

<b>Zeitschrift:</b>	Helvetica Physica Acta
<b>Band:</b>	44 (1971)
<b>Heft:</b>	3
<b>Artikel:</b>	Electron spin resonance of Fe <sup>+3</sup> in ZnAl <sub>2</sub> O <sub>4</sub> spinel and anisotropy energies in ferrites
<b>Autor:</b>	Gerber, P. / Waldner, F.
<b>DOI:</b>	<a href="https://doi.org/10.5169/seals-114290">https://doi.org/10.5169/seals-114290</a>

### **Nutzungsbedingungen**

Die ETH-Bibliothek ist die Anbieterin der digitalisierten Zeitschriften auf E-Periodica. Sie besitzt keine Urheberrechte an den Zeitschriften und ist nicht verantwortlich für deren Inhalte. Die Rechte liegen in der Regel bei den Herausgebern beziehungsweise den externen Rechteinhabern. Das Veröffentlichen von Bildern in Print- und Online-Publikationen sowie auf Social Media-Kanälen oder Webseiten ist nur mit vorheriger Genehmigung der Rechteinhaber erlaubt. [Mehr erfahren](#)

### **Conditions d'utilisation**

L'ETH Library est le fournisseur des revues numérisées. Elle ne détient aucun droit d'auteur sur les revues et n'est pas responsable de leur contenu. En règle générale, les droits sont détenus par les éditeurs ou les détenteurs de droits externes. La reproduction d'images dans des publications imprimées ou en ligne ainsi que sur des canaux de médias sociaux ou des sites web n'est autorisée qu'avec l'accord préalable des détenteurs des droits. [En savoir plus](#)

### **Terms of use**

The ETH Library is the provider of the digitised journals. It does not own any copyrights to the journals and is not responsible for their content. The rights usually lie with the publishers or the external rights holders. Publishing images in print and online publications, as well as on social media channels or websites, is only permitted with the prior consent of the rights holders. [Find out more](#)

**Download PDF:** 15.01.2026

**ETH-Bibliothek Zürich, E-Periodica, <https://www.e-periodica.ch>**

# Electron Spin Resonance of $\text{Fe}^{+3}$ in $\text{ZnAl}_2\text{O}_4$ Spinel and Anisotropy Energies in Ferrites<sup>1)</sup>

by **P. Gerber<sup>2)</sup>**

Physik-Institut Universität Zürich, Switzerland

and **F. Waldner<sup>3)</sup>**

Argonne National Laboratory, Argonne, Illinois 60439, USA

(20. XI. 70)

*Abstract.* The ESR spectra of iron doped  $\text{ZnAl}_2\text{O}_4$  spinel have been measured at 35 GHz at room temperature. The  $\text{Fe}^{3+}$  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  $\text{cm}^{-1}$ :  $D = (-) 0.34017 \pm 0.00015$ ,  $a - F = (+) 0.04707 \pm 0.00021$ ,  $a = (+) 0.0575 \pm 0.0004$ . 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  $\text{Fe}^{3+}$  ions is a main source of the magnetic anisotropy energies in ferrites. The differences to the ESR results of  $\text{Fe}^{3+}$  ions in  $\text{MgAl}_2\text{O}_4$ , 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.

$\text{ZnAl}_2\text{O}_4$  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  $\text{ZnAl}_2\text{O}_4$  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  $\text{Fe}^{3+}$  ions [2, 3] and, at a lower concentration, by  $\text{Cr}^{3+}$  impurities [4]. Additional lines arise from  $\text{Mn}^{2+}$  ions [5].

The ground state of  $\text{Fe}^{3+}$  ( $3d^5$ ,  $S_{5/2}$ ) 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

<sup>1)</sup> Research supported in part by the Swiss National Science Foundation and the U.S. Atomic Energy Commission.

<sup>2)</sup> Present address: Physikalisch-Chemisches Institut, Universität Zürich.

<sup>3)</sup> On leave of absence from University of Zürich.

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  $\xi, \eta, \zeta$ . Choosing a  $\text{Fe}^{3+}$  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  $\xi, \eta, \zeta$ . This interaction gives diagonal and real third off-diagonal matrix elements for  $x$  along  $[1\bar{1}\bar{2}]$  and  $y$  along the two-fold axis  $[\bar{1}\bar{1}0]$ .

If the direction of the applied magnetic field  $H$  relative to  $x, y, z$  is described by the polar angle  $\theta$  and the azimuthal angle  $\varphi$ , 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  $\theta$  and  $180^\circ - \theta$ , hence the lines would have extreme field values at  $\theta = 90^\circ$  for fixed angle  $\varphi$ . However, the last term of the above spin Hamiltonian creates different spectra for  $\theta$  and  $180^\circ - \theta$ . Figure 1 shows different field values for  $\theta$  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  $\text{MgAl}_2\text{O}_4$  a negative  $D$  for  $\text{Fe}^{3+}$  has been found [8]. Diffraction studies [1, 9] gave almost equal structure parameters for  $\text{ZnAl}_2\text{O}_4$  and  $\text{MgAl}_2\text{O}_4$ , therefore a negative sign for  $D$  in  $\text{ZnAl}_2\text{O}_4$  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  $\text{ZnAl}_2\text{O}_4$ , but may be wrong for very large axial distortions.

The main source of the magnetocrystalline anisotropy energy of cubic ferromagnetic substances containing  $\text{Fe}^{3+}$  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].

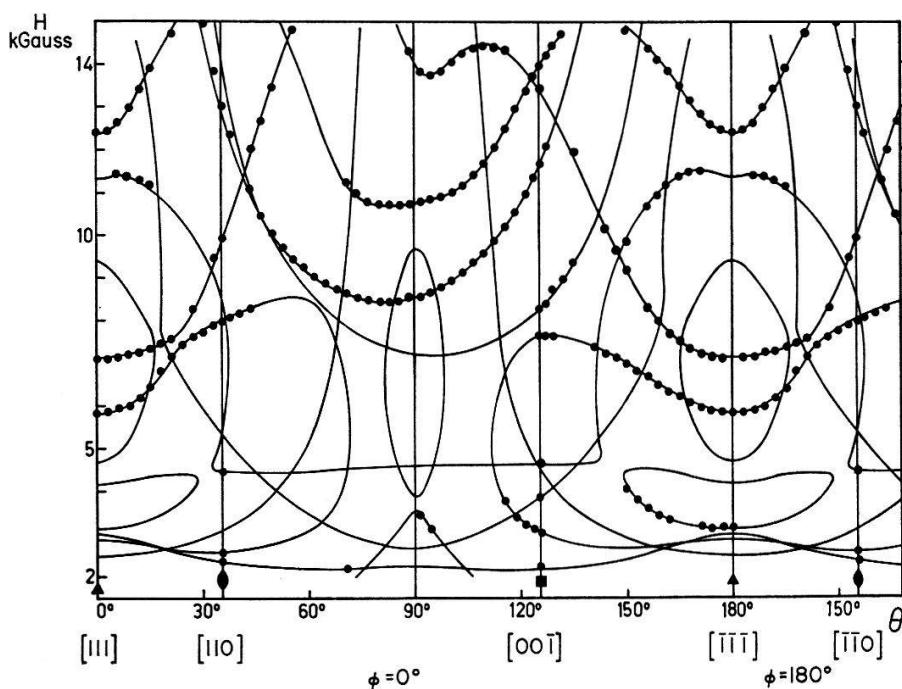


Figure 1

Angular dependence of the  $\text{Fe}^{3+}$  ESR spectra in  $\text{ZnAl}_2\text{O}_4$  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  $\text{Fe}^{3+}$  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  $\text{Fe}^{3+}$  parameters was possible in a natural  $\text{MgAl}_2\text{O}_4$  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  $\text{MgAl}_2\text{O}_4$  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  $\text{Fe}^{3+}$  in octahedral sites alone can account for the measured anisotropy constants  $K_1$  ( $T = 0^\circ$ ) in  $\text{NiFe}_2\text{O}_4$  and  $\text{MnFe}_2\text{O}_4$  [16, 18, 19]. However, the comparison of the parameters for  $\text{Fe}^{3+}$  measured in  $\text{MgAl}_2\text{O}_4$  and  $\text{ZnAl}_2\text{O}_4$  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  $^{27}\text{Al}$  gives equal quadrupole interaction constants in both structures [20, 21]. The parameters  $D$  for  $\text{Cr}^{3+}$  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  $\text{Fe}^{3+}$  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  $\text{MgAl}_2\text{O}$  rises to  $|F| = 0.0104 \pm 0.0005 \text{ cm}^{-1}$  in  $\text{ZnAl}_2\text{O}_4$ . For comparison, the ratio  $[r_{\text{Al}-0(\text{MgAl}_2\text{O}_4)}/r_{\text{Al}-0(\text{ZnAl}_2\text{O}_4)}]^{10}$  is  $1.00 \pm 0.01$ , 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  $\text{Fe}^{3+}$  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  $\text{Fe}^{3+}$  and  $\text{Cr}^{3+}$  at octahedral *B* sites in  $\text{ZnAl}_2\text{O}_4$  and  $\text{MgAl}_2\text{O}_4$  at room temperature.

Growth method	$\text{ZnAl}_2\text{O}_4$ Synthetic	Ref.	$\text{MgAl}_2\text{O}_4$ Natural	Ref.
Lattice constants				
$a_0$	Å	8.086 $\pm$ 0.001 [9]	8.0890 $\pm$ 0.0005	[9]
$u_0$		0.3889 $\pm$ 0.0003 [1]	0.3889 $\pm$ 0.0001	[1]
$r_{\text{Al}-0}$	Å	1.916 $\pm$ 0.002	1.916 $\pm$ 0.001	
ESR $\text{Fe}^{3+}$				
$g_{\parallel}$		2.0001 $\pm$ 0.0004	2.001 $\pm$ 0.003	
$g_{\perp}$		2.0019 $\pm$ 0.0008	2.0 $\pm$ 0.1	
$D$	$\text{cm}^{-1}$	(-) 0.34017 $\pm$ 0.00015	- 0.2467 $\pm$ 0.0005	
$a - F$	$\text{cm}^{-1}$	(+) 0.04707 $\pm$ 0.00021	+ 0.0458 $\pm$ 0.0009	
$a$	$\text{cm}^{-1}$	(+) 0.0575 $\pm$ 0.0004	+ 0.0475 $\pm$ 0.0013	
ESR $\text{Cr}^{3+}$				
$g_{\parallel}$		1.9840 $\pm$ 0.0003 [4]	1.985 $\pm$ 0.001	[22]
$g_{\perp}$		1.9798 $\pm$ 0.0005	1.980 $\pm$ 0.002	
$ D $	$\text{cm}^{-1}$	0.9304 $\pm$ 0.0003	0.9193 $\pm$ 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  $\alpha$  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  $\text{Fe}^{3+}$  in  $\text{ZnAl}_2\text{O}_4$  at room temperature

Angles $\theta$ °	$\varphi$ °	Frequency GHz	Magnetic field Gauss	Theory Gauss	Line width*) 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.

The authors should like to thank E. A. Giess and H. Scheel for the growth of doped  $\text{ZnAl}_2\text{O}_4$  single crystals and D. Schoemaker and R. E. Pixley for helpful comments.

## REFERENCES

- [1] P. FISCHER, Z. Kristallogr. 124, 275 (1967).
- [2] J. E. DRUMHELLER, K. LOCHER and F. WALDNER, Helv. phys. Acta 37, 626 (1964).
- [3] P. GERBER, K. LOCHER, J. E. DRUMHELLER and F. WALDNER, Helv. phys. Acta 42, 585 (1969).
- [4] P. SCHINDLER, P. GERBER, H. R. BOESCH and F. WALDNER, Helv. phys. Acta 42, 583 (1969).

- [5] R. STAHL-BRADA and W. LOW, Phys. Rev. **116**, 561 (1959).
- [6] S. GESCHWIND, Phys. Rev. **121**, 363 (1961).
- [7] S. HAFNER, Schweiz. miner. petrogr. Mitt. **40**, 207 (1960).
- [8] K. A. MÜLLER, private communication (1963), see Ref. [16].
- [9] H. JAGODZINSKI and H. SAALFELD, Z. Kristallogr. **110**, 197 (1958); H. SAALFELD, private communication (1968).
- [10] See for Ref.: K. YOSIDA, J. appl. Phys. **39**, 511 (1968).
- [11] J. H. VAN VLECK, Phys. Rev. **52**, 1178 (1937).
- [12] K. YOSIDA and M. TACHIKI, Progr. theor. Phys. (Japan) **17**, 331 (1957).
- [13] See review in Ref. [23].
- [14] V. J. FOLEN, J. appl. Phys. **31**, 166 S (1960).
- [15] E. BRUN, H. LOELIGER and F. WALDNER, C. r. Colloque Ampère **10**, 167 (1961).
- [16] F. WALDNER, Dissertation Universität Zürich (1963), published (available from University of Zürich on request).
- [17] H. WATANABE, Progr. theoret. Phys. (Japan) **18**, 405 (1957).
- [18] J. F. DILLON, JR., S. GESCHWIND and V. JACCARINO, Phys. Rev. **100**, 750 (1955).
- [19] W. A. YAGER, J. K. GALT and F. R. MERRITT, Phys. Rev. **99**, 1203 (1955).
- [20] E. BRUN and S. HAFNER, Z. Kristallogr. **117**, 37 (1962); **117**, 63 (1962).
- [21] E. BRUN, S. GHOSE and P. SCHINDLER, Helv. phys. Acta **37**, 626 (1964).
- [22] V. A. ATSARKIN, J. exptl. theoret. Phys. (U.S.S.R.) **43**, 839 (1962); Soviet Phys. JETP (Engl. Transl.) **16**, 593 (1963).
- [23] R. F. PEARSON and A. D. ANNIS, J. appl. Phys. **39**, 1338 (1968).