Correlation of Zero-Field Splittings and Site Distortions. IX. Fe^{3+} and Cr^{3+} in β-Ga_2O_3

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Z. Naturforsch. **42 a**, 67–71 (1987); received August 12, 1986

EPR of Fe^{3+} in distorted tetrahedral sites in single crystals of β-Ga_2O_3 has been measured for the first time, and the second-order zero-field splitting (ZFS) parameters and principal axes directions were determined. The data for the sixfold coordinated Fe^{3+} are in good agreement with results from the literature. Comparison of the ZFS patterns with those calculated from the crystal structure data using the superposition model (SPM) shows reasonable agreement in the orientations of the principal axes, but only for the tetrahedral site is a reasonable value of the intrinsic ZFS parameter obtained. Besides large uncertainties in the sizes of the distortions the crystal structure data also appear to be systematically wrong. For Cr^{3+} in sixfold coordinated sites the discrepancies are even larger, but for this ion a reduced validity of the SPM may also be involved.

Introduction

While for Mn^{2+} an almost perfect validity of the superposition model (SPM) has been demonstrated in a large number of cases and a practically complete set of the intrinsic zero-field splitting (ZFS) parameters $\bar{b}_2$ for different ligands is now available [1], corresponding data for the isoelectronic Fe^{3+} are still very scarce. For a large part this can be attributed to the fact that far less host crystals with host ions of the same valence and comparable ionic radius are available in this case, the rather rare Ga^{3+} being almost the only suitable host ion for rigorous tests of the validity of the model and for a determination of the intrinsic ZFS parameters without complication due to local lattice relaxations. β-Ga_2O_3 thus is an extremely welcome host crystal for these purposes since it offers both four- and sixfold coordinated sites of monoclinic (C_s) site symmetry [2]. EPR data for Fe^{3+} in the sixfold coordinated sites are already available [3], and results for Cr^{3+} [4–6] can also be evaluated for comparison although the validity of the SPM for this ion is much more questionable than for Fe^{3+}. β-Ga_2O_3 crystallizes in the monoclinic space group C2/m with four formula units per unit cell; the monoclinic angle β is 103.7°.

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Experimental

Iron-doped crystals of β-Ga_2O_3 grown from flux were kindly supplied by Prof. W. Gunsser. The plate-like crystals with (100) as cleavage plane were oriented according to their morphology and with the help of precession photographs. EPR spectra were measured at Q-band frequencies for rotations around the *a*-, *b*- and *c**-axes. The field positions excluding those of strong overlap and very rapid change with orientation were subjected to a least squares fitting program using full diagonalization of the energy matrix according to the method of Powell [7]. Assuming g to be isotropic and equal to the free electron value, the ZFS parameters b_2^0 and b_2^2 as well as the relations between magnetic, crystallographic and laboratory axis systems could be determined. The sign of b_2^0 was determined from the relative intensity changes of the different transitions at X-band between 300 and 20 K employing a closed cycle refrigeration system model CSA-202 G of Air Products and Chemicals Inc., Allentown, USA.

Results and Discussion

1. EPR of Fe^{3+}

As shown by the example in Fig. 1, spectra due to two crystallographically nonequivalent centers in

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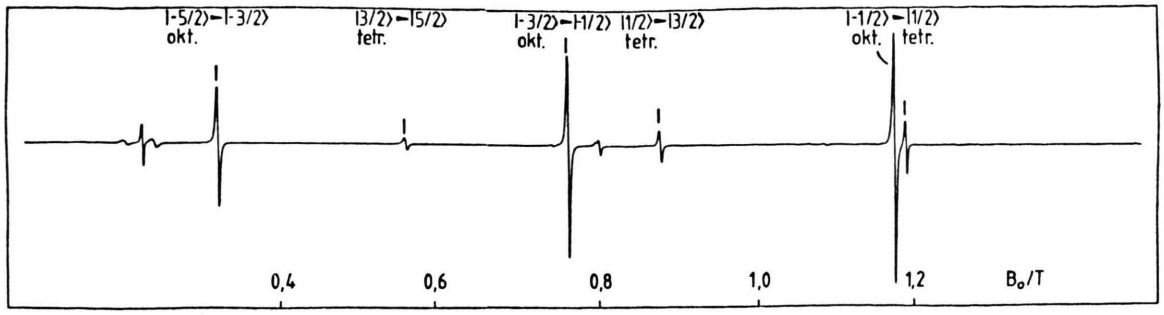

Fig. 1. EPR spectrum of Fe^{3+} in β-Ga_2O_3 at 33.7 GHz and room temperature for B_0 parallel to the b-axis.

the approximate intensity ratio of 5 : 1 were observed. According to earlier Mössbauer measurements [10] they can be unambiguously assigned to the six- and fourfold coordinated Ga sites, respectively. Preferential occupation of sixfold coordinated sites by Fe^{3+} was also observed in yttrium gallium garnet [11]. As required by the space group and site symmetries, one of the principal axes of the ZFS tensors (the z-axis of largest ZFS in both cases) coincides with the crystallographic b-axis. Additional weak signals were observed especially for rotation around the b-axis. They are evidently caused by twinning of the crystal with (100) as the twin plane [6]. The spectra were evaluated using the spin-Hamiltonian

$$\mathcal{H} = \beta B_0 \hat{g} \boldsymbol{S} + b_2^0[S_z^2 - \tfrac{1}{3}S(S+1)] + \tfrac{1}{3}b_2^2(S_x^2 - S_y^2)\,,$$

which together with the usual convention $0 \leqq b_2^2/b_2^0 \leqq 1$ defines the magnetic axes system. Inclusion of fourth order terms did not result in improved agreement of measured and calculated field positions. The numerical results are listed in Table 1. Those for the sixfold coordinated site agree with earlier data from the literature [3], but in that work a total of 11 parameters was determined from only 20 field positions.

Table 1. EPR data for Fe^{3+} in β-Ga_2O_3.

	Fourfold			Sixfold coordination		
b_2^0/cm^{-1}	+ 0.157 (6)			− 0.210 (25)		0.2213 [a]
b_2^2/cm^{-1}	+ 0.133 (6)			− 0.206 (13)		0.2091 [a]
Direction cosines						
	a	b	c^*	a	b	c^*
x	−0.9963	0	−0.0854	0.2130	0	0.9770
y	−0.0854	0	0.9963	−0.9770	0	0.2130
z	0	1	0	0	1	0

[a] Ref. [3].

2. *Superposition analysis for Fe^{3+}*

From the crystal structure data [2] ZFS patterns ("distortion diagrams") for Fe^{3+} and Cr^{3+} at the Ga sites and their limits of error were calculated for the (101) plane using a suitable computer program with $R_0 = 186.5$ and 201.9 pm for four- and sixfold coordinated Fe^{3+}, respectively, $R_0 = 199.6$ pm for Cr^{3+} and $t_2 = 7$ for Fe^{3+}. For Cr^{3+} $t_2 = -0.2$ was used as a weighted average of uniaxial stress data for MgO and $SrTiO_3$ [9].

These crystal structure data of β-Ga_2O_3 are not accurate enough to determine reliable values of $\overline{b_2}$ from them. Thus values from other systems are required for a realistic and reliable comparison of the splitting and distortion patterns. Although none of these systems alone allows a test of the SPM, data for a number of axial sites of Ga^{3+} are available. The $\overline{b_2}$ values calculated from them are collected in Table 2 and compared to that obtained in uniaxial stress measurements for Fe^{3+} in MgO [12, 13]. The results for sixfold coordinated sites are seen to cover a range of almost a factor of 3 whereas those for the distorted tetrahedral sites are in the same range as those for the sixfold coordinated sites in garnets, i.e. on the lower limit of the values for sixfold coordination. A similarly large variation was observed in uniaxial stress measurements for different crystals with values ranging from − 0.225 for CaO to − 0.57 for $SrTiO_3$ [13], but in this case the local compressi-

Table 2. Intrinsic ZFS parameters $\overline{b_2}$ (in cm^{-1}) for Fe^{3+} and Cr^{3+} with oxygen as ligand determined from EPR data for sites of axial symmetry and from uniaxial stress measurements.

Compound	FeO_4	FeO_6	Ref.	CrO_6	Ref.
$ZnGa_2O_4$	–	−0.365(4)	[22, 23]	+0.87(1)	[24]
$Y_3Ga_5O_{12}$	−0.155(8)	−0.288(9)	[25]	–	
$Lu_3Ga_5O_{12}$	−0.183(20)	−0.146(14)	[25]	–	
$Ca_3Ga_2Ge_3O_{12}$	–	−0.208(51)	[25]	–	
$CsGa(SO_4)_2 \cdot 12\ H_2O$	–	±2.21 (71)	[18, 26]	+0.86(26)	[27]
$CsCr(SO_4)_2 \cdot 12\ H_2O$	–	–		+0.79(25)	[26, 27]
MgO	–	−0.412(25)	[12, 13]	+2.36(12)	[9]

bilities for the impurity ion of different size and valence may differ from those for the bulk crystals, and thus we consider the value for MgO to be the most reliable one.

The variations of $\overline{b_2}$ for Fe^{3+} at the axial Ga sites are much larger than those for the isoelectronic Mn^{2+} in different coordinations [14]. Whether this indicates a larger dependence of the intrinsic ZFS parameter on the type of compound as a result of increased importance of contributions of nonsuperponable mechanisms or a beginning breakdown of the necessary conditions for superposability of overlap and covalency contributions [15] is still an open question since quantum mechanical calculations of the type published for Mn^{2+} [15–17] are still lacking for Fe^{3+}. The considerably larger values of $\overline{b_2}$ obtained for Fe^{3+} with H_2O as ligand [18] also contradict the results for Mn^{2+} where $\overline{b_2}$ was always found to be an "atomic" property of the ligand, i.e. practically independent of the nature of the other bonds of this atom. It seems appropriate to use the average values of $\overline{b_2}$ of -0.26 and $-0.17\ cm^{-1}$ from Table 2 for six- and fourfold coordinated Fe^{3+}, respectively, with O^{2-} as ligand.

For Cr^{3+} with oxygen as ligand the $\overline{b_2}$ values for axial sites are always positive and show much less variation. Also, no difference between O^{-2} and H_2O as ligand is found (see Table 2), but the value obtained from uniaxial stress measurements [9] is more than twice as large as those for the uniaxial sites. Again the possibility of a different total compressibility makes this value less reliable. Thus in this case we use the average value of $+0.85\ cm^{-1}$ obtained from the axial sites.

The splitting and distortion diagrams for Fe^{3+} at the fourfold coordinated site in β-Ga_2O_3 are compared in Fig. 2 for the (101) plane. While a satisfactory agreement is obtained for the positions of the principal axes, the x- and z-axes are clearly interchanged. This is not possible within the quoted limits of error of the crystal structure data which are indicated by the bars in the distortion diagram. For Fe^{3+} in sixfold coordination the situation is even worse, as shown in Figure 3. Again x and z are interchanged, but in addition for the y-axis a compression is calculated from the crystal structure data whereas the negative sign of $\overline{b_2}$ indicates an elongation in this direction. Thus a positive sign of $\overline{b_2}$ would lead to a somewhat better agreement, but this choice completely contradicts the results for all other systems for which the sign of $\overline{b_2}$ was experimentally determined.

Likewise, we observe an interchange between x and y for Cr^{3+} and a different sign of distortion and splitting diagrams along b as well. In addition there is also a marked difference in the orientations of the principal axes in the $a-c$ plane in this case, as seen in Figure 4. Reversal of the signs of the a- and c-axes for the EPR measurements as indicated by the dash-dotted curve in Fig. 4 leads to perfect agreement for the principal axes, but to a wrong sign of $\overline{b_2}$ as found for Fe^{3+}.

The discrepancies could have two different origins, namely an almost complete failure of the SPM or systematic errors of the crystal structure data. While a failure of the SPM is easily possible in the case of Cr^{3+} (and in fact was predicted for theoretical reasons [19]) the complete success in the case of Mn^{2+} and the successful application to Fe^{3+} in $CsGaCl_4$ [20] make more than slight deviations rather unlikely for the latter d^5-ion. We are thus inclined to ascribe the largely analogous discrepancies for both Fe^{3+} and Cr^{3+} in the sixfold coordinated sites as well as the significantly smaller dis-

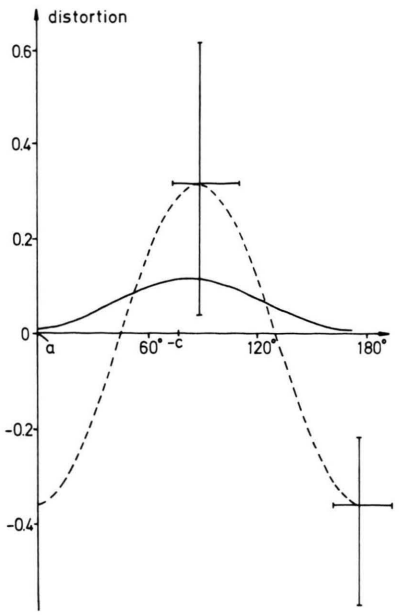

Fig. 2. Splitting (——) and distortion (– – –) diagrams for Fe^{3+} at fourfold coordinated Ga sites in β-Ga_2O_3 at room temperature for rotation around the b-axis. The splitting diagram is given by

$$\frac{1}{2b_2}\left[(3\cos^2\vartheta - 1)\, b_2^0 + \sin^2\vartheta \cos 2\varphi \cdot b_2^2\right],$$

where ϑ and φ are the angles to the z- and x-axes, respectively, the distortion diagram by

$$\tfrac{1}{2}\sum_i (3\cos^2\Theta_i - 1) \cdot \left(\frac{R_0}{R_i}\right) t_2,$$

where Θ_i is the angle between the $M-O_i$ bond and the magnetic field, and the summation runs over all ligands O_i. Thus the distortion is given as "fractional ligand at normal bond distance" [8].

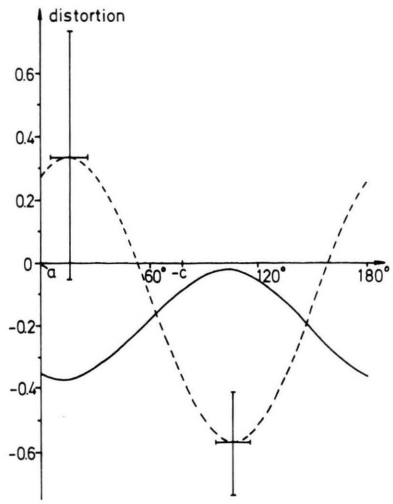

Fig. 3. Splitting (——) and distortion (– – –) diagrams for Fe^{3+} at sixfold coordinated Ga sites in β-Ga_2O_3 at room temperature for rotation around the b-axis.

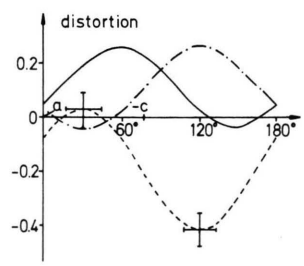

Fig. 4. Splitting (—— and –·–·–) and distortion (– – –) diagrams for Cr^{3+} at sixfold coordinated Ga sites in β-Ga_2O_3 at room temperature for rotation around the b-axis. Reversal of the signs of a- and c-axes for the splitting diagram (–·–·–) results in better agreement in the orientations of the principal axes and with the results for Fe^{3+} and cannot be excluded by the available EPR data.

crepancies for the fourfold coordinated Fe^{3+} to systematic errors in the crystal structure determination. A renewed refinement of the crystal structure thus seems extremely desirable. Even if the existing one proves to be basically correct, at least the remaining doubts can be removed and the accuracy can be increased. Certainly the reported R value of 0.143 is still far from the present state of the art and leaves considerable room for improvement. Doubts have also been raised as to the correctness of the reported space group [21], but our EPR data do not give any indication to support them.

Acknowledgements

This work was supported by grants from the Deutsche Forschungsgemeinschaft. We also thank Professor Dr. W. Gunsser, Universität Hamburg, for supply of the iron-doped crystals of β-Ga_2O_3 used in this study.

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