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Electron Spin Resonance of Fe^{3+} in ZnAl_2O_4 Spinel and Anisotropy Energies in Ferrites¹⁾

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Abstract. The ESR spectra of iron doped ZnAl_2O_4 spinel have been measured at 35 GHz at room temperature. The Fe^{3+} ions occupy only the trigonally distorted B sites in the center of oxygen octahedrons. The g tensor shows a slight asymmetry with $g_{\parallel} = 2.0001 \pm 0.0004$ and $g_{\perp} = 2.0019 \pm 0.0008$. The evaluated electric interaction parameters are in cm^{-1} : $D = (-) 0.34017 \pm 0.00015$, $a - F = (+) 0.04707 \pm 0.00021$, $a = (+) 0.0575 \pm 0.0004$. The sign of a relative to $a - F$ and D could be determined by the asymmetry of the spectra around $\theta = 90^\circ$. The large value of a shows that the 'single-ion' anisotropy energy of Fe^{3+} ions is a main source of the magnetic anisotropy energies in ferrites. The differences to the ESR results of Fe^{3+} ions in MgAl_2O_4 , for which almost equal structure constants have been observed, demonstrate that D , a , and F might be very sensitive to changes in covalent bonding in these fairly ionic crystals.

ZnAl_2O_4 spinels are almost ordered normal spinels [1]. The Zn ions occupy A sites of cubic point symmetry in the center of oxygen tetrahedra, whereas the Al ions are in B sites and surrounded by trigonally distorted oxygen octahedra. The four crystallographically equivalent positions of the B site can be discriminated by electron spin resonance.

Single crystals of iron doped ZnAl_2O_4 were grown by the flux technique. The slightly brown-yellow samples of octahedral habit have been investigated with a 35 GHz superheterodyne electron spin resonance spectrometer at room temperature. The spectra show that the four positions of the B site are equally populated by Fe^{3+} ions [2, 3] and, at a lower concentration, by Cr^{3+} impurities [4]. Additional lines arise from Mn^{2+} ions [5].

The ground state of Fe^{3+} ($3d^5$, $S_{5/2}$) in a site with point symmetry $\bar{3}m$ (D_{3d}) can be described by an effective spin Hamiltonian with $S = 5/2$. In $\bar{3}m$ symmetry there exist only three independent Stark parameters which can be evaluated by investigating differences of energy levels. It is convenient to write the spin Hamiltonian relative

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to a set of axes, x, y, z , which express the point symmetry of the site occupied. In the following, all directions will be given relative to the cubic unit cell axes ξ, η, ζ . Choosing a Fe^{3+} ion in an oxygen octahedron distorted along the $[111]$ direction, the z axis is along this threefold axis of distortion $[111]$. Hence the axial Stark parameters D and F of the second and fourth degree respectively, will contribute only to the diagonal matrix elements. For the cubic Stark parameter a of fourth degree the axes of this specific interaction should be known. In garnets, they must be determined by experiment [6]. In cubic spinels, these axes are fixed by the space group $\text{Fd } 3m (O_h^7)$ [7]. They coincide with the cubic unit cell axes ξ, η, ζ . This interaction gives diagonal and real third off-diagonal matrix elements for x along $[\overline{112}]$ and y along the two-fold axis $[\overline{110}]$.

If the direction of the applied magnetic field H relative to x, y, z is described by the polar angle θ and the azimuthal angle φ , the spin Hamiltonian suppressing some constant terms is written [6] as

$$\begin{aligned} \mathcal{H} = & g_{\parallel} \beta H S_z \cos \theta + (1/2) g_{\perp} \beta H \sin \theta (S_+ e^{i\varphi} + S_- e^{-i\varphi}) + D S_z^2 \\ & - (1/180) (a - F) [35 S_z^4 - 30 S (S + 1) S_z^2 + 25 S_z^2] \\ & - (\sqrt{2}/36) a [S_z (S_+^3 + S_-^3) + (S_+^2 + S_-^2) S_z]. \end{aligned}$$

In the absence of Stark terms of fourth degree the spectra would be equal for θ and $180^\circ - \theta$, hence the lines would have extreme field values at $\theta = 90^\circ$ for fixed angle φ . However, the last term of the above spin Hamiltonian creates different spectra for θ and $180 - \theta$. Figure 1 shows different field values for θ and $180^\circ - \theta$. This asymmetry allows the direct determination of the sign of the parameter a relative to D .

The five parameters evaluated from 25 line positions at three suitable orientations at room temperature are tabulated in Table 1. The signs given are relative signs determined by this experiment. There seems to be an indication of an anisotropic g tensor with $g_{\parallel} - g_{\perp} = -(18 \pm 9) \times 10^{-4}$. In Table 2 the measured line positions are compared to the calculated values. The deviations are small compared to the line widths defined between the extreme values of the derivative of the absorption signal.

In addition, the line positions have been calculated for a rotation of H in the xz plane for 34.85 GHz. The solid lines in Fig. 1 represent all possible transitions disregarding their relative intensity. Most sections without experimental points are due to complex spectra of overlapping lines rather than to the lack of measurable lines.

In MgAl_2O_4 a negative D for Fe^{3+} has been found [8]. Diffraction studies [1, 9] gave almost equal structure parameters for ZnAl_2O_4 and MgAl_2O_4 , therefore a negative sign for D in ZnAl_2O_4 is most probable, resulting in a positive sign for the cubic off-diagonal parameter a (proportional to b_3^4 in other notations) and $F = +0.0104 \pm 0.0005 \text{ cm}^{-1}$. Determinations of the sign of a in other crystals with axial distortions usually must assume that $|F| < |a|$ which is found to be true in ZnAl_2O_4 , but may be wrong for very large axial distortions.

The main source of the magnetocrystalline anisotropy energy of cubic ferri-magnetic substances containing Fe^{3+} is the 'single-ion' anisotropy energy of these

ions [10]. All the 'multi-ion' sources [11] such as anisotropic exchange interaction and higher order magnetic dipole energy are at least an order of magnitude too small to account for the observed anisotropy [12]. The 'single-ion' anisotropy can in principle be measured by electron spin resonance in isomorphous diamagnetic environment and can be expressed in terms of the spin Hamiltonian parameters [12]. Geschwind [6] compared the spin parameters measured in yttrium-gallium-garnet to the anisotropy energy in the isomorphous yttrium-iron-garnet. The experimental value of the anisotropy constant K_1 at $T = 0^\circ$ is twice the value calculated with the 'single-ion' model and further deviations occur at higher temperatures [13]. This discrepancy may arise from the difference of the parameters a and F in these crystals [6].

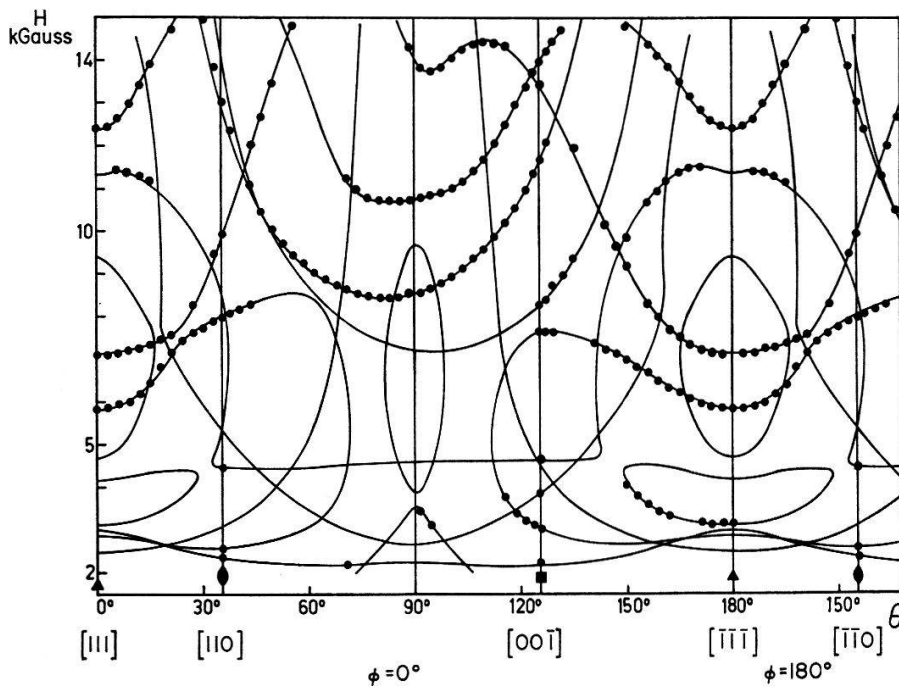


Figure 1

Angular dependence of the Fe^{3+} ESR spectra in ZnAl_2O_4 for 34.85 GHz. The magnetic field H is rotated in the xz plane, containing the $[111]$, $[110]$, $[001]$ directions. The points represent the measured transitions, and the lines the calculated transitions.

The experimental proof of the 'single-ion' model for ferrites has been retarded by the fact that it was difficult to obtain ordered diamagnetic single crystals as host for Fe^{3+} ions, since the lines should not be broad to allow also the determination of the off-diagonal parameter a [14]. A complete determination of the Fe^{3+} parameters was possible in a natural MgAl_2O_4 crystal showing a relatively ordered structure [15, 16]. The parameters were found to be surprisingly large, see Table 1. However, the distances r_{B-0} from the center of the B site to the surrounding oxygens are markedly smaller in MgAl_2O_4 than in many ferrites. In lack of a better theory the prediction of Watanabe [17], that a is proportional to the square of the cubic potential $V_4 \sim (1/r_{B-0})^5$, has been applied. This estimate showed that the contribution of the 'single-ion' anisotropy of Fe^{3+} in octahedral sites alone can account for the measured anisotropy constants K_1 ($T = 0^\circ$) in NiFe_2O_4 and MnFe_2O_4 [16, 18, 19]. However, the comparison of the parameters for Fe^{3+} measured in MgAl_2O_4 and ZnAl_2O_4 demonstrates

clearly, that the proof of the 'single-ion' assumption for the anisotropy energy in ferrimagnets obtained by measuring the spin parameters in diamagnetic isomorphous crystals is limited to a test of the order of magnitude.

These diamagnetic host structures have almost equal structure constants as investigated by x -ray [9] and neutron diffraction [1], and no difference in the Al-O distances could be measured, see Table I. Further, nuclear magnetic resonance of ^{27}Al gives equal quadrupole interaction constants in both structures [20, 21]. The parameters D for Cr^{3+} ions in B sites have a ratio $D_{\text{ZnAl}_2\text{O}_4}/D_{\text{MgAl}_2\text{O}_4} = 1.012 \pm 0.002$ [4, 22]. However, the parameters for Fe^{3+} ions are very different. The ratios $D_{\text{ZnAl}_2\text{O}_4}/D_{\text{MgAl}_2\text{O}_4} = 1.379 \pm 0.002$ and $a_{\text{ZnAl}_2\text{O}_4}/a_{\text{MgAl}_2\text{O}_4} = 1.21 \pm 0.03$ are clearly larger than one. The value $|F| = 0.0017 \pm 0.0016 \text{ cm}^{-1}$ in MgAl_2O rises to $|F| = 0.0104 \pm 0.0005 \text{ cm}^{-1}$ in ZnAl_2O_4 . For comparison, the ratio $[r_{\text{Al-O}(\text{MgAl}_2\text{O}_4)}/r_{\text{Al-O}(\text{ZnAl}_2\text{O}_4)}]^{10}$ is 1.00 ± 0.01 , which should be equal to the ratio of the parameters a given above if the theory of Watanabe [17] would be applicable.

Although in both host crystals the arrangement of the next six oxygen ions and the next six aluminium ions is equal and only the next nearest cations are manganese or zinc respectively, the arrangement may be different around an impurity Fe^{3+} ion, and again these deviations may not be equal for both structures. Till now there is no way to determine whether these deviations are primarily different arrangements of the near nuclei or different distributions of the electrons involved, due to the well known difference in covalency between Mg and Zn.

Table 2

Lattice constants and ESR-parameters of Fe^{3+} and Cr^{3+} at octahedral B sites in ZnAl_2O_4 and MgAl_2O_4 at room temperature.

		ZnAl_2O_4		Ref.	MgAl_2O_4		Ref.
Growth method		Synthetic			Natural		
Lattice constants							
a_0	Å	8.086	± 0.001	[9]	8.0890	± 0.0005	[9]
u_0		0.3889	± 0.0003	[1]	0.3889	± 0.0001	[1]
$r_{\text{Al-O}}$	Å	1.916	± 0.002		1.916	± 0.001	
ESR Fe^{3+}				[3]	[15, 16]		
g_{\parallel}		2.0001	± 0.0004		2.001	± 0.003	
g_{\perp}		2.0019	± 0.0008		2.0	± 0.1	
D	cm^{-1}	(-) 0.34017	± 0.00015		- 0.2467	± 0.0005	
$a - F$	cm^{-1}	(+) 0.04707	± 0.00021		+ 0.0458	± 0.0009	
a	cm^{-1}	(+) 0.0575	± 0.0004		+ 0.0475	± 0.0013	
ESR Cr^{3+}				[4]	[22]		
g_{\parallel}		1.9840	± 0.0003		1.985	± 0.001	
g_{\perp}		1.9798	± 0.0005		1.980	± 0.002	
$ D $	cm^{-1}	0.9304	± 0.0003		0.9193	± 0.0016	

Independent of these speculations, one might expect very large changes in the parameters a and F in arrangements where also the nearest cations are different which is the case for ferrites. Therefore the experimental results reported here may indicate

that the 'single-ion' model can be proved in diamagnetic substances only to about an order of magnitude. In addition, the value of a in ferrimagnets may vary markedly with the concentration in solid solutions, which would make the application of the 'single-ion' model for these systems more difficult [23].

Table 2

Measured and calculated values for ESR transitions of Fe³⁺ in ZnAl₂O₄ at room temperature

Angles		Frequency	Magnetic field	Theory	Line width*)
θ	φ	GHz	Gauss	Gauss	Gauss
0	0	33.759	6976	6980	48
0	0	33.759	5468	5459	121
0	0	33.759	11986	11985	67
0	0	33.759	18515	18515	68
0	0	34.843	7115	7112	48
0	0	34.843	5814	5811	121
0	0	34.843	12375	12377	68
0	0	34.843	18904	18903	88
35.26	0	35.115	9929	9962	268
35.26	0	35.115	2513	2527	112
35.26	0	35.115	8015	8025	90
35.26	0	35.115	16114	16106	102
35.26	0	35.115	2399	2398	41
35.26	0	35.115	13122	13142	235
70.53	0	34.843	11214	11194	272
70.53	0	34.843	2192	2191	50
70.53	0	34.843	8636	8631	80
70.53	0	34.843	7921	7880	424
54.74	180	35.111	13459	13427	334
54.74	180	35.111	2954	2940	115
54.74	180	35.111	7655	7655	225
54.74	180	35.111	14034	14042	94
54.74	180	35.111	2207	2211	64
54.74	180	35.111	11761	11753	291
54.74	180	35.111	8305	8346	483

*) Defined between the extremes of the derivative of the absorption signal.

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