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Structure of *V* Centers in Irradiated $KClO_3$†

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On the basis of the electron spin resonance spectra of a single crystal of $KClO_3$ which has been exposed to x-irradiation, a model is proposed for the V center produced. The center proposed consists of a ClO radical covalently bonded to a neighboring ClO_3^- ion. It is shown that the electron spin resonance spectra predicted for this radical agrees with the observed spectra, both in the number and spacing of the hyperfine components and their orientation dependence in the external magnetic field. It is also proposed that an O_2^- center is produced rather than the usual F center which one might expect to accompany the V center.

INTRODUCTION

THE exposure of crystals to radiation usually results in a change in the properties of the crystal. Since soft x-rays can impart a significant amount of energy only to the electrons in the crystal, any change in the properties must result because of a relocation of electrons in the crystal lattice. In the simple alkali-halide crystals, the fundamental process is the stripping of an electron from a halide ion and the subsequent trapping of this electron in an electron trap, e.g., in an halide vacancy. The trapped electron in an halide vacancy is commonly called an F center, and the negative ion deficiency resulting from the loss of an electron by the halide ion is usually called a V center. Considerable experimental and theoretical work has been done on the nature of these centers in the alkali-halide crystals.[1–6]

The purpose of this paper is to describe the effects of removing an electron from a ClO_3^- ion in a crystal of $KClO_3$.

In order to determine the nature of the centers, the optical, infrared and paramagnetic resonance absorption spectra were observed in single crystals which had been exposed to 50-kv x-irradiation. The paramagnetic resonance spectra proved to be the most useful.

A single crystal of $KClO_3$ was exposed to x-rays from an unfiltered Machlett AEG-50 tube operating at 50 kv and 20 ma for several hours. The crystals turned a deep orange-brown color, and showed a rather intense paramagnetic resonance absorption. Crystals left in the x-ray flux for a day or so began to disintegrate into a fine powder. Figure 1 shows the first derivative of this absorption at three different orientations of the crystal in the external magnetic field. The rotation is about the x crystalline axis. At 0° the y crystalline axis makes an angle of 40° with the magnetic field. The choice of this direction as a reference is discussed below. The spectrum consists of two sets of lines. One set is a single relatively broad line with a g value a little larger than 2. The other set consists of 16 equally intense lines with a line width of about 5 gauss, which show a rather large anisotropy as the crystal is rotated in the external magnetic field.[7]

Figure 2 shows the position in the paramagnetic resonance spectrum of the 16 lines as a function of the angle θ of rotation about the crystal axis x. θ is the angle between the dc magnetic field and the reference direction mentioned above. It is apparent that the 16 lines are four equally spaced groups of four equally spaced lines each. It is also seen that as the separation between the groups decreases, the separation between lines in a group decreases. The separation between lines is the

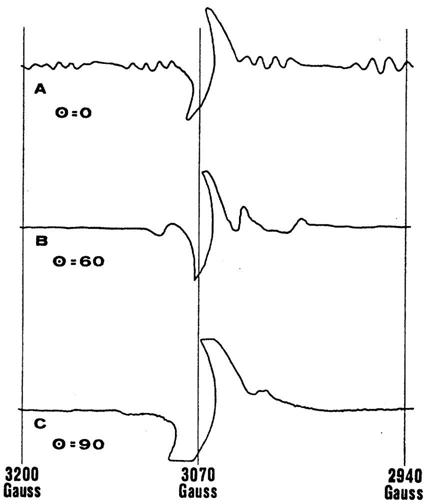

FIG. 1. Derivative of paramagnetic absorption of $KClO_3$ as a function of magnetic field strength for different orientation of the crystal in the external field.

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[6] W. Känzig and T. O. Woodruff, J. Phys. Chem. Solids **5**, 70 (1958).

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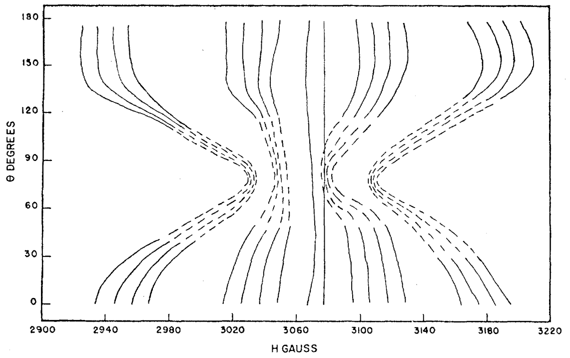

FIG. 2. A plot of the magnetic field at which each line appears as a function of the orientation of the crystal in the field. The dotted sections indicate orientations at which the individual lines in each of the four groups could not be resolved. The straight line down the center of the plot is the position of the DPPH line, and the slightly curved line is the position of the broader strong line attributed to O_2^-.

same in a field of about 7000 gauss, which indicates that the splitting is caused by hyperfine interactions.

All the above data were taken at room temperature, and the intensity of the absorption shows very little change as the crystal is aged at room temperature after irradiation. The crystals were only a few millimeters on a side, since $KClO_3$ seems to prefer to grow in the form of thin wafers, and we have been unable to grow crystals more than a few millimeters thick. However, the thin wafers proved ideal for the optical and infrared absorption measurements.

Optical absorption measurements showed that the radiation produced a single intense band centered at 2.69 ev (461 mμ) with a width between points of half intensity of 0.35 ev. No absorption in the region 0.8 μ to 15 μ was found that could be attributed to the radiation.

In an effort to bleach the crystals, they were annealed for periods of six hours at temperature intervals of 10°C. After each six-hour period, the paramagnetic resonance absorption was observed. After annealing at 85°C, a decrease in the intensity of the 16-line spectrum was observed, and after annealing at 105°C, the 16-line spectrum completely disappeared. The crystal did not become clear, however. It became rather milky in appearance. An unirradiated crystal annealed in this manner remained clear.

No bleaching was observed due to exposure to daylight or to light from a mercury lamp.

STRUCTURE OF THE PARAMAGNETIC CENTERS

It is probable that the primary effect of an x-ray on the crystal would be the removal of an electron from a ClO_3^- ion, leaving a ClO_3 radical. The experimental evidence indicates that this radical is unstable in the $KClO_3$ lattice. If this radical were stable, the radiation damage to the lattice would be reversible. The bleaching experiments, however, show that the damage is permanent. The ClO_3 radical probably breaks up into ClO and O_2. We propose that the O_2 molecule diffuses into the lattice and becomes trapped at negative ion vacancy, and that the ClO, which has an electron deficiency in its valence shell, shares this deficiency with the nearest ClO_3^- ion. This should result in a loosely-bound $ClO-ClO_3^-$ ion.

The nearest ClO_3^- ions in the $KClO_3$ lattice are the ions in the upper right-hand corner of one unit cell and the lower left-hand corner of the unit cell diagonally above it (see Fig. 3). The separation between these ions is 3.65 A.[8] The angles between the line joining these ions (dashed line in Fig. 3) and the x, y, and z crystalline axes are α, β, and γ, respectively, where $\alpha=87.3°$, $\beta-40.1°$ and $\gamma=53.9°$.

PREDICTED PARAMAGNETIC ENERGY LEVELS OF THE *V* CENTER

A method of successive perturbation developed by Pryce[9] can be used to determine the energy levels responsible for paramagnetic resonance absorption. This method can be modified to include the hyperfine interaction of the electron with two nuclei.

The Hamiltonian for the odd electron (in this case an electron hole) is $\mathcal{H}$,

$$\mathcal{H}=\mathcal{H}_0+\lambda\mathbf{L}\cdot\mathbf{S}+\beta(\mathbf{L}+2\mathbf{S})\cdot\mathbf{H}$$

$$+\sum_{i=1}^{2}\left\{2\gamma\beta\beta_n\left[\frac{(\mathbf{L}-\mathbf{S})\cdot\mathbf{I}_i}{r_i^3}+\frac{3(\mathbf{r}_i\cdot\mathbf{S})(\mathbf{r}_i\cdot\mathbf{I}_i)}{r_i^5}\right]\right.$$

$$\left.+\frac{8\pi}{3}\delta(r_i)\mathbf{S}\cdot\mathbf{I}_i\right\}$$

$$+\sum_{i=1}^{2}\frac{e^2Q}{2I_i(I_i-1)}\left[\frac{I_i(I_i+1)}{r_i^3}-\frac{3(\mathbf{r}_i\cdot\mathbf{I}_i)^2}{r_i^5}\right], \quad (1)$$

where $\mathcal{H}_0$ includes the kinetic energy of the electron and potential energy due to coulomb interactions.

It is assumed that the ground-state eigenfunction of the above Hamiltonian can be made up of p orbitals of the ClO radical and the ClO_3^- ion. There will be a certain amount of s character, however, due to the polarization of the radicals. The ground-state wave function will be ϕ, where

$$\phi=a\phi_1\pm b\phi_2, \quad (2)$$

and

$$\phi_i=\alpha_iF(r_i)Y_{1,m}(\theta_i,\phi_i)\pm\beta_iG(r_i). \quad (3)$$

α_1 and β_1 designate the fraction of p and s character in $-ClO$, and α_2 and β_2 designate the p and s character in ClO_3^-. The coefficients satisfy the condition,

$$a^2+b^2=\alpha_1^2+\beta_1^2=\alpha_2^2+\beta_2^2=1. \quad (4)$$

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[8] R. W. G. Wyckoff, *Tables of Crystal Structure* (Interscience Publishers, Inc., New York, 1948–51).

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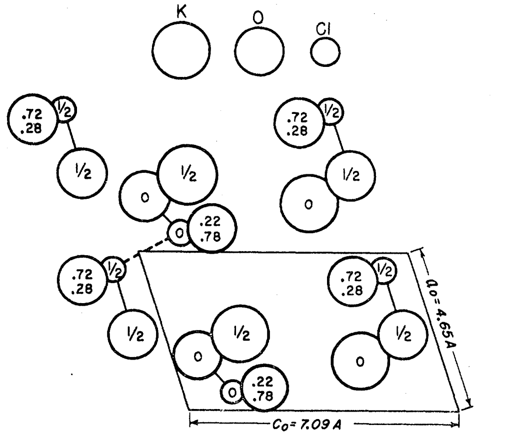

FIG. 3. Location of the atoms in the $KClO_3$ structure. The dotted line at the upper left corner of the unit cell connects the two ClO_3^- ions that form the $ClO-ClO_3^-$ *V* center.

If the quadrupole interactions are neglected, and it is assumed that only the lowest orbital level is populated, a straightforward application of first-order perturbation theory gives the following result for the energies of the paramagnetic levels:

$$E^n=\langle m_1m_2|\langle SM_s|\mathcal{H}|SM_s\rangle|m_1m_2, \qquad (5)$$

where

$$\mathcal{H}=g\beta\mathbf{H}\cdot\mathbf{S}+A_1\mathbf{I}_1\cdot\mathbf{S}+\eta_1L(L+1)(3\cos^2\theta_1-1)\mathbf{I}_1\cdot\mathbf{S} +A_2\mathbf{I}_2\cdot\mathbf{S}+\eta_2L(L+1)(3\cos^2\theta_2-1)\mathbf{I}_2\cdot\mathbf{S}. \qquad (6)$$

The terms with subscript (1) are due to coupling with the chlorine nucleus in the ClO group, and terms with subscript (2) are due to coupling with the chlorine nucleus in the ClO_3 group. θ_1 and θ_2 are the angles between the axes of quantization of the ClO and ClO_3^-, respectively, and the external magnetic field. The axis of quantization can be determined from the observed paramagnetic transitions. Evaluation of Eq. (5) gives

$$E^n=g\beta M_sH+A_1m_1M_s+K_1m_1M_s(3\cos^2\theta_1-1) +A_2m_2M_s+K_2m_2M_s(3\cos^2\theta_2-1). \qquad (7)$$

The values of S, I_1, I_2, M_s, m_1, and m_2 are given below:

$$S=\tfrac{1}{2},$$
$$I_1=I_2=\tfrac{3}{2},$$
$$M_s=\pm\tfrac{1}{2},$$
$$m_1=m_2=\pm\tfrac{3}{2},\ \pm\tfrac{1}{2}.$$

The coefficients A_1, A_2, K_1, K_2 must be determined empirically.

There will be 32 energy levels corresponding to a $(2S+1)$ $(2I_1+1)$ $(2I_2+1)$ multiplicity.

The transitions that are observed correspond to the following selection rules:

$$\Delta M_s=1, \quad \Delta m_i=0. \qquad (8)$$

The equation for the frequency of these transitions is:

$$h\nu=g\beta H+A_1m_1+K_1m_1(3\cos^2\theta_1-1) +A_2m_2+K_2m_2(3\cos^2\theta_2-1). \qquad (9)$$

This can be rewritten in terms of the magnetic field at which resonance occurs:

$$H=H_0-a_1m_1-k_1m_1(3\cos^2\theta_1-1) -a_2m_2-k_2m_2(3\cos^2\theta_2-1). \qquad (10)$$

where

$$a_i=A_i/g,\quad k_i=K_i/g,\quad \text{and}\quad H_0=h\nu/g\beta. \qquad (11)$$

The effect of second-order perturbations will be to add terms quadratic in H and S. Since $S=\frac{1}{2}$, the only contribution to Eq. (9) will be that g should be written as $ge+f$, where ge is the "g" value of the free electron and f is a tensor with the same symmetry as the crystalline field. The sign of f would be negative for an electron excess, and positive for an electron deficiency. In this case, f is positive. No appreciable anisotropy in f could be determined from the spectra.

COMPARISON WITH EXPERIMENTAL RESULTS

In order to determine whether or not Eq. (11) leads to the correct angular variation, it is necessary to fit the four constants a_1, a_2, k_1, k_2 to the experimental curve. Since the maxima and minima of the hyperfine splitting for both chlorine nuclei occur at the same orientation it is assumed that for any orientation, $\theta_1=\theta_2$. Hence θ_1 and θ_2 will be replaced by θ.

The part of the hyperfine splitting which arises from the *s* character of the electron deficiency, is independent of the angle beteeen the axis of quantization and the external magnetic field. Thus, the values of a_1 and a_2 will not depend on the axis through which the crystal is rotated. This is not true, however, for the part of the hyperfine interaction which arises from the *p* character of the wave function.

The equations developed above were based on the assumption that the crystal was being rotated about an axis perpendicular to the axis of quantization. In cases when the crystal is rotated about an axis not perpendicular to the axis of quantization the axis of quantization will make some minimum angle ϕ with the plane of the magnetic field. K must then be resolved into its components parallel and perpendicular to the plane of the magnetic field.

These components are:

$$k_\perp=k\sin\phi, \qquad (12)$$

and

$$k_\parallel=k\cos\phi. \qquad (13)$$

The perpendicular component will remain at right angles to the external field, but the parallel component will make with the field an angle θ, which depends on the orientation of the crystal. Thus, the equation for the *p* contribution to the hyperfine splitting must be modified to:

$$H_p=\sum_{i=1}^{2}\left[m_ik_i\sin\phi\left(3\cos^2\frac{\pi}{2}-1\right)+m_ik_i\cos\phi(3\cos^2\theta-1)\right].\quad(14)$$

The total hyperfine splitting is given by:

$$H=\sum_{i=1}^{2}m_i[a_i-k_i\sin\phi+k_i\cos\phi(3\cos^2\theta-1)].\quad(15)$$

Since ϕ will remain constant for a particular orientation of the crystal, the constant term is actually $(a_i-k_i\sin\phi)$, rather than a_i. Thus, both the value for k_i and the apparent value for a_i will depend on the axis about which the crystal is being rotated. For the case $\phi=0$, Eq. (15) reduces to Eq. (10). Only in this case can the actual values of a_i and k_i be measured. For the case when $\phi=\pi/2$, the spectrum will show a minimum splitting for all values of θ.

Since the line joining the ClO and the nearest ClO_3^- is the most logical as the axis of quantization, the crystal was rotated around the x crystal axis. This axis is almost perpendicular to the line between the ions ($\alpha=87.3°$). Proof that the line joining the ions is the correct axis of quantization is that the minimum splitting occurs when this line is perpendicular to the magnetic field, and rotation of the crystal about an axis parallel to this line showed minimum splitting for all orientations. The data for rotation about the x axis is used to determine a_1, a_2, k_1, and k_2.

The position of the curve at $\theta=0°$ was used to determine k_1 and k_2. The values of a_1 and a_2 were measured at $\theta=57°$.

The values from the experimental curve of Fig. 2 are

$$a_1=41.0\text{ gauss},$$
$$a_2=5.0\text{ gauss},$$
$$k_1=22.4\text{ gauss},$$
$$k_2=2.6\text{ gauss}.$$

Using these values for the constants, Eq. (10) describes the angular dependence that is shown in Fig. 2 very well.

The spectrum of the V center is complicated by the fact that there are two principal isotopes of chlorine present. These isotopes are chlorine-35, which has a natural abundance of 75.4%, and chlorine-37, which is 24.6% abundant. Since both of these isotopes have a spin of $\frac{3}{2}$, they will give the same number of hyperfine lines, but there will be a slight difference in the magnitude of the splitting of these lines, due to the difference in the nuclear magnetic moments of the two isotopes. Chlorine-35 has a magnetic moment of 0.82 nuclear magneton, and chlorine-37 has a magnetic moment of 0.68 nuclear magneton.

The presence of these isotopes allows four different types of V centers to be formed. They are as follows:

1. Both radicals of the V center contain chlorine-35.
2. The ClO radical contains chlorine-35, and the ClO_3 radical contains chlorine-37.
3. Both radicals contain chlorine-37.
4. The ClO radical contains chlorine-37, and the ClO_3 radical contains chlorine-35.

We could only detect a difference in splitting for the cases where the ClO radicals contain different isotopes. The hyperfine interaction from the chlorate is far too small for separate lines to be detected for the different isotopes. The presence of two isotopes in the chlorate radical should only broaden the line. The maximum broadening that one would expect is about 5 gauss.

We should be able to resolve a difference in the hyperfine splitting, due to the two different isotopes that can occur in the ClO radical. At the position of maximum splitting, the center of the outer line should be about 19 gauss smaller for centers containing chlorine-37 than for those containing chlorine-35. The intensity of these lines should be about one third as great as for those containing chorine-35. The extra lines due to the chlorine-37 can be clearly seen in Fig. 1(a).

THE O_2^- CENTER

The center which produces the strong central line is believed to be an O_2^- molecule ion. Evidence that this center is associated with a trapped oxygen molecule is brought out by the heating experiments. As previously mentioned, the crystal became milky when it was heated to a temperature sufficient to bleach out this center. A phenomenon of this type could easily be produced by the liberation of this trapped oxygen. It might be mentioned at this point that at no time was the crystal raised to such a temperature as to cause the normal potassium chlorate to dissociate. This would indicate that any oxygen that was liberated would be that which was trapped in lattice vacancies, and not from a chlorate ion.

The necessity for postulating the existence of an O_2^- molecule ion is twofold. First, in order to be consistent with our theory of the V center, we would have at least as many O_2 molecules trapped in the crystal as we have V centers. The O_2 molecule is naturally paramagnetic with a spin of 1. This is due to the fact that there are two electron vacancies in the outer shell of the O_2 molecule. A trapped oxygen molecule would exhibit a two line spectrum, corresponding to a $2S$ fine structure splitting. However, if the oxygen molecule gains an additional electron, the net spin of the system will be $\frac{1}{2}$. This system would exhibit a single line. The paramagnetic susceptibility of this system would be due to a trapped hole. Secondly, from purely electrostatic considerations, we would expect as many electron traps in the crystals as we have hole traps. We have evidence that the *V* center is a hole trap. Thus, we would expect the other paramagnetic center to be an electron trap. However, from the paramagnetic resonance spectrum, we see that the *g* value of the central line is greater than that of a free electron. This indicates that this center is also due to a trapped hole. We must conclude that this center is actually an electron trap which behaves paramagnetically as if it were a hole trap. The O_2^- molecule ion provides such a center.

Although there is no conclusive evidence that the trapped O_2^- molecule ion is responsible for the large central line, it is in agreement with the other assumptions, and with the observed data.

The question now arises as to the mechanism by which the O_2^- molecule ion is formed. The most probable mechanism by which this center may be formed is as follows:

When the chlorate radical dissociates, the liberated oxygen molecule will probably diffuse through the crystal until it is trapped in an existing Schottky defect. A defect of this type is a vacancy which is normally occupied by a ClO_3^- radical. It is surrounded by six neighboring $K+$ ions. Thus, we might also expect an electron to become trapped in this vacancy. This electron would probably exist in one of the vacancies of the outer shell of the oxygen molecule leaving an O_2^- molecule ion. One might notice at this point the distinct difference between this type of paramagnetic center and the *F* center of the alkali halides.

The Hamiltonian for this system could again be made up of terms of the Hamiltonian for the free ion. The term H_0 would have a very similar appearance to the H_0 term for the *V* center, the only difference being that the O_2^- molecule ion contains only two nuclei. The terms arising from the spin orbit coupling and from the interaction with the external magnetic field would have the same form as those for the *V* center. Since the oxygen nucleus has a spin of zero, the Hamiltonian will contain no hyperfine or quadrupole terms.

The width of the absorption line was approximately 12 gauss at room temperature. The line width decreased to about 3 gauss at liquid nitrogen temperature, indicated that the principal broadening mechanism was the spin-lattice interaction. We were unable to determine whether or not the line width had any angular dependence since, for orientations near 90 degrees, the lines of the *V* center merged with the central line.

CONCLUSION

In order to determine the energy levels of the *V* center, certain assumptions about the wave function of the unpaired electron were made. The assumption that the wave function has a large amount of *p* character is in agreement with the fact that the positions of the hyperfine lines are strongly dependent on the orientation of the crystal in the external magnetic field. It is also consistent with the assumption that the center is held together largely by a covalent bond. It has been suggested by Townes[10] that the percentage of *p* character in a wave function is a direct measure of the percentage of the bond that is covalent, while the *s* character is a measure of the amount of the bond that is ionic. One might be tempted to say that the ratio of *k* to *a* is the ratio of the amount of the covalent part to the ionic part of the chemical bond. This is not true, however, since the hyperfine coupling constants also depend on the radial parts of the wave function. The ratio of k_1 to k_2 was found to be 22.4/2.6. This ratio is the same as the ratio a_1/a_2 to within 5%. One is led to conclude that the deficiency has the same character about each of the two chlorine nuclei. From these ratios, the coefficients *a* and *b* of Eq. (2) are computed to be 0.94 and 0.33, respectively.

ACKNOWLEDGMENTS

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