EPR of Ferric Ions in Sodium Alum

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The EPR of single crystals of sodium aluminum alum doped with ferric ions were studied at room temperature. The resonance linewidths are relatively narrow and the fine structures well resolved. The ferric ions are found to occupy sites of trigonal symmetry. There are four chemically equivalent but magnetically non-equivalent sites of ferric ions in the crystal. The trigonal axis for each site is along one of the [111] directions of the crystal lattice. The crystal field splittings are much larger than those in rubidium and potassium alums. The axial component of the crystal field is much larger than the cubic component for ferric ions in sodium alum. The second-order perturbation theory, which is usually good for s-state ions, is not applicable for ferric ions in sodium alum. The Zeeman levels of ferric ions must be solved by finding the eigenvalues of a six by six matrix. The best-fit spin Hamiltonian parameters are $g=2.007, D/g\beta=390$ gauss, $A/g\beta=35$ gauss and $F/g\beta=-91$ gauss.

INTRODUCTION

THE electron paramagnetic resonance (EPR) of Fe$^{3+}$ and Mn$^{2+}$, which are isoelectronic, has been the subject of extensive research both experimentally and theoretically. In a crystal field of trigonal symmetry, the resonance spectra of $S=5/2$ ions are generally complicated. Bleaney and Trenam have used a spin Hamiltonian with four parameters to explain the EPR of Fe$^{3+}$ in rubidium sulfate alum and potassium selenate alum. The axial field parameters $D$ and $F$ are much smaller than the cubic field parameter, $A$, in these two alums, hence a second-order perturbation formula given by Bleaney and Trenam is quite satisfactory to account for the observed resonance spectra. Kemp has observed and discussed the EPR of Fe$^{3+}$ in methylamine alum. The resonance lines of Fe$^{3+}$ in this alum observed at 300 K were very broad and not well-resolved. At 77 K, the resonance spectrum can be accounted for only when an additional rhombic term is added to the spin Hamiltonian. This implies that the local symmetry is no longer axial. The broad linewidths observed from alum crystals doped with Fe$^{3+}$ indicates the presence of growth inhomogeneity in the sample crystals as indicated by the above authors. We have grown crystals of Na-alum, NaAl(SO$_4$)$_2\cdot$12H$_2$O, doped with Fe$^{3+}$ which show relatively sharp resonance lines even at room temperature. The fine structure of Fe$^{3+}$ in Na-alum are well resolved at room temperature. The observed angular variations of the resonance lines when the magnetic field is in the (111) and the (100) planes of the crystal indicates that the local symmetry of the Fe$^{3+}$ ions in Na-alum is axial as in Rb- and K-alum. The fine-structure splitting of the ferric ion in Na-alum is experimentally observed to be quite large. Furthermore, the axial components of the crystal field ($D$ and $F$) is much larger than the cubic component ($A$), hence the second-order perturbation formula given by

The spin Hamiltonian for an Fe$^{3+}$ ion in an axial crystal field may be written as,

$$
\mathcal{H} = g \beta H S + \frac{1}{6} a \left[ S_1^2 + S_3^2 - \frac{1}{2} S(S+1) \right] + D \left[ S_2^2 - \frac{1}{3} S(S+1) \right] + \frac{1}{180} F \left[ 35 S_2^2 - 30 S(S+1) S_3^2 + 25 S_1^2 - 6 S(S+1) + 3 S_3^2 \right]$$

(1)

where $S=5/2$, $g$ is the g-factor, $\beta$ the electronic Bohr magneton, $H$ the applied magnetic field, $S_z$ the z-component of the spin operator, the $z$-axis is parallel to the trigonal axis of the crystal field.

The $\xi\eta\zeta$ axes are three mutually perpendicular axes which are the cubic axes of the crystal field. $D$ and $F$ are the axial field parameters and $a$ is the cubic field parameter.

Fe$^{3+}$ replaces Al$^{3+}$ in a Na-alum crystal. The nearest neighbors of Fe$^{3+}$ in the crystal lattice consists of six water molecules located at the corners of a distorted octahedron. In Na-alum, the trigonal axis of the water-octahedron coincides with the $[111]$ direction of the crystal, but its cubic axes do not coincide with the cubic axes of the crystal, rather, the two sets of cubic axes are related by a rotation of an angle $\alpha=39.6$ degrees around a body-diagonal of the crystal lattice. This fact plus the fact that in Na-alum the spin Hamiltonian parameters $D$ and $F$ are much larger than a makes the resonance spectrum of the ferric ions fairly complicated.

The spin Hamiltonian given in eq. (1) adopted two different coordinate systems, but it reflects more closely the local environment of the ferric ions in the crystal. To calculate the eigenvalues of this spin Hamiltonian, the $\xi\eta\zeta$ system must be rotated first to a new coordinate system whose $z$-axis is along the trigonal axis of the crystal field. Such a coordinate system can be chosen as the following: Without loss of generality, we can consider the case when the trigonal axis is parallel to the $[111]$ axis of the crystal. Hence,

$$
\tilde{x} = (2\tilde{a} - \tilde{b} - \tilde{c})/\sqrt{6} \quad \text{(2a)}
$$

$$
\tilde{y} = (\tilde{b} - \tilde{c})/\sqrt{2} \quad \text{(2b)}
$$

$$
\tilde{z} = (2\tilde{a} + \tilde{b} - \tilde{c})/\sqrt{6} \quad \text{(2c)}
$$

In terms of the $xyz$ coordinate system, the $\xi\eta\zeta$ system can be written as,

$$
\tilde{x} = \frac{2}{3} \cos \alpha \tilde{x} + \sqrt{\frac{2}{3}} \sin \alpha \tilde{y} + \frac{1}{\sqrt{3}} \tilde{z} \quad \text{(3a)}
$$

$$
\tilde{y} = -\sqrt{\frac{2}{3}} \sin(\alpha + 30) \tilde{x} + \sqrt{\frac{2}{3}} \cos(\alpha + 30) \tilde{y} + \frac{1}{\sqrt{3}} \tilde{z} \quad \text{(3b)}
$$

$$
\tilde{z} = \sqrt{\frac{2}{3}} \sin(\alpha - 30) \tilde{x} - \sqrt{\frac{2}{3}} \cos(\alpha - 30) \tilde{y} + \frac{1}{\sqrt{3}} \tilde{z} \quad \text{(3c)}
$$

In terms of the $xyz$ coordinate system, the spin Hamiltonian in eq. (1) is now transformed into,

$$
\mathcal{H} = g \beta H S \cos \theta + \frac{1}{2} g \beta H (e^{i\Psi} S_x + e^{-i\Psi} S_x) + \frac{1}{180} \left[ a(\cos 3\alpha \Psi + \sin 3\alpha \Psi^2) \right] \quad \text{(4)}
$$

In the above equation, $\theta$ is the angle between the magnetic field and the trigonal axis of the crystal field, $\varphi$ is the angle between the projection of the magnetic field on the (111) plane and the $z$ axis, $S_x$ and $S_y$ are the raising and lowering spin operators. $\Theta_0^0, \Theta_0^1$ and $\Theta_0^2$ are Stevens' 5 equivalent spin operators $\hat{\phi}$.

The spin Hamiltonian in eq. (4) can be rearranged in the following form,

$$\mathcal{H} = g \beta H S + B \Theta_0^1 + B \Theta_0^2 + H \Theta_0^2 = \mathcal{H}$$

Where $B_0 = D/3, B_1 = -(a-F)/180, B_2 = \sqrt{2}/9 a \cos 3\alpha$, and $C_1 = \sqrt{2}/9 a \cos 3\alpha$. The quantization axis is normally chosen as parallel to the direction of the magnetic field. To do this, the spin operators in eq. (5) have to be transformed again. Mankowitz and Low, V. Lupei et al., in discussing the forbidden transitions of Mn$^+$ ions (isoelectronic with Fe$^{2+}$), have derived the required spin Hamiltonian.

$$\mathcal{H} = g \beta H S + B \Theta_0^1 \left[ \frac{1}{2} (3 \cos^2 \theta - 1) \Theta_0^1 + 6 \sin \theta \cos \Theta_0^1 + \frac{3}{2} \sin^2 \theta \Theta_0^1 \right]$$

$$+ B_1 \left[ \frac{1}{2} (3 \cos^2 \theta - 30 \cos^3 \theta + 3) \Theta_0^1 - 5 \sin \theta \cos \Theta_0^1 (7 \cos^3 \theta - 3) \Theta_0^1 \right]$$

$$+ \frac{5}{2} \sin^3 \theta (7 \cos^3 \theta - 1) \Theta_0^1 - 35 \sin^3 \theta \cos \Theta_0^1 + \frac{35}{2} \sin^3 \theta \Theta_0^1 \right]$$

$$+ \frac{\sqrt{2}}{9} a \cos 3 (\varphi - \alpha) \left[ \frac{1}{2} \sin^3 \theta \cos \Theta_0^1 + \frac{3}{4} \sin^3 \theta (4 \cos^3 \theta - 1) \Theta_0^1 \right]$$

$$+ \frac{3}{4} \sin \theta \cos \Theta_0^1 \Theta_0^1 + \frac{1}{4} (4 \cos^3 \theta + 3 \cos^3 \theta - 3) \Theta_0^1 \right]$$

$$- \frac{\sqrt{2}}{9} a \sin 3 (\varphi - \alpha) \left[ \frac{1}{4} \sin^3 \theta \cos \Theta_0^1 \right]$$

$$+ \frac{1}{4} \sin \theta (3 \cos^3 \theta - 1) \Theta_0^1 + \frac{1}{4} \cos \theta (9 \cos^3 \theta - 3) \Theta_0^1 \right] \right]$$

$$- \frac{1}{8} \sin \theta (1 + 3 \cos^2 \theta) \Theta_0^1 \right]$$

(6)

Where the new $z$-axis is now parallel to the magnetic field, $\theta$ and $\varphi$ are the polar angles of the magnetic field with respect to the $xyz$ coordinates system.

For computational purposes, the spin Hamiltonian in eq. (6) can be rearranged in the following form,

$$\mathcal{H} = g \beta H S + A \Theta_0^0 + A \Theta_0^1 + A \Theta_0^2 + A \Theta_0^3 + A \Theta_0^4 + A \Theta_0^5 + A \Theta_0^6$$

$$+ B \Theta_0^1 + B \Theta_0^2 + B \Theta_0^3 + B \Theta_0^4 \right]$$

(7)

The eigenvalues are the roots of the following six by six determinantal equation.

$$\begin{vmatrix}
C_1 - E & F_e e^{-i \psi} & F_e e^{-i \psi} & F_e e^{-i \psi} & F_e e^{-i \psi} & 0 \\
F_e e^{i \psi} & C_1 - E & F_e e^{i \psi} & F_e e^{i \psi} & 0 & F_e e^{i \psi} \\
F_e e^{-i \psi} & F_e e^{i \psi} & C_1 - E & 0 & F_e e^{i \psi} & -F_e e^{i \psi} \\
F_e e^{i \psi} & F_e e^{-i \psi} & 0 & C_1 - E & F_e e^{i \psi} & F_e e^{i \psi} \\
F_e e^{-i \psi} & 0 & F_e e^{i \psi} & -F_e e^{i \psi} & C_1 - E & -F_e e^{i \psi} \\
iC_1 & F_e e^{-i \psi} & -F_e e^{-i \psi} & F_e e^{-i \psi} & -F_e e^{-i \psi} & C_1 - E
\end{vmatrix} = 0$$

(8)

Where

The roots of the secular equation in (8) can be expressed in closed forms only in the case when the magnetic field is parallel to the trigonal axis. At this orientation of the magnetic field, if the high-field quantum numbers are used to designate the eigenstates, then the Zeeman levels are given by:

\[
E_{s/2} = \pm \frac{1}{2} g \beta B + \frac{1}{3} D - \frac{1}{2} (a-F) \pm \frac{1}{2} \left[ 3g \beta B \pm 6D \pm \frac{1}{3} (a-F) \right]^{1/2} + \frac{80 \alpha}{g} a^{1/2} \]

\[
E_{fJ_z} = \pm \frac{1}{2} g \beta B + (a-F) \]

\[
E_{s+1} = \pm \frac{1}{2} g \beta B + \frac{1}{3} D - \frac{1}{2} (a-F) \pm \frac{1}{2} \left[ 3g \beta B \mp 6D \mp \frac{1}{3} (a-F) \right]^{1/2} + \frac{80 \alpha}{g} a^{1/2} \]

At other orientations of the magnetic field, the eigenvalues have to be obtained by numerical methods. We expand the six by six determinant equation into an ordinary equation of the sixth order. The roots of this equation is then solved by using a routine called the 'iterative rootfinder for user-defined functions'. An HP 9825 desk-top calculator was used to find the roots. The roots can be found to any desired degree of accuracy in a reasonably short time.

**EXPERIMENTAL RESULTS**

The crystal samples of the Na-alum doped with ferric ions used in this experiment were grown by the method of slow evaporation of aqueous solution. Equal molar quantities of sodium sulfate and aluminum sulfate, and a small amount of ferric sulfate were dissolved into distilled water. The crystals were grown at a constant temperature in between 15 and 20 degrees centigrade. Two types of crystals, though not at the same time, were obtained. One type of crystal, whose growth habit is very similar to that of potassium alum, is cubic in structure. The other type of crystal, which appeared as elonged tablets, is monoclinic in structure. The as-grown sodium alum crystals were octahedral in shape which shows prominently the (111) and the (100) types crystal planes. The crystals were transparent and showed no noticeable absorption trace in the visible region of:

the spectrum. Even when a relatively large amount of ferric sulfate was added into the solution during growth, the crystals obtained still appear to be colorless, and its EPR signals were not enhanced to any great degree. Apparently, only a small concentration of ferric ions can be doped into sodium alum.

The crystals were studied by using a commercial X-band EPR spectrometer at room temperatures. As the magnetic field is rotated in a (111) plane of the crystal sample, the recorder traces show five resonance lines whose resonance fields were independent of the orientations of the magnetic field in the (111) plane. In addition to these, three groups of lines with a periodicity of 120 degrees in magnetic angle with respect to each other were also observed in the recorder traces. The same type of resonance spectrum was recorded no matter which one of the (III)-type planes of the octahedral shape of the crystal sample was studied. This indicates that the ferric ions retain the trigonal symmetry occupied by the aluminum ions.

Fig. 1 shows part of the recorded resonance lines when the magnetic field was perpendicular to one of the (111) planes of the crystal sample. The strong, high-field lines are due to the allowed fine-structure transitions and the weak, low-field lines are due to forbidden transitions of the types $\Delta m=\pm 2, \pm 3, \pm 4$ and $\pm 5$. The observed spectrum is consistent with the model that there are four chemically equivalent but magnetically non-equivalent sites of the ferric ions inside the crystal. At this orientation of the magnetic field, the polar angle $\theta$ is zero for one of the site and is $\theta=\cos^{-1}(1/\sqrt{3})=\approx 70^\circ$ for the other three sites. As is evident from the form of the spin Hamiltonian given in eq. (6), the eigenvalues, and hence the resonance fields, have a periodicity of 120 degrees with respect to the azimuthal angle $\varphi$. Therefore, when the magnetic field is parallel to one of the body-diagonals of the crystal lattice, three of the ferric ions sites become degenerate and its resonance spectra coalesce with each other.

Numerical analysis of the resonance conditions at $\theta=0^\circ$ as derived from eq. (10) shows that the magnitudes of the resonance fields depend strongly on the spin Hamiltonian parameters $D$ and the difference $a-F$. As long as $D$ and $a-F$ are kept constant, the values of, the resonance fields do not vary appreciably for different sets of $a$ and $F$. The same can be said for the case when the magnetic field is in a (111) plane of the crystal. As a consequence, only $D$ and $a-F$ can be determined from the resonance fields at $\theta=0$ and $\theta=90$, but not the values of $a$ and $F$ separately. The tilt angle $\alpha$ can not be determined from these two orientations of the magnetic field also, for at these two orientations the resonance fields are independent of this angle. $D/g\beta=390$ gauss and $(a-F)/g\beta=126$ gauss gives the best fit between the experimental values and the calculated values of the resonance fields at $\theta=0$ and $\theta=90$. To determine separately the values of the parameters $a$ and $F$, at least one other orientation of the magnetic field must be considered. One such orientation is $\hat{\phi}=\cos^{-1}(1/\sqrt{3})$, which occurs when the magnetic field is along the [111] direction of the crystal. Another such orientation which has the most simple resonance spectrum is when the magnetic field

![Fig. 1](image-url)
Fig. 2. Energy-level diagram of the $S=\frac{5}{2}$ manifold of ferric ions in sodium alum as a function of the magnetic field for the case when the magnetic field is parallel to the trigonal axis of the crystal field.

Fig. 3. Energy-level diagram of the $S=\frac{5}{2}$ manifold of ferric ions in sodium alum as a function of magnetic field for the case when the magnetic field is parallel to a cubic axis of the crystal lattice.
Fig. 4. Energy-level diagram of the $S=\frac{1}{2}$ manifold of the ferric ions in sodium alum as a function of the magnetic field for the case when the magnetic field makes an angle of $\theta = 0^\circ$ with the trigonal axis of the crystal field.

Fig. 5. Energy-level diagram of the $S=\frac{1}{2}$ manifold of the ferric ions in sodium as a function of magnetic field for the case when the magnetic field is perpendicular to the trigonal axis of the crystal field.
**Table I.** Comparison between the experimental values and the calculated values of the allowed fine structure of ferric ions in sodium alum for the case when the magnetic field is along the trigonal axis of the crystal field. The spin Hamiltonian parameters used to calculate the theoretical values are cited in the text.

<table>
<thead>
<tr>
<th>Experimental values (G)</th>
<th>Calculated values (G)</th>
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<tbody>
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<tr>
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</tr>
<tr>
<td>1856</td>
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</tbody>
</table>

**Table II.** Comparison between the experimental values and the calculated values of the allowed fine structure of ferric ions in sodium alum for the case when the magnetic field is along a cubic axis of the crystal.

<table>
<thead>
<tr>
<th>Experimental values (G)</th>
<th>Calculated values (G)</th>
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<tbody>
<tr>
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</tr>
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<td>2848</td>
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</tbody>
</table>

**Table III.** Comparison between the experimental values and the calculated values of the allowed fine structure of ferric ions in sodium alum for the case when the magnetic field makes an angle of $\theta = \cos^{-1}(1/3)$ with the trigonal axis of the crystal field. The azimuthal angle of the magnetic field is chosen as $\phi = 180^\circ$.

<table>
<thead>
<tr>
<th>Experimental values (G)</th>
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<td>2649</td>
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</tbody>
</table>

**Table IV.** Comparison between the experimental values and the calculated values of the allowed fine structure of ferric ions in sodium alum for the case when the magnetic field is in a (111) plane of the crystal lattice. The azimuthal angle of the magnetic field is chosen as $\phi = 0^\circ$.

<table>
<thead>
<tr>
<th>Experimental values (G)</th>
<th>Calculated values (G)</th>
</tr>
</thead>
<tbody>
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<tr>
<td>2451</td>
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</tbody>
</table>
is perpendicular to a (100) plane of the crystal. At this orientation of the magnetic field, all four sites become degenerate. For the angle \( \alpha \) we have used the value of 36.9 as determined from diffraction experiment. At the microwave frequency of 9.14 GHz, the best-fit spin Hamiltonian parameters are \( g_z = 2.007, D/g_B = 390 \) gausses, \( a/g_B = 35 \) gausses and \( F/g_B = -91 \) gausses for the Fe\(^{3+}\) ions in sodium alum.

Using this set of spin Hamiltonian parameters, we have calculated the Zeeman splittings as a function of the magnetic field for \( \theta = 0, 55, 70 \) and 90 degrees. The results are plotted in Fig. 2 to Fig. 5. Table 1-4 tabulate the experimental resonance fields of the allowed transitions and the calculated values for these four orientations.

In conclusion, we find that good crystal samples of sodium alum doped with ferric ions can be grown from aqueous solutions. The resonance linewidths of these samples at room temperature are small as compared with other alums doped with Fe\(^{3+}\). The trigonal distortion of the water-molecule octahedron surrounding the ferric ion sites is relatively large, in view of the fact that the experimentally determined axial-field spin Hamiltonian parameters \( D \) and \( F \) are much larger than the cubic-field parameter \( a \).