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SIGN OF THE GROUND-STATE CUBIC CRYSTAL FIELD SPLITTING PARAMETER IN Fe^{3+}

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Recent interest has focused on the mechanism of the splitting of the nominally spherically symmetric $6S_{5/2}$ ground state of Fe^{3+} in cubic crystalline fields. Watanabe[1] has shown that a splitting arising from perturbations by excited states derived from the $3d^5$ configuration involve the cubic crystalline potential, $V = C(x^4 + y^4 + z^4 - \frac{3}{5}r^4)$, to even powers only and will first appear as V^2. Consequently the sign of a in the cubic term of the ground-state spin Hamiltonian, $a(S_\xi{}^4 + S_\eta{}^4 + S_\zeta{}^4)$, should be independent of the sign of V. Thus, even though the cubic potentials have opposite signs at the center of a tetrahedron of point charges to that of an octahedron, the sign of a should be the same for both. We have verified that this is indeed the case for Fe^{3+} from the paramagnetic resonance spectrum of Fe^{3+} in octahedral and tetrahedral O^{2-} coordination in single crystals of yttrium gallium garnet, $3Y_2O_3 \cdot 5Ga_2O_3$ (hereinafter called YGaG), a being positive in both sites. This result led us to re-examine the spectrum of Fe^{3+} in rubidium aluminum sulphate where a negative sign for a was reported earlier.[2] However, we find that a is positive in this case also.

YGaG is isostructural with yttrium iron garnet[3] (YIG). There are 16 octahedral sites and 24 tetrahedral sites per unit cell which are occupied by Ga^{3+}. A 0.1 % Fe impurity enters as Fe^{3+} substitutionally for the Ga with a roughly 10:1 preference for the octahedral site. The octahedra are distorted by a stretching along the four different [111] directions (site symmetry C_{3i}), and the tetrahedra by a pulling along the three different cube edges (site symmetry S_4) giving rise to axial terms in the spin Hamiltonian for each site which are considerably larger than the cubic terms. The spin Hamiltonian for Fe^{3+} is given in reference 2. With the magnetic field in an arbitrary direction in the crystal, as many as seventy lines corresponding to $\Delta m = \pm 1$ transitions are possible (5 for each nonequivalent site as far as crystal field orientation is concerned). However, by confining the magnetic field to a (110) plane some of the sites will give identical spectra and an even further simplification results with H_{dc} along one of the principal axes. From the spectra with H_{dc} parallel to a [111] direction ($\theta = 0$ spectrum), D and $(a-F)$ for the octrahedral sites were determined with the signs found from the relative intensity of the lines at 4.2°K. Similarly, with H_{dc} parallel to the [100] direction, D and $(a + \frac{2}{3}F)$ were determined for the tetrahedral sites. To determine a separately, a detailed knowledge of the crystal structure is needed.

Among those tetrahedral sites having a common [100] axis of distortion, there are two types of sites. They differ from each other in that they are rotated about this [100] direction from a position in which the cubic axes of the tetrahedra are coincident with unit cell edges, through angles $+\alpha$ and $-\alpha$, respectively, for the two types of sites which we will call $d_{(1)}$ and $d_{(2)}$. These two sites will give rise to two distinct spectra corresponding to the term $a[S_+{}^4 e^{i4(\varphi \pm \alpha)} + S_-{}^4 e^{-i4(\varphi \pm \alpha)}]$ in the cubic part of the spin Hamiltonian for the tetrahedral site. Here φ is the angle between the projection of H_{dc} on the (100) plane and the [010] axis. As H_{dc} is rotated in the (100) plane, two perpendicular spectra ($\theta = 90°$) will be observed as is shown in Fig. 1 for the $-1/2 \to +1/2$

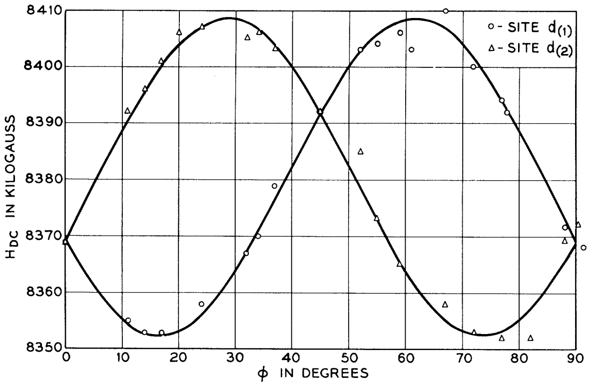

FIG. 1. Perpendicular spectrum of $-1/2 \rightarrow +1/2$ transition of Fe^{3+} in the tetrahedral site, with H_{dc} rotated in a (100) plane. The failure of some of the points to fall on the curve is due to extreme pulling of these lines by much stronger lines from the octahedral sites at certain angles of the field.

transition. The variation with φ will be of the form $C_T a \cos[4(\varphi \pm \alpha)]$, where C_T is a constant determined from first-order perturbation by diagonalization of the major portion of the spin Hamiltonian with parameters D and $(a+\frac{2}{3}F)$ determined from the parallel spectrum. As is seen from Fig. 1, α is either 16.5° or 28.5° and these two values give opposite signs for a. In the isostructural YIG, α was found to be 15.6° and we would expect it to be very much the same here, so that we can rule out with certainty 28.5° and therefore a is found to be positive.

Similarly, for those octahedral sites having the same [111] direction of distortion there are two types of sites rotated from each other about this [111] direction by an angle 2α. The site symmetry being C_{3i}, the cubic part of the spin Hamiltonian now has an $e^{+i3(\varphi \pm \alpha)}$ azimuthal dependence. Proceeding in the same manner as for the tetrahedral site and again using the crystal structure of YIG, one concludes that a is positive as Low[4] found for a similar O^{2-} coordination in MgO. The room-temperature parameters for both sites are listed in Table I.

Table I. Room-temperature parameters for both sites.

	Octahedral	Tetrahedral
D	-1384 ± 3 oersteds	-947 ± 5 oersteds
a	$+ 198 \pm 5$ oersteds	$+ 66 \pm 3$ oersteds
F	$+ 28 \pm 4$ oersteds	$- 42 \pm 4$ oersteds
g	2.003 ± 0.001	2.0047 ± 0.0005

The constant appearing in the cubic potential V is $-35q/9d^5$ and $+35q/4d^5$ for tetrahedral and octahedral sites, respectively, where d is the distance from the center of the site to the charges q located at the corners. If, in accordance with Watanabe,[1] $a \sim V^2$, then $a_{\text{oct}}/a_{\text{tet}} = (9/4)^2(d_{\text{tet}}/d_{\text{oct}})^{10}$. Using the Fe-O distances given in reference 3, one predicts $a_{\text{oct}}/a_{\text{tet}} = 2.72 \pm 0.3$, the error arising from the error in d. This is in very good agreement with the experimental value 3.00 ± 0.1.

A study of the earlier work on Fe^{3+} in rubidium aluminum sulphate showed that under the conditions encountered, i.e., 20°K and 9000 Mc/sec, a difference of intensity of only 8.5 % is to be expected between the $-3/2 \rightarrow -5/2$ and $+3/2 \rightarrow +5/2$ transitions. We re-examined the spectrum at 4.2°K and 1.6°K at 24 000 Mc/sec and it is shown in Fig. 2 for the external magnetic field parallel to a [100] direction in the crystal. The increase

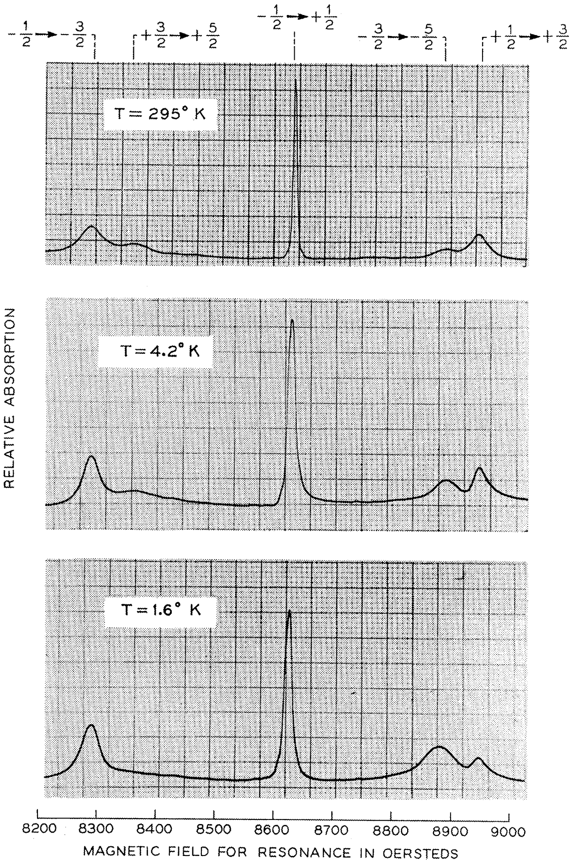

FIG. 2. Paramagnetic resonance spectrum at K-band of Fe^{3+} in rubidium aluminum sulphate with H_{dc} parallel to a [100] direction. The relative intensity at low temperature establishes the ground-state cubic field splitting parameter a as positive.

of the relative intensity of the inner high-field line and the outer low-field lines labels them as the -3/2 → -5/2 and -1/2 → -3/2 transitions, respectively, and establishes the positive sign of a for Fe^{3+} in octahedral water coordination.

Further details including the relation of the crystal field splitting parameters to ferrimagnetic anisotropy as well as a more detailed summary of splitting of S-state ions will appear in forthcoming publications.

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CANTED SPIN ARRANGEMENTS*

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The aim of this Letter is to discuss two spin systems where canted spin arrangements are very likely to occur. These are (1) the ordered iron aluminum alloys[1]; (2) the tin-substituted yttrium iron garnets.[2]

(1) Iron aluminum alloys.—A very attractive model for exchange interactions in this system has been proposed by Arrott and Sato.[1] In the "ordered" alloys there are three sublattices. One of them, A, is only partially filled up with iron, and has the saturation magnetization $M_A = I\frac{1}{2}(1-2c)$ where I is the saturation magnetization of pure iron, and $c(<\frac{1}{2})$ the aluminum percentage. The other two sublattices B' and B'' are completely filled with iron and have magnetizations $M_{B'} = M_{B''} = \frac{1}{4}I$. The assumed spatial arrangement is made of planes $B'AB''AB'\ldots$ normal to a (100) direction of the bcc structure. The $B'B''$ coupling takes place through Al atoms and is antiferromagnetic. The AB' and AB'' couplings are taken as ferromagnetic. The resultant molecular fields may be written, in the notation of Yafet and Kittel,[3]

$$H_A = -n(M_{B'} + M_{B''}),$$
$$H_{B'} = -n(M_A - \gamma_2 M_{B''}),$$
$$H_{B''} = -n(M_A - \gamma_2 M_{B'}); \qquad (1)$$

n and γ_2 are negative here. $|\gamma_2| = 4c/\mu$ where μ is the absolute value of the ratio between ferromagnetic exchange integrals as defined in reference 1. A discussion similar to that of reference 3 then gives the following results:

	Ground state	Upper transition point
$0 < c < c'$	Ferro	Ferro
$c' < c < c''$	Triangular	Ferro
$c'' < c < \frac{1}{2}$	Triangular	Antiferro

c' and c'' are defined by the equations

$$\mu(1-2c') - 4c' = 0, \qquad (2)$$
$$\mu^2(1-2c'') - 8(c'')^2 = 0. \qquad (3)$$

Typical values are quoted below:

	$\mu = 2.00$	$\mu = 1.60$	Exp.[1]
c'	0.25	0.22	0.28
c''	0.36	0.33	0.33

The ground state is never antiferromagnetic (the different, incorrect result of reference 1 stems from the use of the Ising model). The spontaneous magnetization at $T=0$ is

$$M_0 = I(1-c), \qquad c < c'$$
$$M_0 = \tfrac{1}{2}I(1-2c)(1+\mu/4c), \qquad c > c'. \qquad (4)$$

The M_0 vs c curve displays a typical change in slope which is indeed observed (Fig. 1). The low-temperature susceptibility, due to changes

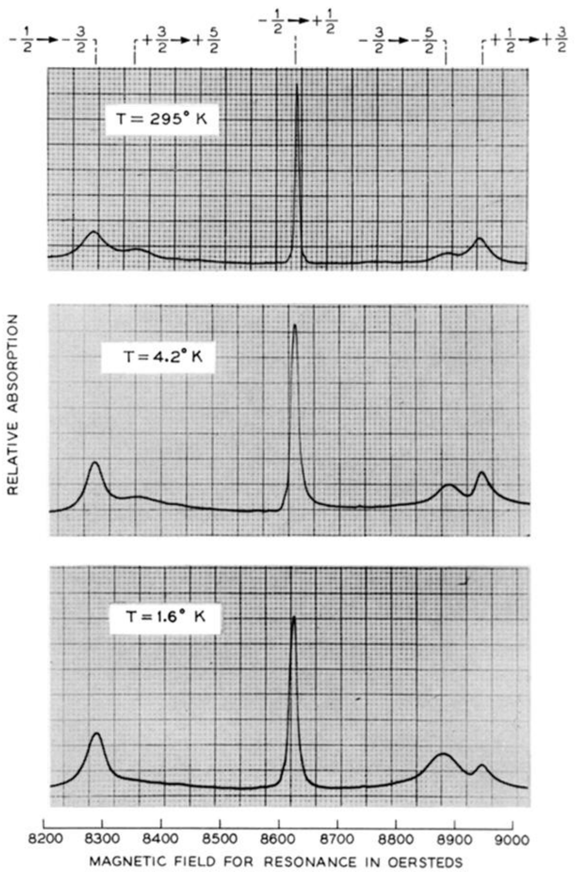

FIG. 2. Paramagnetic resonance spectrum at *K*-band of Fe^{3+} in rubidium aluminum sulphate with H_{dc} parallel to a [100] direction. The relative intensity at low temperature establishes the ground-state cubic field splitting parameter a as positive.