in the a.c. plane of the $KMnO_4$ crystal. $x$ and $y$ are the $g$ tensor axes; 2 and 3 are the $A$ tensor axes.

Calculations were also made to determine the error introduced by neglecting the nuclear Zeeman term, $g_n\beta_nH_0$. For manganese in a field of 3200 G, $g_n\beta_nH_0 = 9{\cdot}5$ MHz. This introduces a maximum error of about 1/2 MHz and hence can be neglected. The error in calculating the $Q$'s is approximately ± 3 MHz. The error for the other hyperfine constants is about ± 1 MHz. The $g$ value error is estimated to be ± 0·0002.

## 4. DISCUSSION

There remains the question of the identification of the species observed. We will first consider radical '$B$'. There are six main groupings of lines in the spectrum and this would indicate a coupling with a nucleus of spin 5/2. $^{55}$Mn has a spin of 5/2 and would fulfill this requirement. A manganese ion of some sort can be ruled out since there is no fine structure evident in the spectrum. We considered the electronic structure of the oxides of manganese and then predicted the ESR spectrum that would result from such structures. In constructing molecular orbitals from a linear combination of atomic orbitals for these species we considered mainly 2$s$ and 2$p$ orbitals on the oxygen and 3$d$ orbitals on manganese. This was a very rough approximation but was made for simplicity of description. Calculations by Ballhausen and Gray[18] on the $MnO_4^-$ ion indicate that 4$p$ and 4$s$ orbitals from manganese do not make a significant contribution except in high energy antibonding orbitals. However, we introduced the 4$p$ and 4$s$ orbitals when they were pertinent to the argument. Further details of the following arguments are given in Ref. [19].

The unpaired electron in MnO occupies the $\pi^*$ orbital which consists of the $d_{zy}$ and $d_{zx}$ from Mn and the $p_y$ and $p_x$ from oxygen.

This will yield a hyperfine splitting depending on the magnitude of the coefficient of the *d* orbital. It can be shown that the *g* values will be equal to or greater than 2·0023. From the above arguments it is unlikely that either '*A*' or '*B*' is MnO.

Similar calculations were done for $MnO_2$, $MnO_3$ and $MnO_4$. These showed that the hyperfine splitting would be quite small since the unpaired electron occupied an orbital that was mainly nonbonding and localized on the oxygens. Thus species '*B*' could not be identified with any of these.

The paramagnetic species $MnO_4^{-2}$ was observed and analyzed in two papers by Carrington, *et al.*[20] and Schonland[21], henceforth referred to as CS. They carried out electron spin resonance studies of single crystals of potassium chromate containing manganate ($MnO_4^{-2}$) ions. The results of their experiments and analysis yield the constants given in Table 3.

*Table* 3. *g and A tensor elements from Ref.* [20]

| | |
|---|---|
| $g_x = 1\cdot970$ | $A_x = 75$ MHz |
| $g_y = 1\cdot966$ | $A_y = 99$ MHz |
| $g_z = 1\cdot938$ | $A_z = 405$ MHz |
| | $A_{yz} = -66$ MHz |

A calculation by CS indicated that these data were consistent if the unpaired electron resided in an orbital of species *e* of the $T_d$ symmetry group. Furthermore, considering spin-orbit coupling and crystal field distortion, the ground state can be represented as essentially the $d_{xy}(e)$ orbital from the manganese and approximately *p* orbitals from oxygen. (Because of the way in which the coordinate system was chosen the $d_{xy}(e)$ and $d_{x^2-y^2}(t_2)$ are interchanged in irreducible representations from their conventional designation).

These data are very similar to ours but there are some important differences that should be noted. In the first place we observed a superhyperfine spectrum as well as a hyperfine spectrum. In CS no such splitting was observed. This could be accounted for from the fact that the neighboring species for the paramagnetic center in this work were made up of $K^+$ and $MnO_4^-$ ions. In the CS report the neighboring species were the $K^+$ and $CrO_4^=$ ions. Since we have observed six components the most likely nucleus that could cause this splitting is manganese. $^{52}Cr$, however, has a spin of zero and could not cause any superhyperfine splitting. Secondly our experiment was carried out at 77K whereas in CS the spectrum could not be observed above 20K. Thirdly, the *g* and *A* tensors had common *x* (the *b* axis in Fig. 5) axes in CS but in our case the *z* axes were coincident. This last difference has important implications on the orientation of the radical. If one assumes a symmetric hyperfine tensor and then diagonalizes the tensor given in Table 3 one finds that the new diagonalized tensor has the values listed in Table 4.

*Table* 4. *Hyperfine tensor elements after diagonalization of a tensor in Table* 3

$A_3 = 420$ MHz
$A_2 = 87$ MHz
$A_1 = 75$ MHz

It turns out that $A_3$ is almost coincident with the $C_2$ axis which is, very roughly speaking, the *y* axis in Fig. 5.

In this work we have found the relative orientation of the *g* and *A* axis as given in Fig. 5. Note that the molecular structure in the figure represents the permanganate ($MnO_4^-$) ion in the unirradiated $KMnO_4$ matrix. The maximum hyperfine constant axis is perpendicular to the a.c. plane. CS found this axis to be in the a.c. plane. This means that the manganate ion ($MnO_4^{-2}$) must be rotated 90° relative to the permanganate ion orientation. Under these circumstances the reflection symmetry (the a.c.

plane) is lost and the site symmetry is reduced to $C_1$. As a result all $d$ orbitals will mix to form the ground state molecular orbital. This contrasts with CS who indicated that the reflection symmetry of that plane remained. In our case it is assumed that the ground state ($d_{xy}$) and first excited state ($d_{x^2}$) are basically the same as those determined by Schonland. The total wave function including mixing is given by

$$|0\rangle = N_0[|xy\rangle + a_1|z^2\rangle + a_2|xz\rangle + a_3|x^2-y^2\rangle + a_4|yz\rangle],$$

$$|1\rangle = N_1[|z^2\rangle + b_1|xy\rangle + b_2|xz\rangle + b_3|x^2-y^2\rangle + b_4|yz\rangle].$$

The $xyz$ axis system is fixed in the radical. Experimentally it was found that $g_{xz} = g_{yz} = 0$ and also that $A_{xz} = A_{yz} = 0$. To calculate components of the $g$ and $A$ tensor it is necessary to construct $|+\rangle$ and $|-\rangle$, the two spin functions, taking into account the spin orbit coupling which mixes $|0\rangle$, $|1\rangle$ and other excited states such as $|xz\rangle$, $|x^2-y^2\rangle$ and $|yz\rangle$. If it is assumed that the $z$ axis of the radical is perpendicular to the a.c. plane then it is found that $a_4 = b_4 = a_2 = b_2 = 0$ in order that $g_{xz}$, $g_{yz}$, $A_{xz}$ and $A_{yz}$, be equal to zero.

With these conditions in mind we now calculate $A_{xx}$, $A_{yy}$, $A_{xy}$, and $A_{zz}$.

$$A_{zz} = -2\beta + \alpha_0 \qquad A_{yy} = \beta + \alpha_0 - \beta'$$

$$A_{xx} = \beta + \alpha_0 + \beta' \qquad A_{xy} = A_{yx} = \gamma$$

where $\alpha_0$ is the isotropic coupling constant and

$$\gamma = a_1 < xy \left|\frac{3xy}{r^3}\right| z^2 > g\beta g_n\beta_n N_0{}^2$$

$$\beta' = \frac{2\lambda k b_3 N_0 N_1}{\Delta E} < xy\left|\frac{3xy}{r^3}\right|z^2 > g\beta g_n\beta_n.$$

For $d_{xy}$ orbitals,

$$\beta = N_0{}^2\frac{2}{7}g\beta g_n\beta_n\left\langle\frac{1}{r^3}\right\rangle.$$

$\lambda$ is the spin orbit coupling constant, $\Delta E$ is the energy difference between $|0\rangle$ and $|1\rangle$ and and

$$ik = \langle zx|L_x|xy\rangle.$$

As defined in CS, pure $3d$ orbitals would have $k = 1$ but the admixture of oxygen and $4p$ manganese orbitals reduces $k$ below this value. Diagonalizing this matrix we get,

$$A'_{zz} = A_{zz} = -2\beta + \alpha_0,$$

$$A'_{xx} = \beta + \alpha_0 + \chi,$$

$$A'_{yy} = \beta + \alpha_0 - \chi,$$

where

$$\chi = [(\beta')^2 + \gamma^2]^{1/2}.$$

The signs of the hyperfine constants given in Table 2 cannot be determined experimentally. However, certain reasonable assumptions can be made in order to determine the sign of $A'_{zz}$. For most manganese systems the isotropic coupling constant is negative and on the order of $-170$ MHz. As determined from a calculation[19], $2\beta$ is a positive quantity for a $d_{xy}$ orbital and has a maximum value of about 275 MHz. Consequently $A'_{zz}$ must be negative, i.e., $-386$ MHz. Nonetheless the ambiguity of signs of $A'_{xx}$ and $A'_{yy}$ remains. The values of $\beta'$, $\alpha_0$ and $|\chi|$ for the various combinations of signs for $A'_{xx}$ and $A'_{yy}$ are given in Table 5.

*Table 5. $\alpha_0$, $\beta$, and $|\chi|$ for various combinations of signs of $A'_{xx}$ and $A'_{yy}$*

| $A'_{xx}$ MHz | $A'_{yy}$ MHz | $\alpha_0$ MHz | $\beta$ MHz | $\lvert\chi\rvert$ MHz |
|---|---|---|---|---|
| +87 | +20 | −93 | +147 | 34 |
| −87 | −20 | −164 | +111 | 34 |
| +87 | −20 | −106 | +140 | 54 |
| −87 | +20 | −151 | +118 | 54 |

If the unpaired electron was completely localized in a $d_{xy}$ orbital on manganese then $2\beta$ would equal 275 MHz. The values shown in Table 5 indicate a range of from 81 to 100 per cent manganese '*d* character' for the unpaired electron. These values must be considered as rough approximations since only $d_{xy}$ orbitals were used in evaluating $2\beta$. There will be contributions from other parts of $|0>$ such as $d_{z^2}$, etc..

If we had chosen $d_{z^2}$ as our ground state instead of $d_{xy}$ we would have found that

$$A_{zz} = +2\beta + \alpha_0.$$

Again, assuming that $\alpha_0$ is approximately $-170$ MHz then the maximum value for $A_{zz}$ would be 100 MHz which is inconsistent with the experimental results. Consequently, it was felt that $d_{xy}$ was indeed the ground state.

One of the shortcomings of the above analysis is the assumption that the radical ion has rotated 90° (out of the a.c. plane) relative to the original orientation of the permanganate ion. An alternate explanation has been suggested* by one of the referees. The premise here is that the radical ion maintains roughly the same orientation in the crystal matrix as the permanganate ion. As a consequence the a.c. reflection plane remains a symmetry element and the site symmetry is $C_s$.

Assume that ground state wave function is

$$|a'\rangle = a_0|zx\rangle + a_1|z^2\rangle + a_3|x^2-y^2\rangle$$

where (see Fig. 5) the $y$ axis is parallel to the $b$ crystalline axis, the $z$ axis is coincident with the $y$ axis and the $x$ axis remains the same.

The $A$ tensor terms will be:

$$\begin{aligned}A_{zz} &= \alpha_0 - 2\beta(a_0{}^2 - a_1{}^2 + a_3{}^2)\\ A_{xx} &= \alpha_0 + \beta(a_0{}^2 - a_1{}^2 + a_3{}^2 - 2\sqrt{3}a_1a_2)\\ A_{yy} &= \alpha_0 + \beta(a_0{}^2 - a_1{}^2 + a_3{}^2 + 2\sqrt{3}a_1a_3)\\ A_{xy} &= A_{yx} = -2\sqrt{3\beta}a_0a_1\end{aligned}$$

where $N_0{}^2 = 1$.

If we assume $\alpha_0 = -152$ MHz and $\beta = 123$ MHz then a good fit to the data is found if

$$|a'\rangle = a_1|z^2\rangle + a_3|x^2-y^2\rangle$$

where $a_1{}^2 = 0{\cdot}85$ and $a_3{}^2 = 0{\cdot}15$

This assumes that the ground state is mainly $d_{z^2}$ rather than $d_{xy}$. The problem with this explanation is in the rather large value of $a_3$. The $d_{z^2}$ orbital belongs to the $E$ representation and $d_{x^2-y^2}$ belongs to the $T_2$ representation (in this coordinate system, previous to the lowering of the symmetry to $C_s$.) The $E \rightarrow T_2$ energy separation of $MnO_4^-$ is on the order of 10,000 $cm^{-1}$[29] and the spin-orbit coupling constant is approximately 150 $cm^{-1}$. As a consequence the mixing would have to come through an exceptionally large crystal field distortion. This seems unlikely under these circumstances hence the large value of $a_3{}^2$ remains unexplained.

We now wish to consider paramagnetic center '*A*'. Unfortunately, without resolvable hyperfine splitting the identification of this species becomes very difficult. However, numerous investigators[23–26] have observed a paramagnetic species that possesses $g$ values very similar to this radical. Atkins, *et al.*[23], have identified this as the $O_3^-$ radical. This radical has a bent structure[27] with the $x'$-axis perpendicular to the radical plane, the $z'$-axis parallel to the bisector of the apex angle, and the $y'$-axis perpendicular to both $x'$ and $z'$.

This radical has nineteen valence electrons and it can be shown[27] that $\Delta g_{x'} \simeq 0$, $\Delta g_{y'}$ will be large and greater than zero and $\Delta g_{z'}$ will be between 0 and $\Delta g_{y'}$. Referring to Fig. 5 it is seen that if $x' \rightarrow x$ and $z' \rightarrow y$ then $O_3^-$ radical would approximately coincide with the position of the manganese atom and the two oxygen atoms lying above and below the c.a. plane. A similar substitution was observed by Tagaya[26] for $O_3^-$ in $AgNO_3$ where $O_3^-$ occupied a $NO_3^-$ vacancy.

Manganese dioxide also has nineteen valence electrons. In this case the 3*d* orbitals

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*The author is indebted to one of the referees for this suggestion.

are the main bonding orbitals from manganese with minor contributions from 4*s* and 4*p*[18]. Using the Walsh diagrams as outlined by Atkins and Symons[27] the electrons take up the following configuration, assuming $D_{\infty h}$ symmetry with the *z* axis in the OMnO direction:

$$(s_1)^2(s_2)^2(\sigma_g)^2(\pi_g)^4(\delta_g)^4(\sigma_u)^2(\pi_u)^3.$$

$s_1$ and $s_2$—consist of the 2*s* orbitals on the oxygen;

$\sigma_g$—consists of the $d_{z^2}$ from Mn and the $p_z$ from the oxygens;

$\pi_g$—consists of the $d_{zy}$ and $d_{zx}$ from Mn and the $p_y$ and $p_x$ from the oxygens;

$\delta_g$—consists of the $d_{x^2-y^2}$ and $d_{xy}$ from Mn which are nonbonding orbitals localized on Mn;

$\sigma_u$—consists of the $p_z$ from Mn and the $p_z$ from the oxygen;

$\pi_u$—consists of the $p_x$ and $p_y$ from Mn and the oxygens.

There could be some question of the order of the last three energy levels $\delta_g$, $\sigma_u$, and $\pi_u$. If one chooses the scheme used by Ballhausen and Gray[18] and uses the calculated Coulomb integrals for the Mn(3*d*), Mn(4*p*), and O(*p*), ones finds from a very rough calculation that the $\sigma_u$ and $\pi_u$ levels are higher in energy than $\delta_g$. In such a case the unpaired electron occupies a $\pi_u$ or $\sigma_u$ level which are mainly localized on the oxygen atoms with a small contribution from the $p_x$ and $p_y$ orbitals located on the manganese. Because of this small contribution the anistropic hyperfine splitting due to manganese will be very small. If the molecule is bent, the $\pi_u$ orbital will split into $b_1$ and $a_1$ orbitals with $E(a_1) > E(b_1)$. In this case the unpaired electron will occupy the $a_1$ orbital. Defining the $x'$, $y'$, $z'$ axes system in the same way as for the $O_3^-$ radical we now find that $\Delta g_{z'} \cong 0'$ $\Delta g_{y'}$ is a large positive number and $\Delta g_{x'}$ between 0 and $\Delta g_{y'}$. This would mean that the measured value of 2·0020 which makes an angle of 18° to the *a* axis (see Fig. 5) would correspond to the $z'$ axis of the radical. The other *g* values would place the oxygen atom symmetrically above and below the a.c. plane.

It can also be shown that for $MnO_3$ the unpaired electron would occupy the $2a_2^*$ level. Lancaster and Gordy[28] have found that the average *g* value for $MnO_3$ was 1·96. The *g* values for '*A*' were all considerably higher than this hence it is unlikely that this species would be $MnO_3$.

We have not as yet analyzed the possibility of the species '*A*' being $MnO_4$ as the study is quite complex and, in the final analysis, would be only qualitative in nature. It can be said that the $t_1$ orbital for the unpaired electron would exhibit no anisotropic hyperfine splitting. Experimentally it was observed that there was some small unresolved anisotropic hyperfine splitting, and if this was due to manganese in the paramagnetic center then $MnO_4$ could be eliminated. However, if it was due to some superhyperfine coupling with neighboring manganese or potassium, then it would still leave $MnO_4$ as a possibility.

## 5. CONCLUSIONS

The γ-irradiation of $KMnO_4$ produces at least two paramagnetic species. The first one generated by room temperature irradiation has not been completely identified but some of the possible species are $O_3^-$, $MnO_2$ and $MnO_4$. There is some unresolved hyperfine structure in the spectrum and further work will be needed to resolve the identity of this species. The second paramagnetic center is generated by irradiation at 77°K and is unstable at slightly higher temperatures. This has been identified as the $MnO_4^{-2}$ radical which is in a completely different orientation with respect to the parent $MnO_4^-$ ion. For the radical, two of the oxygen atoms of the tetrahedron lie above the a.c. plane and the other two below this plane. For the ion, two oxygen atoms lie in the plane and the other two lie symmetrically above and below the plane. This new orientation should produce a great deal mixing of states. However, the data show that for consistent results some of this expected mixing does not occur.

The measured constants and the final electronic structure largely agree with the results of CS. The unpaired electron resides principally in a $d_{xy}$ orbital located on the manganese with some coupling to the oxygens. We have not made any attempt to interpret the superhyperfine splitting which was observed, other than to note that it may be due to a coupling with neighboring $MnO_4^-$ ions.

It would be appropriate here to make some comment on Boldyrev's theory[8] of the effect of high energy radiation on the decomposition of $KMnO_4$. He assumes that $KMnO_4$ undergoes the reaction, $2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$. The initial step in this process is the electron transfer mechanism

$$2MnO_4^- \rightarrow MnO_4^{-2} + MnO_4^{\circ}$$

$$MnO_4^{\circ} \rightarrow MnO_2 + O_2.$$

He claims that the manganate ion is more stable than the permanganate ion and has shown that the introduction of $K_2MnO_4$ inhibits decomposition of the compound, but that introduction of $MnO_2$ accelerates the decomposition. $MnO_2$ has a work function of 5·48 eV while that of $KMnO_4$ is 4·76 eV. $MnO_2$ may act as an electron acceptor in the $KMnO_4$ lattice. He believes that the electron acceptor characteristic of $MnO_2$ produced in preliminary irradiation overshadows the stabilizing effect of $MnO_4^{-2}$ which is also produced by irradiation, and accounts for the increased decomposition rate. We have found that the manganate ion does not appear to be stable in the matrix at room temperature. However, radical '*A*' which could be identified as $MnO_2$ is stable up to and beyond room temperature. This could account for his prediction that the destabilizing effect of $MnO_2$ overshadows the stabilizing effect of $MnO_4^{-2}$.

These conclusions must be considered highly tentative as several other experiments should be carried out in order to put them on a firmer base. For one, an attempt should be made to observe the $MnO_4^{-2}$ at lower temperatures. As was mentioned, CS were not able to observe the manganate radical at a temperature higher than 20 K. It could be that the irreversible loss of our signal at about 100K actually is a reorientation of the radical to a new position. The new orientation might have a significantly different spin-lattice relaxation time and render the radical unobservable at 77K as was reported by CS. More work needs to be done on understanding the photolytic mechanism which causes the irreversible disappearance of $MnO_4^{-2}$ when it is irradiated with visible light.

A further experiment that should be carried out would be an electron-nuclear double resonance (ENDOR) study of radical '*A*'. Resolution of the hyperfine splitting could be very helpful in making a positive identification of this radical.

In closing we may note that some progress has been made on the understanding of the initial steps on the decomposition mechanism. Until now a great many assumptions have been made on the details of the mechanism from somewhat indirect data. We have been able to make a few direct observations on the predictions of one of the theories of decomposition and hope to make considerable progress in the future.

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