Paramagnetic Defects in Irradiated KClO₄

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Electron magnetic resonance (EMR) studies of X-ray damaged single crystals of KClO₄ indicate the presence of two types of stable paramagnetic defects at room temperature. One type of defect appears to be a trapped ClO₄⁻ molecule.

Single crystals of KClO₄ were grown by slow evaporation of an aqueous solution. Potassium perchlorate is orthorhombic with 4 molecules per unit cell. Cell
dimensions are $a = 8.834\ \text{Å}$, $b = 5.650\ \text{Å}$, $c = 7.240\ \text{Å}$; the space group is $V_{16}^n$ (Pnma). Irradiations were performed at room temperature in air with 50 kv X-rays from a tungsten target tube operating at 20 ma. After irradiations of from 10 minutes to two hours the crystals exhibited color ranging from pale yellow to brown. EMR spectra were observed with a Varian V 4500 spectrometer using a cylindrical cavity operating in the TE$_{01}$ mode at 9536 Mc.

Figure 1 shows a typical EMR spectrum of an irradiated and aged single crystal;

![EMR Spectrum](image)

its main features are (1) four groups labeled $A_1$, $A_2$, $B_1$, and $B_2$, each group having four lines of nearly equal spacings and (2) a group of closely spaced lines labeled $P$. Spacings of lines within each group as well as the relative positions of the groups depend upon the crystal orientation relative to the applied magnetic field. Immediately after irradiation only the $P$ group was observed; thereafter the other four groups appeared and increased in intensity to the terminal value shown in Figure 1. A third set of lines appeared concurrently with the $A$ and $B$ groups but two days after irradiation their intensity began to decrease, becoming too weak to observe after about 10 days. Observed spectra of aged crystals can be accounted for by the following assumptions.

(a) The species producing group $A_1$, $A_2$, $B_1$, and $B_2$ contains only one Cl nucleus; $A_1$ and $B_1$ a Cl$^{35}$, $A_2$ and $B_2$ a Cl$^{37}$.

(b) There are two nonequivalent sites for the Cl associated defect. Figure 2 illustrates the orientation of the principal axes of the hyperfine tensors ($x$, $y$, $z$; $x'$, $y'$, $z'$) of the two sites relative to the unit cell axes. These two sites give rise to the $A$ and $B$ groups.

(c) In the set of defect axes labeled $x$, $y$, $z$ for $A$ and $x'$, $y'$, $z'$ for $B$ the molecular spin Hamiltonian is,

$$\mathcal{H} = \beta S \cdot g \cdot B_0 + g_\alpha \beta_s I \cdot B_0 + I \cdot A \cdot S + Q \cdot \nabla E$$

(1)
Fig. 2.—Orientation of defect hyperfine axes relative to the unit cell axes. Axes b, x, and x' are perpendicular to the plane of the figure.

$B_0$ is the applied magnetic field $S$ and $I$ the electron and nuclear spin operators, $A$ the hyperfine coupling tensor, $g$ the electronic $g$ tensor, $Q$ the nuclear quadrupole tensor and $\nabla E$ the field gradient tensor. $\beta$ and $\beta_n$ are the electronic and nuclear magnetons respectively. The first and second terms in (1) are the electronic and nuclear Zeeman terms, respectively, while the third and fourth are the hyperfine and nuclear quadrupole energies. Principal values of the diagonalized $A$ and $g$ tensors determined for Cl$^{15}$ were:

$$A_{zz} = 44 \pm 4 \text{ Mc} \quad g_{zz} = 2.0183 \pm 0.0005$$
$$A_{yy} = 32 \pm 4 \text{ Mc} \quad g_{yy} = 2.0088 \pm 0.0005$$
$$A_{xx} = 204 \pm 2 \text{ Mc} \quad g_{zz} = 2.0036 \pm 0.0005$$

The nuclear Zeeman and quadrupole terms produced only small effects in the EMR spectra, in particular the quadrupole term was estimated to be less than 10 Mc. Diagonal values for $A$ in the Cl$^{17}$ defects were found to be smaller by a factor of 0.83 (equal to the ratio of nuclear magnetic moments). Diagonal values of $g$ for Cl$^{17}$ defects were the same as for Cl$^{16}$ defects.

(d) The $P$ group of lines arises from other paramagnetic species.

The identification of the Cl associated defect as ClO$_2$ rests on three points. First, $\frac{1}{2} \text{Tr } g$ is 2.010 in agreement with the value found for ClO$_2$ in solution by Bennett and Ingram; the isotropic hyperfine interaction given by $\frac{1}{2} \text{Tr } A$ is 43 Mc, again in agreement with the value of 46.5 Mc found for ClO$_2$. The value of 43 Mc is obtained if $A_{xx}$ and $A_{yy}$ are opposite in sign to $A_{zz}$. Secondly, $g$ and $A$ being noncylindrically symmetric eliminate species such as ClO$_2$ and ClO. Lastly, the values given above for the diagonal components of $A$ are in semiquantitative agreement with hyperfine components calculated from MO theory. Further studies are in progress to determine nuclear quadrupole interactions and to identify the transient species mentioned above.
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2 Bennett, J. E., and D. J. E. Ingram, Phil. Mag., 1, 109 (1956).

CONTINUOUS ELECTROPHORETIC FRACTIONATION STABILIZED BY ELECTROMAGNETIC ROTATION*

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The objective of the experiments described below is to achieve continuous separation of ions in solution by making charged particles of different mobilities follow divergent paths. Similar aims have been pursued by other authors employing different means. Grassman and Hannig utilized in their paper curtain electrophoresis gravitational descent of a flowing zone of the dissolved mixture of ions along a curtain of filter paper in a transverse electric field. Svensson and Brattsten aimed to achieve the same result by using glass powder as a medium to suppress thermal convection. Mel used a density gradient for stabilization, putting gradient zone electrophoresis on a continuous flow basis, and Dobry and Finn relied on suppression of thermal convection in a viscous vertical flow column. The present approach differs from the previous ones in that no porous media or concentration gradients are required for stabilization against thermal convection, and in the use of electromagnetic forces in combination with an electric field to obtain the desired motion of the ions in a free solution, stabilization being achieved by revolution of the electrophoretic column about a horizontal axis. The resulting stability is so great that high current densities in cooled liquid columns can be employed permitting continuous application of potential gradients in the vicinity of 50 Volts/cm and brief application of fields exceeding 100 Volts/cm. The use of very thin and sharp "streaks" of ions in strong electric fields leads to clear-cut separations within time intervals of the order of a few seconds (Fig. 10d). The method is applicable to suspended particles as well as to ions in solution.

The application described below is designed for separation on a micro-scale, processing mixtures at the rate of less than 0.01 cc/min. No attempt has been made as yet to construct an apparatus for large-scale separations.

Principle of the Method.—The main experimental difficulty to be overcome is thermal convection. In addition to the above mentioned methods of stabilization, there are two stabilization principles which have not been used as yet for continuous flow separations: (a) Stabilization by an electromagnetic force field, which has been used so far only in experiments on electromagnetophoresis, and (b) stabilization by rotation of the fluid, which has been used practically so far only with zone electro-