Electron Spin Resonance of Cr^{3+} in $ZnAl_2O_4$ Spinel Parameters and Linewidths[1])

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Abstract. The ESR spectra of Cr^{3+} in synthetic $ZnAl_2O_4$ spinel have been measured at 35 and 9 GHz. The parameters of the spin Hamiltonian are at $300\,°K$: $g_{||} = 1.9840 \pm 0.0003$, $g_{\perp} = 1.9798 \pm 0.0005$, $|D| = (0.9304 \pm 0.0003)$ cm^{-1}. The strongly varying linewidths are interpreted quantitatively by a simple model which is consistent with small disorder effects.

Introduction

The comparison of $ZnAl_2O_4$ spinel with $MgAl_2O_4$ spinel is interesting particularly with respect to order-disorder phenomena: on one hand they have almost equal structure constants [1], their nuclear quadrupole interaction of ^{27}Al is the same [2, 3], and the hyperfine splitting of Mn^{2+} impurities shows no difference [4, 5], although this value should depend on covalency [6]. On the other hand one observes distinct differences in their order-disorder behavior. Natural $MgAl_2O_4$ crystals are almost ordered, but an irreversible disorder can be induced by a short heating above about $900\,°C$. They show then similar disorder effects as synthetic crystals. This disorder has been observed by nuclear magnetic resonance [2] and electron spin resonance [7, 8]. Contrarily, synthetic $ZnAl_2O_4$ samples are ordered and give relatively narrow magnetic resonance lines [3]. Fischer [1] has investigated this different behavior by neutron diffraction.

Are there measurable indications of this different disorder behavior still in the ordered phase? The splitting parameters of paramagnetic impurities should be very sensitive to slight variations in the arrangement of their surroundings and to changes in covalency. Cr^{3+} ions as an example show in fact small but significant differences in their electron spin resonance parameters.

Further, the linewidths of the Cr^{3+} spectrum show a marked anisotropy. Their behavior can be described by a simple model which agrees with the assumption of a small disorder present in the samples. Hence both structures may have the same disorder phenomena and they may differ only in their quantitative amount.

Theory

(a) *Spinel Structure* [9]

The ordered spinel structure AB_2O_4 has the space group $Fd3m$ (O_h^7). The oxygen ions form an almost perfect cubic closed package. The A ions occupy a site of cubic point symmetry $\overline{4}3m$, surrounded by four oxygens in the corners of a tetrahedron. This site is in general referred to as the 'A site'. The B ions are surrounded by six oxygens arranged in a octahedron which is distorted in one of the four directions of the space diagonals of a cube. The 'B site' has the point symmetry $\overline{3}m$.

In disordered spinels the distribution of the ions of type A and B among the sites A and B is changed, additional interstitial positions are also possible. A special type of disorder is the inverse spinel, where all A type ions are at B sites, the B type ions half at A, half at B sites. A description of the actual disorder in a sample could be given by the amount of ions at 'wrong' sites, but it would also be of interest how these imperfections are distributed in the crystal.

(b) *Spin Hamiltonian*

The grounnud state of a Cr^{3+} ion in the B site of an ordered spinel is usually described by an axial spin Hamiltonian

$$\mathcal{H} = g_{\parallel} \beta H S_z \cos\theta + (1/2) g_{\perp} \beta H (S_+ + S_-) \sin\theta + D [S_z^2 - (1/3) S (S+1)] \quad (1)$$

where $S = 3/2$, the z axis is along the actual threefold axis of the B site occupied by the Cr^{3+} ion, and θ is the angle between the static magnetic field H and z. The g tensor can here be described by the parameters $g_{\parallel}$ and $g_{\perp}$, β is the Bohr magneton, the axial second degree crystal electric field parameter is D, and S_z, S_+, S_- are spin operators.

Disorder effects would lower the symmetry of the B site. But for small disorder one can assume that the center of the still symmetric lines would correspond in first approximation to the spectrum in the ideal structure.

Experimental Results and Discussion

Our experiments have been made for the major part with two synthetic $ZnAl_2O_4$ spinel single crystals doped with Cr_2O_3 and grown by the flux technique. The clear pink crystals of octahedral forms have a size of about 1 and 2 mm respectively. Conventional K- and X-band spectrometers have been used. The magnetic field H has been rotated in a plane from the [001]-direction through the [111]-direction to the [110]-direction. The spectra obtained indicate by their angular dependence that Cr^{3+} is at the B site.

In Figure 1 there are two ESR spectra taken at two different frequencies with the magnetic field H parallel to a threefold axis of the crystal. Among the intense lines there is one with an outstanding shift to lower field for higher frequency, but the
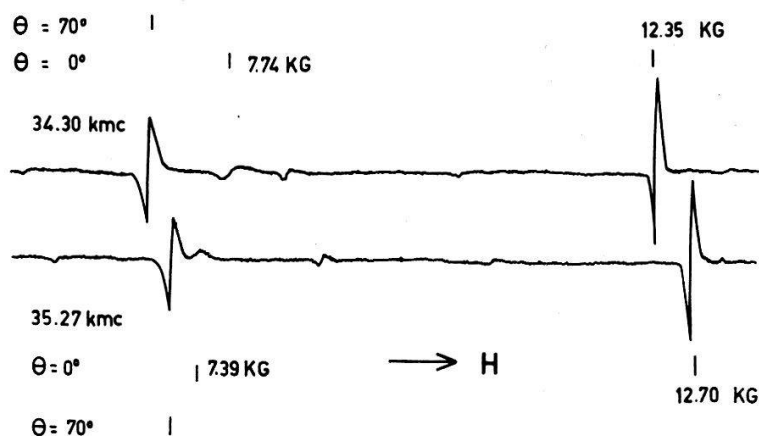
Figure 1

ESR spectra of Cr^{3+} doped $ZnAl_2O_4$ spinel with H parallel [111] at 300 °K. θ is the angle between H and the trigonal axis of the appropriate position of the Cr^{3+} ions. Lines of lower intensity are due to Fe^{3+} present as impurities.

absolute value of the shift is equal to that of the $1/2 \leftrightarrow -1/2$ transition. This behavior together with the symmetric angular dependence in $\pm \theta$ leads to its assignment to the 'low field' $-3/2 \leftrightarrow -1/2$ transition. The position of this line is proportional to D and is therefore strongly influenced by disorder.

The three parameters $g_\parallel$, $g_\perp$ and D can easily be calculated if the assignment of the $-3/2 \leftrightarrow -1/2$ transition at $\theta = 0°$ and for the $1/2 \leftrightarrow -1/2$ transition at $\theta = 0°$ and 90° to three observed line positions is possible. The parameter values at room temperature are [10]:

$$g_\parallel = 1.9840 \pm 0.0003 \,,$$

$$g_\perp = 1.9798 \pm 0.0005 \,,$$

$$|D| = (0.9304 \pm 0.0003)\ \text{cm}^{-1}\ (27.894 \pm 0.008\ \text{GHz}) \,.$$

Furthermore, comparison of the angular dependence of the spectrum at constant frequency in K-band (34.237 GHz) were made with computer solutions of the spin Hamiltonian with the above parameters. The measured positions together with the calculated curves are given in Figure 2. The calculated values are within the measured positions with an error of about 1/20 of the actual linewidths defined between the peaks of the derivative of the absorption curve. No systematic deviation proposed by Koster and Statz [11] could be detected.

In addition, the calculated initial splitting at zero magnetic field would be $|2D| = (1.8608 \pm 0.0006)\ \text{cm}^{-1}$ in agreement with 1.86 cm^{-1} determined directly by Overmeyer [12].

We have not determined the sign of D, although this should in principle be possible by measuring the change in relative intensity of the two lines observed at $\theta = 0°$ as a function of temperature. One can guess the sign by applying the rather doubtful rule [13] that the expression $D/(g_\parallel - g_\perp)$ should be a first approximation for the positive spin orbit coupling constant of Cr^{3+}. For an assumed positive D this expression would give $(+440 \pm 60)$ cm^{-1}.
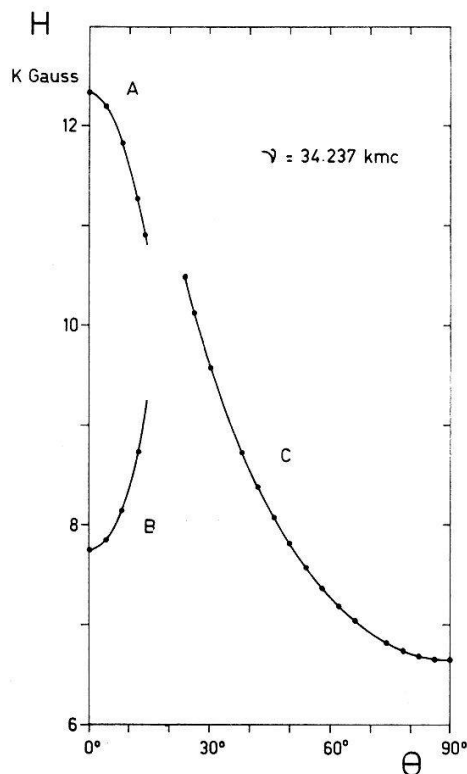
Figure 2

ESR spectra of Cr^{3+} in $ZnAl_2O_4$: resonance magnetic field H vs. θ at 34.237 GHz. Points: measured, lines: calculated with $g_\parallel = 1.9840$, $g_\perp = 1.9798$, $D = 0.9304$ cm^{-1}.

Thus $|D|$ is about 1.012 ± 0.002 times larger in $ZnAl_2O_4$ than in $MgAl_2O_4$ where Atsarkin [8] found $|D| = (0.9193 \pm 0.0016)$ cm^{-1} in an almost ordered natural sample. The differences of the above structures are also reflected in the spin Hamiltonian parameters of Fe^{3+} $(3\,d^5)$ at B sites: the ratio for the $|D|$ values is 1.379 ± 0.002 and for the cubic parameters a 1.21 ± 0.03 [14–17].

These results demonstrate that electron spin resonance is able to observe differences of structures where conventional crystallographic diffraction methods find no difference. However, the interpretation of the observed parameter values still remains incomplete.

Linewidth and Disorder

Electron spin resonance line shapes and widths are determined by a great number of effects, but in general it is rather difficult to evaluate their relative importance. Shaltiel and Low [18] attempted to explain the anisotropic broadening of Gd^{3+} lines in thorium oxide by a mosaic structure of the sample. Recently, Pavlovskaya et al. [19] applied a similar method for the determination of the disorientation angles of blocks in ruby by nuclear magnetic resonance. Another approach was made by Grant and Strandberg [20] with a statistical theory of spin interaction based on a pair concept.

Other authors based their models on a random distribution of internal strain and stress. The shifts of the resonance magnetic field as a function of externally applied uniaxial stress have been previously measured in the same structure and described by a 'gradient elastic tensor'. In addition, an intrinsic isotropic residual linewidth has been assumed which the line would have in the absence of internal stress. Elsa Feher [21] accounted for the linewidth of Mn^{2+} and Fe^{3+} in MgO ranging from 0.5 up to

20 Gauss. Wenzel and Kim [22] studied the linewidth of Cr^{3+} in ruby before and after neutron irradiation. The linewidth increased anisotropically up to 140 Gauss. The strain-source model yields an almost satisfactory fit to the observed broadening. However, the measured azimuthal dependence of the line broadening has a period of 60° instead of a calculated 120° period and no azimuthal dependence could be observed before irradiation, although this should be an inherent feature of the strain-source model for ruby because of the rotated oxygen triangles. Kirby and Thorp [23] applied the strain-source model to show that the internal strain values in ruby are growth dependent.

Clough and Scott [24] described a general theory of saturation applicable to dilute spin systems and inhomogeneously broadened lines. Recently, Stoneham [25] presented a review on inhomogeneously broadened resonance lines.

Before we discuss further possible interpretations, we present our observations in $ZnAl_2O_4$:

The line labeled A in Figure 2 has a nearly Gaussian shape for small values of θ but in the region of $|\theta| > 8°$ small but distinct deviations occur. Unequal enlarged wings make these lines anisotropic.

The line B is strongly affected by Fe^{3+} lines. One can only guess the linewidth by graphical interpolation, which becomes more difficult for large $|\theta|$ due to the reduced signal amplitude.

The line C is nearly Gaussian from $\theta = 90°$ to about 30°. This line has enlarged wings for smaller values of θ, but the shape remains almost symmetric.

If the spectra would have axial symmetry, they should obviously depend only on the absolute value of θ. Small departures from this symmetry could be observed for θ of equal magnitudes but opposite signs. They are more pronounced in line shape than in linewidth whereas the magnetic fields of the centre of the lines are independent of the sign of θ.

In Figure 3 the measured linewidths have been plotted, using the peak distance of the derivative of the absorption curve.

In order to interpret these experimental facts we now make the following assumptions:

1. Spin-spin interactions with other Cr ions and with nearest neighbor ^{27}Al nuclei of the form $\boldsymbol{S}_i \cdot \underset{\sim}{K} \cdot \boldsymbol{S}_j$, $\boldsymbol{S}_i \cdot \underset{\sim}{K}' \cdot \boldsymbol{I}_j$ respectively are assumed, with $\boldsymbol{S}$, $\boldsymbol{I}$ as the appropriate spin vectors. The interaction tensors $\underset{\sim}{K}$, $\underset{\sim}{K}'$ are supposed to be isotropic. For measurements at fixed magnetic field H and variable frequency ν shifts $\Delta\nu$ occur which are independent of the orientation for the above assumption. For measurements at fixed frequency ν and variable magnetic field H there would be shifts $\Delta H = (\partial H/\partial \nu) \cdot \Delta \nu$. The derivative $\partial H/\partial \nu$ is dependent on the orientation of the crystal relative to the magnetic field, causing an anisotropic angular variation of this contribution, although the interaction itself is assumed to be isotropic [5]).

2. Point imperfections will be distributed at random among crystallographical equivalent positions. Thus, we exclude clustering.

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[5]) This assumption would reduce the discrepancies between the observed and calculated values in ref. [22].
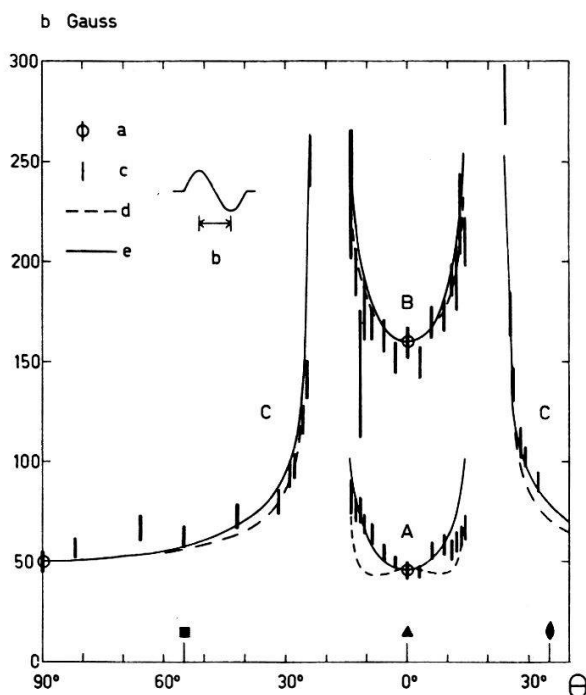
Figure 3
Linewidths b of Cr^{3+} in $ZnAl_2O_4$ vs. θ at 34 GHz. (a), (c) measured, (d), (e) calculated. The three measured widths (a) lead to $k_v = 127$ mc, $k_D = 213$ mc, $k_E = 100$ mc and to the calculated curve (d) with $k_\theta = 0$. The curve (e) has identical parameters, except $k_\theta = 1/3°$.

3. For a possible mosaic structure Gaussian distributions are assumed for the angles involved.

4. For small point disorder the linewidth is almost determined by these Cr ions which have only imperfections at large distances. Because we have excluded clustering we treat these imperfections in cubic crystals as if they were continuously distributed with equal probability over all solid angles. However, if they act through stress on the Cr spectra, the ensemble of the shifts produced can have a non spherical distribution with the point symmetry of the Cr site in the ideal structure as lowest possible symmetry.

5. Imperfections at short distances give distinct sets of spectra, because the possible positions of the imperfections are 'quantized' in space. This 'quantization' is independent of the type of interaction involved, and is a consequence of the discrete lattice structure. The ensemble of these individual spectra should have a symmetry not lower than the point symmetry of the Cr site in the ideal structure, if the imperfections are distributed at random over the possible positions. However, the symmetry of the spectra can be higher than in pos. 4, if the possible positions for the imperfections alone would create a higher point symmetry at the Cr position than the entire ideal structure.

6. The point symmetry of the site occupied by the Cr ions may be lower than the symmetry of the ideal unit cell. The different possible positions inside one unit cell are then related by symmetry operations of the space group of the unit cell. If the Cr ions are distributed at random among the possible positions of this site, the spectra of these Cr ions are obviously related by these symmetry operations. If the spectra coincide for no imperfections present, these symmetry operations can result in a higher symmetry of the shifts in imperfect crystals than predicted from pos. 4 and 5 alone.

7. Furthermore, as the disorder increases, the Cr ions at positions with near lying imperfections will give a greater contribution to the observed line. Thus the resulting increase in linewidth is rather due to changes in the relative population of the possible individual spectra than to a broader continuous distribution of the local strains and deformations. Therefore the line shape will change. Hence the linewidth alone is no longer a sufficient description how disorder affects the line. One should further note that the number of paramagnetic centers which contribute to the line inside the linewidth may drastically be different for different lines observed at equal direction of the magnetic field H and may also change for one transition at different angle settings.

The symmetry of the observed spectrum can provide important information: for example, the symmetry should be trigonal in ruby, if long range stress effects described by the gradient elastic tensor are involved, whereas this symmetry would be hexagonal, if near lying cation imperfections are dominant. The higher hexagonal symmetry has been observed by Wenzel and Kim [22]. This leads together with the recorded changes in line shape and the absolute magnitude of the measured linewidths to the conclusion that the long range stress effects used as description are strongly modified by near lying point imperfections, for which the measured gradient elastic tensor is at least doubtful.

In spinel, both effects would result in trigonal symmetry, they can therefore not be distinguished by this argument. In addition, the deviations observed from axial symmetry are small. Hence the application of the strain-source model would be rather inadequate, even if the 'gradient elastic tensor' would be known. Further, the recorded variations of line shape and the absolute magnitude of the linewidths suggest again heavy influence from near lying imperfections.

A single Cr^{3+} ion in a disturbed surrounding would give a spectrum having as lowest symmetry mmm if one neglects the possible determination of the lack of inversion symmetry be externally applied electric fields. The energy levels of this ion numbered j can be described by a spin Hamiltonian

$$\mathcal{H}_j = g_{jz}\,\beta\,H\,S_{jz}\cos\theta_j + (1/2)\,g_{jx}\,\beta\,H\,(S_{j+} + S_{j-})\,\sin\theta_j\,\sin\varphi_j +$$

$$+ (1/2\,i)\,g_{jy}\,\beta\,H\,(S_{j+} - S_{j-})\,\sin\theta_j\,\cos\varphi_j + D_j\,[S_{jz}^2 - (1/3)\,S\,(S+1)] +$$

$$+ (1/2)\,E_j\,(S_{j+}^2 + S_{j-}^2)\,. \tag{2}$$

The $\underset{\sim}{g_j}$-tensor has the diagonal components g_{jx}, g_{jy}, g_{jz}, the parameter D_j is a measurement of the deviation from cubic to axial point symmetry and E_j indicates the further rhombohedral deformation. The direction of the magnetic field H is indicated by the polar angle θ_j and the azimuthal angle φ_j, and S_{jz}, S_{j+}, S_{j-} are spin operators. All values are related to the symmetry directions of the second degree electric interaction of the ion numbered j, which are in general not in coincidence with the symmetry directions of the point symmetry in the ideal structure.

A crude model would now be to assume independent Gaussian distributions for the parameters D_j, E_j, θ_j, φ_j centered at the values for the ideal structure, although a better description would consist in a superposition of all the spectra of the individual

ions $j = 1, n$. For the residual width we assume an isotropic energy spread of Gaussian form, described by $k_\nu \, \partial H/\partial \nu$ in terms of the transition frequency ν. Defining in a similar way k_D, k_E, k_θ, k_φ as proportional to the standard deviations of the appropriate distributions, H the resonant magnetic field for the transition of a Cr^{3+} ion in the ideal structure, we can write for the linewidth b in first approximation:

$$b^2 = \left(k_\nu \, \frac{\partial H}{\partial \nu}\right)^2 + \left(k_D \, \frac{\partial H}{\partial D}\right)^2 + \left(k_E \, \frac{\partial H}{\partial E}\right)^2$$
$$+ \left(k_\theta \, \frac{\partial H}{\partial \theta}\right)^2 + \left(k_\varphi \, \frac{\partial H}{\partial \varphi}\right)^2. \tag{3}$$

Further, the derivative $\partial H/\varphi$ vanishes for an axial spin Hamiltonian. Therefore we have only the four parameters k_ν, k_D, k_E, k_θ to adjust. The derivatives have been evaluated by calculating the resonant magnetic fields for the experimental microwave frequency with slightly varied spin Hamiltonian parameters on a computer.

The values of k_ν and k_D can directly be determined from the two lines at $\theta = 0°$, then the line at $\theta = 90°$ gives k_E and the finer adjustment for the remaining angles θ leads to $k_\theta = 1/3°$. In Figure 3 the observed widths are compared to the computed widths. The dotted line shows the calculated values with the same set of parameters k_ν, k_D, k_E but with $k_\theta = 0$. One clearly sees that this assumption of no mosaic effect at all would not drastically change the fit. On the other hand, we can certainly exclude that a mosaic structure alone is responsible for the linewidth variations. Therefore we can say that the hypothesis of a slight inversion present in the sample is not in contradiction to the observations.

The limits of this statistical model can easily be demonstrated by checking the linewidths measured at 9.5 GHz with the parameters obtained at 35 GHz, which is shown on Figure 4 by the solid line. Although distinct deviations occur, these deviations are not larger than 30%. While it is possible to obtain again a good fit for this frequency as shown by the dotted line on Figure 4, the parameters are very different.

The reason for different parameters may be that the model assumed is a strong oversimplification. It neglects correlation terms linear in E_j and D_j, and all higher order terms. The different linewidth of the $1/2 \leftrightarrow -1/2$ transition at $\theta = 0°$ for different microwave frequencies may indicate the presence of higher order terms, because the bilinear correlation vanishes for these lines. Further, correlation terms evaluated for 35 GHz would give no valuable contribution at 9.5 GHz due to the extreme insensitivity for changes in D-values in this frequency region. For example, if a Cr ion j has $E_j = 0$ but $D_j \neq D$ producing a shift of 100 Gauss for the line B at $\theta = 0°$, 35 GHz, the largest shift of the $1/2 \leftrightarrow -1/2$ transition at 9.5 GHz would be smaller than 0.2 Gauss for every angle θ. Therefore, the number of Cr ions contributing to the signal inside the linewidth is much larger at 9.5 GHz than at 35 GHz. Hence one cannot expect that the same model for linewidths will give equal parameters at both frequencies.

Finally, our model has at least its justification as a simple description of the observed linewidths at fixed frequency. It may be a useful tool to compare the

qualities of different crystals and their growing methods as done by Kirkby and Thorp [23] for ruby.

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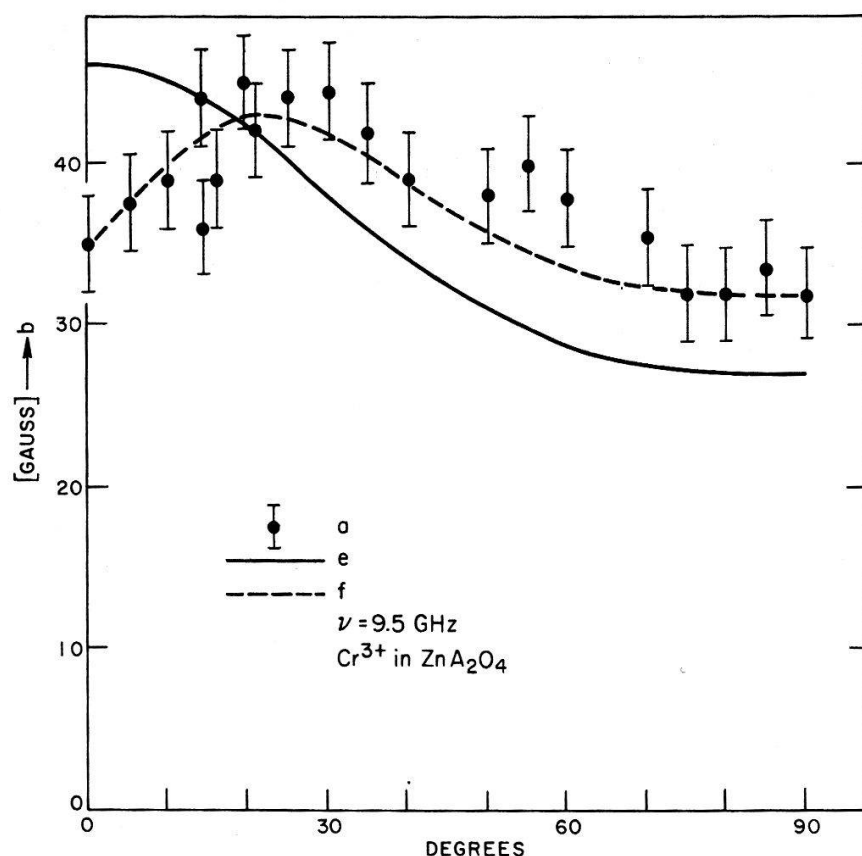

Figure 4

Linewidths b of Cr^{3+} in $ZnAl_2O_4$ vs. θ at 9.5 GHz. (a) measured; (e) calculated with the parameters of curve (e) in Figure 3; (f) calculated with $k_v = 97$ mc, $k_E = 252$ mc, $k_\theta = 0.7°$. The line positions are at X-band extremely insensitive to variation in the value of D, therefore k_D cannot be determined.

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