PHYSICAL REVIEW B VOLUME 20, NUMBER 7 1 OCTOBER 1979

EPR of Fe^{3+} and Mn^{2+} in single-crystal $ZnGa_2O_4$ spinel

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(Received 1 May 1979)

The EPR spectra of Fe^{3+} and Mn^{2+} in the single crystal $ZnGa_2O_4$ have been measured. The room-temperature spin-Hamiltonian parameters of Fe^{3+}, which are related to the magnetocrystalline anisotropy in the spinel ferrites, are $g_{\parallel} = 2.005(2)$, $g_{\perp} = 2.008(3)$, $D = -0.2442(2)$ cm^{-1}, $a = +0.0444(8)$ cm^{-1}, and $a - F = 0.0353(4)$ cm^{-1}. For Mn^{2+} the parameters are $g = 2.0011(6)$ and $A = -76.2(2) \times 10^{-4}$ cm^{-1}. The details of the Mn^{2+} spectra indicate a small degree of *A*-*B* disorder in this normal spinel. The Fe^{3+} and Mn^{2+} are located on *B* and *A* sites, respectively.

The spin-Hamiltonian parameters of Fe^{3+} in spinel crystals are relevant to the "single-ion" mechanism[1] of cubic anisotropy in the isomorphous ferrites. We have made an EPR examination of well-formed crystals of $ZnGa_2O_4$ and have identified the spectra of three ions: Cr^{3+}, Fe^{3+}, and Mn^{2+}. The first conforms with the properties reported by Kahan and Macfarlane.[2] The other two have not been reported and are the subject of this communication.

$ZnGa_2O_4$ is a normal cubic spinel of space group O_h^7 and lattice parameter[3] $a_0 = 8.33$ Å, with Zn in tetrahedral (T_d) *A* sites and Ga in trigonally distorted octahedral (D_{3d}) *B* sites. The crystals, which have a faint yellow color, were grown using the method described by Van der Straten *et al.*[4] No attempt was made to deliberately dope the crystals and the reagents used were nominally 99.99% pure. The EPR signal intensities gave estimates of 100 and 3 ppm for the Fe^{3+} and Mn^{2+} concentrations, respectively.

Spectra were obtained at room temperature and 4.5 K with a Varian E-9 *X*-band spectrometer with a Helitran refrigeration insert. Data were taken at magnetic field orientations throughout the $(1\bar{1}0)$ plane of the sample. Field values for resonance for $\vec{H}$ parallel to [001], [110], and [111] were calibrated with an NMR magnetometer and used for computer optimization of the spin-Hamiltonian parameters.

a. Fe^{3+}. The Fe^{3+} spectra can be fit by a spin Hamiltonian suitable to the trigonally distorted *B* sites. Suppressing constant terms, for $S = \frac{5}{2}$ this takes the form[5]

$$\begin{aligned}\mathcal{H} = {} & g_{\parallel}\mu_B H_z S_z + g_{\perp}\mu_B(H_x S_x + H_y S_y) \\ & + D S_z^2 + \tfrac{1}{180} F (35 S_z^4 - \tfrac{475}{2} S_z^2) \\ & + \tfrac{1}{6} a (S_\xi^4 + S_\eta^4 + S_\zeta^4) \ ,\end{aligned}$$

where ξ, η, ζ refer to cube edge directions and in the set *x*, *y*, *z* the *z* direction is along the trigonal axis which is one of the $\langle 111 \rangle$ directions. The spin-Hamiltonian parameters of Fe^{3+}, derived from 20 well-defined lines observed in the three orientations, are shown in Table I. The rms error of 16 G is much less than a typical linewidth. The sign of *D* was confirmed by population differences at the two temperatures. Only a slight improvement in fit is achieved using our tabulated *g* values instead of average isotropic values.

In the "single-ion" explanation[1] of the cubic anisotropy constant K_1 of the spinel ferrites, *D*, *a*, and *F* all play a role. The dominant contribution arises from the *a* term. Because of averaging over equivalent sites, K_1 is less sensitive[6] to *F*, while *D* affects K_1 only via the small second-order Wolf term D^2/H_m in which H_m is the molecular field. In Table II we summarize the room-temperature values of *a*, *F*, and *D* for Fe^{3+} in single-crystal spinel samples. It should be noted that the lattice constant of $ZnGa_2O_4$ is more nearly equal to those of the ferrites than are the lattice constants of the $ZnAl_2O_4$,[7] $MgAl_2O_4$,[8] and $Li_{0.5}Al_{2.5}O_4$ hosts[9] studied earlier by EPR. Since the Fe^{3+} is located on an *A* site in ordered $Li_{0.5}Al_{2.5}O_4$ rather than on a *B* site as in the other spinels, direct comparison is not possible but it is given for completeness.

b. Mn^{2+}. For Mn^{2+} in *A* sites one expects resonance patterns similar to those found by Soulié

TABLE I. Spin-Hamilontian parameters of Fe^{3+} in $ZnGa_2O_4$

	Room Temp.	4.5 K
$g_{\parallel}$	2.005(2)	2.006(2)
$g_{\perp}$	2.008(3)	2.008(4)
D (cm^{-1})	−0.2442(2)	−0.2476(2)
$a - F$ (cm^{-1})	+0.0353(4)	+0.0372(5)
a (cm^{-1})	+0.0444(8)	+0.0465(9)

TABLE II. Room-temperature zero-field splitting parameters for Fe^{3+} in spinel single crystals.

Host	a (cm^{-1})	F (cm^{-1})	D (cm^{-1})	a_0 (Å)	Ref.
$ZnGa_2O_4$	0.0444	0.0091	−0.2442	8.33	this work
$ZnAl_2O_4$	0.0575	0.0104	−0.3402	8.086	7
$MgAl_2O_4$	0.0475	0.0017	−0.2467	8.089	8
$Li_{0.5}Al_{2.5}O_4$	≃0.01[a]	∼ ±0.0067[a]	±0.104[a]	7.92	9

[a] Fe^{3+} is on an A site in ordered $Li_{0.5}Al_{2.5}O_4$ rather than a B site. The a value is preliminary.

et al.[10] for Mn^{2+} in $ZnAl_2O_4$, in which the members of the characteristic hyperfine-split sextet of Mn^{2+} have an orientation-dependent splitting and variable widths due to combined effects of a small cubic field term and second-order hyperfine terms. Instead we observe a situation more like that found[11,12] for Mn^{2+} in $MgAl_2O_4$, in which the components are all of constant width (18 G here) and show additional broadening or structure only near $\vec{H} \parallel [001]$. It appears that there is sufficient lattice disorder to introduce ill-defined lower-symmetry crystal fields which broaden and eliminate from observability all but the $M=\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transitions. The collapse of trigonal field contributions at the [001] orientation apparently allows some additional transitions to become distinguishable. We observe no "forbidden" doublets between sextet lines. From this we conclude that the magnitude of the lower-symmetry terms is less than 0.01 cm^{-1}. If crystal-field contributions are assumed to average away, evaluation of the parameters in the simple Hamiltonian $\mathcal{H} = g\mu_B \vec{H}\cdot\vec{S} + A\,\vec{I}\cdot\vec{S}$ leads to the room-temperature [4.5 K] values $g=2.0011(6)$ [2.0012(6)] and $A=-76.2(2)\times 10^{-4}$ $[-76.9(2)\times 10^{-4}]$ cm^{-1}, assumed negative. The g and A values are quite compatible with those for Mn^{2+} in $ZnAl_2O_4$ and $MgAl_2O_4$.[11]

From the identified spectra, which essentially exhaust the features observed, we conclude that Fe^{3+} is substitutional for Ga in $ZnGa_2O_4$ and Mn^{2+} replaces Zn. The difficulties with the Mn^{2+} spectra, which also are reflected in moderately broad asymmetric line shapes for Fe^{3+}, indicate that the ordering of Zn and Ga on the A and B sites, respectively, is imperfect.

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