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Behavior of the Yb^{3+} Ion on Anomalous Sites in Ytterbium-Doped Yttrium Iron Garnet*†

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The theoretical behavior of the Yb^{3+} ion on octahedral a sites in ytterbium-doped YIG is examined with regard to some of the so-called anomalous properties of this substance. First, a simple spin Hamiltonian is proposed and discussed in the light of the crystal-field properties of the anomalous site. Next, the implications of the model for static torque are derived and compared with experiment. Excellent agreement may be achieved provided that the maximum separation of the doublet levels is taken to be 55 cm^{-1}. The minimum level spacing is not precisely determined, but is surely less than 2 cm^{-1}, and is thus the smallest to be observed in rare-earth-doped YIG. Last, the prediction of the model for the resonance anomaly is derived in a molecular-field model. A version of the theory involving only two adjustable parameters may be used to explain many details of the resonance measurements, including the variation of properties with angle and, to a lesser extent, with frequency. Since measurements are available at frequencies above the assumed level splitting, the degree of agreement is very sensitive to the form chosen for the susceptibility of the anomalous ytterbium ions to the exchange field. None of the forms examined produced quantitative agreement for the entire range of frequencies, although a form of inhomogeneous broadening is indicated. A more complete understanding of the problem could probably be achieved if resonance measurements at higher frequencies, and torque measurements at lower temperatures, became available.

1. INTRODUCTION

RARE-EARTH-DOPED yttrium iron garnet (RE-doped YIG) is a useful material for the study of the behavior of magnetic ions in insulators. Most commonly, the observed effects are associated with RE ions which substitute for yttrium on c sites in the YIG structure. However, there is convincing evidence that the phenomena which are discussed in this paper are to be ascribed to a small fraction of ytterbium ions which settle on the energetically less favorable a site normally occupied by Fe^{3+} ions.

The anomalous effects have been measured experimentally by a number of workers. The effects which I consider in detail consist of the sharp peak in the field for ferrimagnetic resonance, the peak in linewidth,[1–3] and the corresponding peak in the derivative of the static torque,[4] all of which occur whenever the magnetization is perpendicular to any $\langle 111\rangle$ crystallographic direction.

The agent responsible for the anomalous effects was something of a mystery for several years, as the Kramers doublets of the c-site Yb's, widely spaced by the exchange field,[5] failed to explain the sharp peaks and their low-temperature behavior. In 1965, Mrs. G. Donnay and S. Geschwind[6] independently suggested that the Yb^{3+} ion on a sites might be responsible. Dillon, Remeika, and Walker[1] have collected extensive evidence supporting this view by examining the symmetry of the peaks and their variation with the growth environment of different samples. As will be shown, only a small fraction of the ytterbium ions, of the order of a few percent, need settle on the a sites in order to account for the magnitude of the observed effects.

2. HAMILTONIAN

The electronic structure of the Yb^{3+} ion is $(4f)^{13}\,{}^2F$. Spin-orbit coupling is very strong, and the lowest J multiplet, $J=\frac{7}{2}$, is well separated from higher states. Barring coincidental degeneracies, the crystal field will split the $J=\frac{7}{2}$ multiplet into four Kramers doublets. These doublets may in turn be split via magnetic interactions. Insofar as the crystal-field separation of the doublets is relatively large compared with the interaction between them, the paramagnetic Hamiltonian for the ground doublet is entirely determined by the g tensor. Analogously, the exchange interaction of a doublet will be given by a tensor of coefficients which will here be denoted by $\mathbf{G}$. As has been shown by Wickersheim,[5] the G tensor and the g tensor need not be proportional.

In a molecular-field approximation, well justified for this case,[7] the exchange spin Hamiltonian takes the form[8]

$$H=\mathbf{M}_{Fe}\cdot\mathbf{G}\cdot\mathbf{S}'. \qquad (1)$$

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[1] J. F. Dillon, J. P. Remeika, and L. R. Walker (to be published).

[2] B. F. Clarke, J. Appl. Phys. **36**, 1211 (1965).

[3] T. Penney, thesis, Harvard University, 1966 (unpublished).

[4] R. F. Pearson, Proc. Phys. Soc. (London) **86**, 1055 (1965).

[5] K. A. Wickersheim, Phys. Rev. **122**, 1376 (1961).

[6] J. H. Van Vleck (private communication) and J. Dillon (private communication).

[7] J. H. Van Vleck, Progr. Sci. Tech. Rare Earths **2**, 1 (1966).

[8] W. P. Wolf, Proc. Phys. Soc. (London) **74**, 665 (1959).

Here, $\mathbf{M}_{\mathrm{Fe}}$ is the magnetization of the YIG lattice, i.e., the contribution of the iron spins. $\mathbf{S}'$ are the effective spin-$\frac{1}{2}$ operators of the lowest doublet.

The g tensor is given by the detailed composition of the ground states and thus depends in a complicated way on the crystal fields. The G tensor has still more involved origins; however, the fact remains that the tensor itself, in general, involves no more than three independent parameters, and in this case actually is specified by two. Thus it is far more convenient to base the discussion on the spin Hamiltonian of Eq. (1) rather than on the underlying crystal-field and exchange interactions. For this reason, I delay consideration of the detailed crystal-field theory of Yb until the role of the G tensor in parametrizing the exchange interaction is made clear.

First, note that there is a relation of the G tensor to the paramagnetic g tensor, which stems from the fact that both involve factors which relate the true angular momentum to the effective spin. In particular, if the basic exchange interaction is of the isotropic Heisenberg form—$H\sim 2(g_J-1)\mathbf{J}\cdot\mathbf{M}_{\mathrm{Fe}}$—then the two tensors are proportional. In reality, the isotropic Heisenberg exchange Hamiltonian is not expected to be an adequate description of the exchange interaction for Yb^{3+}. The departure of the interaction from the isotropic form is often referred to as anisotropic exchange, and insofar as such terms are present, the tensors are not proportional. Even so, some relation between them would be expected to persist, and thus a great deal of insight into the G tensor, which is, theoretically speaking, a rather inaccessible quantity, may be gained by examining the more understandable g tensor through the formalism of crystal-field theory.

Second, consider the general properties which the G tensor would be expected to have. It is clear that the spin Hamiltonian can be written in such a manner as to reflect the symmetry associated with the observed effects. In particular, the anomalous anisotropy peaks seem to reflect the C_{3i} symmetry associated with the normal a site, i.e., that a site as measured with an Fe^{3+} ion in place. In the principal axis system where z corresponds to the appropriate $\langle 111\rangle$ direction, Eq. (1) takes the form

$$H=G_{\|}M_zS_z+G_{\perp}M_xS_x+G_{\perp}M_yS_y. \tag{2}$$

The most general form of Eq. (1) which is necessary to describe the anomaly thus involves only two parameters.

Furthermore, the general nature of the anisotropy peaks enables us to surmise that $G_{\perp}$ is to be small compared with $G_{\|}$. Kittel[9] has pointed out that giant anisotropy anomalies are to be associated with a near coincidence of energy levels. It is clear upon examining the eigenvalues of Eq. (2) for the case where $\mathbf{M}$ is in the anomaly direction, i.e., $M_z=0$, that a near coincidence may be achieved only if the parameter $G_{\perp}$ is very small. It is this anticipated property of $G_{\perp}$ which I will now attempt to justify from crystal-field considerations of the related quantity $g_{\perp}$. It will not be possible in this analysis to limit closely the values of any of the parameters. The purpose is merely to illustrate reasonable situations in which the desired value of $g_{\perp}$ might be expected.

3. CRYSTAL-FIELD THEORY FOR Yb^{3+} ON a SITES

The interaction of an ion with the electrostatic fields of its environment may be represented in appropriate cases by a crystal-field Hamiltonian of the form[10]

$$H=\sum_{nm} B_n{}^mO_n{}^m. \tag{3}$$

$O_n{}^m$ are spherical tensors to which the Stevens' operator-equivalent procedure[11] may be applied, and $B_n{}^m$ are numerical coefficients determined by the distribution of electrostatic charges of the surroundings. In C_{3i} symmetry, the nonzero $B_n{}^m$'s, expressed with respect to the appropriate $\langle 111\rangle$ axis, are limited to those for which (n, m) have the values (2, 0), (4, 0), (4, 3), (6, 0), (6, 3), and (6, 6).

The usual starting point for estimating the crystal fields is the "point-charge model" in which the electrostatic fields are determined from elementary considerations of the crystal structure. The geometry of the a site in pure YIG has been measured by Geller and Gilleo.[12] The nearest-neighbor oxygen ions are pictured in Fig. 1. The polygon, whose vertices represent O^{--} ions, may be regarded as an octahedron, distorted by stretching along a trigonal axis so the deviations from cubic symmetry are considerable. There are four distinct kinds of a sites corresponding to the four $\langle 111\rangle$ axes of the cubic lattice along which the distortion may occur. Note that the site pictured in Fig. 1 represents a configuration about an Fe^{3+} ion.

First consider the level structure as determined by the nearest-neighbor point charges of this "normal" a site. This is shown in Fig. 2, along with the g factors for each doublet. It is encouraging to note that for most doublets the ratio of $g_{\|}$ to $g_{\perp}$ is quite large, a reflection of the fact that the field is trigonal rather than cubic. However, for the particular field values of this case, the

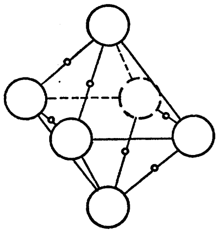

FIG. 1. The a site. The nearest-neighbor oxygens which surround an a-site Fe^{3+} ion are shown. Distances indicated by lines with open circles are 2.63 Å; other lines indicate 2.99 Å. Measurements are from Ref. 12.

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[9] C. Kittel, Phys. Rev. **117**, 681 (1960).

[10] M. T. Hutchings, Solid State Phys. **16**, 227 (1964).

[11] K. W. H. Stevens, Proc. Phys. Soc. (London) **A65**, 209 (1952).

[12] S. Geller and M. A. Gilleo, J. Phys. Chem. Solids **3**, 30 (1957).

ground doublet is predominantly comprised by the states $j_z=+\frac{1}{2}$, $j_z=-\frac{1}{2}$, and therefore the significant $g_\perp$ is quite large.

In fact, it turns out that for the range of crystal-field parameters having the same sign as those indicated by the point-charge model, there are no situations for which $g_\perp$ is sufficiently small.

Now, although point-charge calculations do not usually give proper magnitudes for the crystal fields acting on rare earths, they are generally thought to give the correct signs.[13] However, because of the distortion introduced by the Yb substitution, the above calculation is not to be taken too seriously. For example, should an additional stretching along ⟨111⟩ of 5% of the altitude of the octahedron have taken place, then the sixth-order crystal-field term, as given by a point-charge model, would change sign. Considering that the ytterbium ion is about 20% larger than Fe^{3+}, a distortion of this magnitude does not seem unlikely.

Once the restriction on the sign of the crystal field is removed, extensive ranges of parameters may be found for which $g_\perp$ is very small in the ground state in C_{3i} symmetry. The most likely situation occurs for negative sixth-order crystal fields, here taken as having the cubic relationship among terms of the same order. Figure 3 shows a situation in which the states labeled by $j_z=\pm\frac{3}{2}$ become the ground doublet. It might be recalled that this is the ground doublet found in Yb ethylsulphate.[14] If there is perfect C_{3i} symmetry, then these states are precisely $j_z=\pm\frac{3}{2}$, and clearly $g_\perp$ is exactly zero. Nonetheless, terms third-order in the exchange field would still connect these levels, so there would still be a finite level separation at near crossing. If there were some distortion of the site, as, for example, magnetostriction, some of the states $j_z=\pm\frac{1}{2}$ would be mixed in, and some first-order interaction with the transverse field would result. In either case, the situation is still describable to an excellent approximation by Eq. (2).

In summary, for reasonable crystal fields, the g factors may assume a wide range of values. Thus crystal-field theory does not provide a numerical estimate of the parameters. However, any values of these parameters, such as are necessary to explain the torque and resonance data, are not to be considered unreasonable from the point of view of crystal fields.

Doublet (Principal Constituent)	Energy (cm^{-1})	Exchange g-Factors	
		$g_\perp$	$g_\parallel$
1/2, -1/2	-788	1.04	.09
3/2, -3/2	-526	0.	.86
-5/2, 5/2	+17	.092	-1.21
7/2, -7/2	+1287	.010	+1.39

FIG. 2. Energy levels and g factors for "point-charge" a-site crystal-field values. The effect of the large axial component of the crystal field is apparent in the disparity between $g_{||}$ and $g_\perp$. Note that contrary to what is expected for the ground doublet of the anomalous ion, in this case $g_\perp$ is quite large.

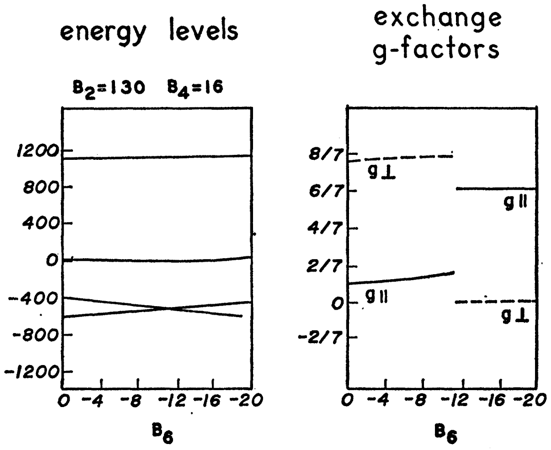

FIG. 3. Case where $j_z=+\frac{3}{2}$, $j_z=-\frac{3}{2}$ becomes the ground doublet. Values of energies and crystal fields are in cm^{-1}. For the values of the second- and fourth-order crystal fields indicated, $j_z=\pm\frac{3}{2}$ is the ground state for large negative sixth-order cubic crystal fields. In this doublet, $g_\perp$ is zero. A situation similar to this seems to be the most likely explanation of the anomaly.

4. STATIC TORQUE

In a static-torque experiment, one measures the torque necessary to prevent a sample from turning toward its easy axis when held at some fixed orientation in a magnetic field. Static torque depends only the derivative of the equilibrium free energy, and not on the dynamical details of the relaxation process by which that equilibrium is achieved; it is a simple manifestation of the energy-level structure of the ytterbium ion.

As derived from the Hamiltonian of Eq. (2), the static torque is

$$T=-6.31\times10^{21}G_\perp MN\delta'(\theta)\times\tanh[G_\perp\times M\delta(\theta)]/2KT\ \mathrm{erg/cm^3}. \qquad (4)$$

Here, N is the number of contributing ions given as a fraction of the number of c sites. The angular-dependent quantity δ is proportional to the splitting. [δ and δ' are given explicitly in Eq. (6).] The angle θ measures the angle to the local ⟨111⟩ axis, and therefore $\theta=90°$ is to be associated with an anomaly direction. The sign of the torque is such as to indicate that the anomaly is a local hard direction of the magnetization. Finally, I should point out that Eq. (6) only applies when the torque is measured in a plane which contains the local ⟨111⟩ axis, for example, a {110} plane. For other planes a simple modification must be made.

The torque anomaly consists of an abrupt change in the torque as the magnetization is passed through the anomaly direction. The change is small compared to torques associated with other constituents of the sample. However, because of the abruptness of the change,

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[13] G. Burns, J. Chem. Phys. **42**, 377 (1965).

[14] A. H. Cooke, F. R. McKim, H. Meyer, and W. P. Wolf, Phil. Mag., **2**, 928 (1957).

the torque derivative of the anomaly contrasts rather dramatically with the contributions of the slowly varying background. The torque derivative, which is a sharply peaked function, is given by

$$T' = 6.31\times 10^{21} G_{\perp} M N[\delta'' \tanh(G_{\perp}\times M\delta/2KT) + (\delta')^2 (G_{\perp}M/2KT)\,\mathrm{sech}^2(G_{\perp}M\delta/2KT)]. \quad (5)$$

The angular-dependent quantity δ and its first two derivatives are

$$\delta = \{1+[(G_{\|}/G_{\perp})^2-1]\cos^2\theta\},$$

$$\delta' = [(G_{\|}/G_{\perp})^2-1](\sin 2\theta/2\delta),$$

$$\delta'' = [(G_{\|}/G_{\perp})^2-1]\{(\cos 2\theta/\delta) + [(G_{\|}/G_{\perp})^2-1](\sin 2\theta/4\delta^3)\}. \quad (6)$$

The predictions given in the above equation are now to be compared with experiment.

Measurements of static torque have been published by Pearson.[4] Many of the data presented represented the torque with the sample constrained to rotate in a (100) plane. This configuration leads to some difficulty, because at the anomaly direction in that plane, [110], the contributions of two distinct sets of anomalous sites are superimposed. A small amount of misalignment of the sample can lead to a great distortion in the appearance of the observed effect. Fortunately, some data were also taken representing the (110) plane, in which a distinct anomaly occurs at [112].[15] Despite some considerable scatter in these data, the (110) plane measurements were used to obtain a representation of the intrinsic shape of the torque-derivative anomaly. First, the theoretical equations were fitted to the observations by choosing the G parameters. The concentration N, which is to be regarded as a scale factor, will be discussed later.

It was found that the shape of the observed anomaly in the torque derivative in the (110) plane could be duplicated rather closely, provided that the parameters $G_{\|}$ and $G_{\perp}$ obeyed a certain relation, which need not be elaborated here. All sets of parameters obeying that relation generated curves of approximately the same shape, so that shape alone could not be used to determine both parameters independently. It might be noted, however, that for assumed values of $MG_{\perp}$ less than about 2 cm^{-1}, the relation reduced to the simple requirement that $MG_{\|}$ equal about 55 cm^{-1}, independent of $G_{\perp}$. A sample of the kind of fit which can be generated is illustrated in Fig. 4.

The analysis of the shape of the torque derivative at one temperature (1.5°K) effectively fixed one of the spin-Hamiltonian parameters. In order to find another relation between the parameters, it is necessary to consider the torque at different temperatures. The only datum available for such an analysis is the dependence of the peak magnitude of the [110] torque-derivative anomaly in the (100) plane. As mentioned above, this quantity is somewhat confused by the coincidence of two anomalies from two different sites. Nonetheless, the conclusion reached either by a simple consideration of the term $\tanh(MG_{\perp}/2KT)$, or by a more complicated attempt to account for possible misalignment of the crystal, is essentially the same; it is only possible to say that $G_{\perp}M$ is less than 2 cm^{-1}. In order for $G_{\perp}$ to be determined unequivocally by this approach, measurements at temperatures of the order of $G_{\perp}M/2KT$ would have to be performed.

The last quantity of interest in Eq. (4) is N, the fraction of contributing ions. This is not known merely from the doping of the sample. N may be determined for the sample in question, however, by establishing the scale of magnitude of some quantity which does not depend sensitively on the value of the unknown parameter $G_{\perp}$. Such a quantity is the integrated area under the torque-derivative curve taken between limits a few degrees removed from the anomaly direction, that is, the change in torque as the magnetization passes through the anomaly. This quantity ΔT is given by

$$\Delta T = 4.2\times 10^4\, N G_{\|} M \text{ erg/cm}^3. \quad (7)$$

Upon taking account of the fact that torque measured in the (100) plane is not quite described by Eq. (4), we arrive at the conclusion that for the sample studied, $N = 3.7\times 10^{-4}$. Since one-half of the ions on anomalous sites contribute to the [110] anomaly and, furthermore, since the total ytterbium doping for this sample was 5%, it follows that about 1.5% of the ytterbium ions settled on the anomalous sites. There is evidence that the number of anomalous Yb's depends strongly on the method of preparation.[1] However, it is notable that only a small number of ions is required to produce the effects which have been observed, and this explains

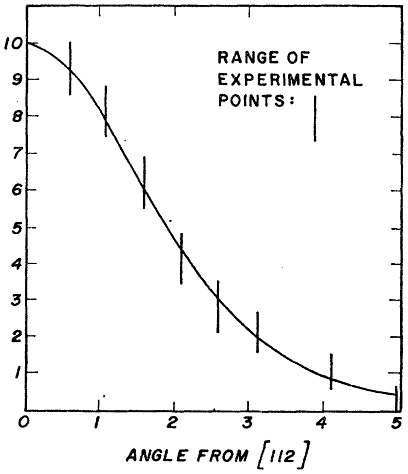

FIG. 4. The [112] torque-derivative anomaly. A theoretical prediction for the torque-derivative anomaly is compared to the (normalized) experimental results. The parameters for the theoretical curve are $G_{\|}M = 55$ cm^{-1}, $G_{\|}/G_{\perp} = 70$.

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[15] R. F. Pearson (private communication).

why, at directions not perpendicular to [111] axes, the anomalous sites have not been found to have any observable effects.

In summary, the analysis of static-torque data has enabled the determination of one of the spin-Hamiltonian parameters, $G_{||}$, as being about 55 cm^{-1}. Also, it has been estimated that about 1.5% of the ytterbium ions present settle on anomalous sites for the sample studied. It would have been valuable if the other spin-Hamiltonian parameter could have been determined, but the temperatures at which measurements have been done were not sufficiently low for this to be possible. As the ferromagnetic-resonance data are considered in the next section, the parameter $G_\perp M$ will have to be regarded as free to assume any value less than 2 cm^{-1}.

5. FERRIMAGNETIC RESONANCE

A. Summary of Results

The most interesting aspect of the ytterbium anomaly appears in ferrimagnetic-resonance measurements. As the frequency of measurement is increased, the single peak in the field for resonance as plotted against the angle of the magnetization separates into two peaks.[1] At still higher frequencies, the linewidth peak also splits. It has been suggested by Dillon and others that this sort of behavior is a manifestation of the fact that at the higher frequencies the incident frequency is somewhat higher than the minimum level separation of the ionic levels of the rare-earth ion. As the magnetization is moved away from the anomaly direction, the level spacing increases until some sort of resonant effect is achieved. This process is illustrated in Fig. 5.

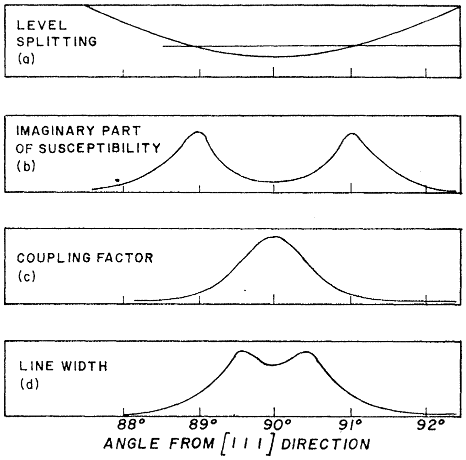

FIG. 5. General behavior at near-crossing-double peak in linewidth. (a) The splitting is shown as a function of angle from a [111] axis in a (110) plane. The incident frequency is indicated by the horizontal line. Here the incident frequency is taken as greater than the minimum value of the splitting so at some angle a resonance may be achieved. (b) The imaginary part of the rare-earth ion susceptibility is peaked at the resonance angles. (c) However, the coupling between the precessing iron magnetization and the ion is strongly peaked at the center of the anomaly. (d) The linewidth is the product of the susceptibility and the coupling. Even if there is a double peak in the susceptibility, the linewidth may appear as only a single peak, although in the case illustrated, some evidence of the double peaks remain.

The reader should be aware at the outset that although the above picture of the situation is fundamentally the one which will be pursued, certain difficulties immediately present themselves. For example, when the details of the coupling between the magnetization and the rare-earth moment are taken into account, the splitting of the various peaks must be associated with a relatively undamped system which undergoes a sharp resonance as the level spacing becomes equal to the ferrimagnetic-resonance frequency. However, for such systems, it would be expected that at fixed angle of the magnetization, which corresponds to a fixed splitting, the resonant response would take place over a correspondingly limited frequency range. Nonetheless, in point of fact, it is found that the effect occurs over a very broad range of incident frequencies. Indeed, the linewidth is seen to be increasing at the highest frequency at which measurements have been performed. This difficulty should become more clear as the detailed theory is developed.

B. Equation for a Kramers Doublet

The theory of the ferromagnetic resonance of an isotropically coupled rare-earth–iron system, without crystal-field effects, was presented by Kittel.[16] The theory for the case when crystal fields are important was developed by Walker[17] for the case of terbium. An equivalent, and more expeditious approach for the specific case of a Kramers doublet is contained in the work of Hartmann-Boutron[18] and Van Vleck and Orbach[19] on longitudinal relaxation. Although the anomaly is rather primarily a transverse effect, it is their approach which is closest to the one adopted below.

The procedure for considering the resonance anomaly is basically to find an equivalent linear paramagnetic problem for each system. That is to say, the Hamiltonian must assume a form in which there is one large static effective field, and all time-varying fields are small. The small transverse fields give rise to a paramagnetic resonance, the longitudinal fields to the nonresonant longitudinal effects, such as have been described by Gorter[20] for the ordinary paramagnetic case, and by Clogston[21] and others for longitudinal relaxation in ferrimagnets.

The problem is most conveniently analyzed by relating it to an equivalent isotropically coupled paramagnetic system. In order to achieve the analogy, it is necessary to construct a scaled effective field whose components are related to those of the ordinary effective

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[16] C. Kittel, Phys. Rev. **115**, 1587 (1959).

[17] J. F. Dillon and L. R. Walker, Phys. Rev. **124**, 1401 (1961).

[18] F. Hartmann-Boutron, Compt. Rend. **256**, 4412 (1963).

[19] J. H. Van Vleck and Orbach, Phys. Rev. Letters **11**, 65 (1963).

[20] C. J. Gorter, *Paramagnetic Relaxation* (Elsevier Publishing Company, Inc. New York, 1947).

[21] A. M. Clogston, Bell System Tech. J. **34**, 739 (1955).

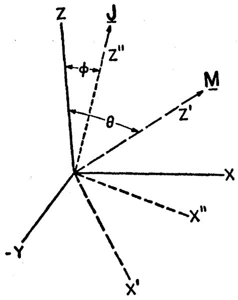

FIG. 6. Coordinate systems for describing the moments. If M_{Fe} lies along z', then its static scaled field will be along z''. A simple calculation reveals that $G_{||}\tan\Phi = G_{\perp}\tan\theta$. The Yb^{3+} ion responds with a static moment along the scaled field.

field by absorbing the corresponding coupling factors. Once the scaled field is constructed, the moment may be regarded as isotropically coupled to it. Then, the only deviation from azimuthal symmetry of the unperturbed Hamiltonian about the axis of the large static scaled field occurs via damping terms. Thus, if anisotropic damping is neglected, simple forms for the susceptibility become appropriate to describe the response to the scaled fields.

In analyzing the complete Yb–Fe system, we first solve the equivalent paramagnetic problem of the response of the Yb ion in the effective field created by the iron magnetization. Next, we solve the equivalent paramagnetic problem for the magnetization in the effective field due to the rare-earth ion, added to the external magnetic field.

The above procedure requires the construction of three coordinate systems as outlined in Fig. 6. The unprimed coordinate system is the one in which the appropriate [111] crystal axis corresponds to the z axis. The Hamiltonian [Eq. (2)] has been written in this unprimed system. The primed system is constructed so that the z' axis corresponds to the equilibrium position of the magnetization. This will also be taken as the direction of the static external field, since it may be shown that the distinction between the two directions is of little consequence. Last, there is the double-primed system, which is arranged so that the equilibrium position of the anomalous ytterbium moment lies along z''. The relation of this system to the other two is indicated on the figure. These three coordinate systems have the advantage that, by construction, the large static part of each moment appears along the appropriate z axis. Thus the transverse components of both $\mathbf{M}_{\mathrm{Fe}}$ and $\mathbf{J}$ may be regarded as small quantities and therefore will be designated by small letters, for example, $m_{y''}$, $j_{x''}$.

The Hamiltonian for this system in the presence of an external field with transverse, time-varying components is, in the unprimed system,

$$H = G_{||}M_zJ_z + G_{\perp}M_xJ_x + G_{\perp}M_yJ_y - \mathbf{H}\cdot\mathbf{M}. \tag{8}$$

The direct interaction of the external field with the rare earth is ignored, since it is always small compared with exchange, provided most of the anisotropy is ascribed to the ordinary g factor. For simplicity, it is assumed that there is one Yb^{3+} ion in 1 cc of material.

Now consider the Hamiltonian as it affects the ytterbium ion. In the appropriate coordinate systems, this is

$$\begin{aligned} H = {} & J_{z''}(G_{\perp}\delta' m_{x'} + G_{\perp}\delta M_{z'}) \\ & + j_{x''}(m_x G_{||}/\delta) + j_{y''}(m_{y'}G_{\perp}). \end{aligned} \tag{9}$$

The quantities δ and δ' are defined in Eq. (6). Equation (9) is written in such a way that it is clear that the quantities in brackets play the role of effective fields in an isotropic-paramagnetic experiment, as described earlier.

We start by observing that the only large static term, which is proportional to $M_{z'}$, does indeed act only on $J_{z''}$, and this will give rise to static-z'' component of the rare-earth moment. The external field causes the magnetization to precess, giving rise to time-varying effective fields through the factors proportional to $m_{x'}$ and $m_{y'}$. Note that the anisotropic coupling leads to the scaled effective fields having a quite different direction from that of the magnetization. The rare-earth ion responds to them with both longitudinal and transverse time-varying moments. The exact form of the response may be conveniently written if we first define a susceptibility χ as follows: Let there be an "isotropic" Hamiltonian of the form[22]

$$H = H_zJ_z + h_zJ_z + h_xJ_x + h_yJ_y, \tag{10}$$

where H_z is a large static field, and h_i are small time-varying fields. χ_{ij} is then the function which gives the linear response of ith moment to the jth field. For example,

$$J_y = \chi_{yx}h_x + \chi_{yy}h_y. \tag{11}$$

In the above notation, the rare-earth response is formally expressed as follows:

$$\begin{aligned} J_{z''} &= J_0 + m_{x'}\chi_{zz}G_{\perp}\delta', \\ J_{x''} &= \chi_{xx}(G_{||}/\delta)m_{x'} + \chi_{yy}G_{\perp}m_{y'}, \\ J_{y''} &= \chi_{yx}(G_{||}m_{x'}/\delta) + \chi_{yy}G_{\perp}m_{y'}. \end{aligned} \tag{12}$$

J_0 is the static moment and is given by

$$J_0 = -\tfrac{1}{2}\tanh(G_{\perp}\times M\delta/2KT). \tag{13}$$

The above values for the rare-earth moment may now be returned to Eq. (8) and the effective field acting on the magnetization constructed. With a few simplifications, the Hamiltonian becomes

$$\begin{aligned} H = {} & -M_{z'}(-G_{\perp}\delta J_0 + H) - m_{x'}[G_{\perp}\delta' J_0 - \chi_{zz}(G_{\perp}\delta')^2 m_{x'} \\ & - (G_{||}/\delta)m_{x'}\chi_{xx} - (G_{||}G_{\perp}/\delta)m_{y'}\chi_{xy} + h_{x'}] \\ & - m_{y'}[-(G_{||}G_{\perp}/\delta)m_{x'}\chi_{yx} - G_{\perp}^2\chi_{yy}m_{y'} + h_{y'}]. \end{aligned} \tag{14}$$

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[22] Note that the H field in Eq. (10) need have no particular relation to the magnetic field. It just represents a set of numerical coefficients, here having the units of energy.

Note that there is a small static term multiplying $m_{x'}$. This is just a manifestation of the static magnetocrystalline anisotropy associated with the anomaly, and may be accounted for by noting that the angle between the static magnetization and the external field actually changes somewhat as the magnetization is rotated through the anomaly. For small doping, this effect is not important.

The response of the iron lattice to the effective field is well approximated to be that of an inherently undamped system. The imaginary part of the susceptibility to the external fields alone, which manifests itself as linewidth, arises explicitly via the interaction of the Fe magnetization with the rare earths. Near resonance of the iron system, only the m^+ component of the time-varying magnetization need be considered. First, we define the function R:

$$R=(G_{||}/\delta)^2\chi_{xx}+G_{\perp}^2\chi_{yy}+i(G_{||}G_{\perp}/\delta)(\chi_{yx}-\chi_{xy}). \qquad (15)$$

In terms of this function, the magnetization is given by

$$m^+=\frac{M}{-G_\perp\delta J_0+H-(\omega\hbar/g\beta)} \times\{h^+-\tfrac{1}{2}m^+[\chi_{zz}(G_\perp\delta')^2+R]\}. \qquad (16)$$

Here, M denotes the magnitude of the iron magnetization. The self-consistent solution to Eq. (16) is

$$m^+=\frac{Mh^+}{-G_\perp\delta J_0+H-(\omega\hbar/g\beta)+\frac{1}{2}MR+\frac{1}{2}M\chi_{zz}(G_\perp\delta')^2}. \qquad (17)$$

The shift in the field for resonance will be called δH:

$$\delta H=G_\perp\delta J_0-\mathrm{Re}[\tfrac{1}{2}MR+\tfrac{1}{2}M\chi_{zz}(G_\perp\delta')^2]. \qquad (18)$$

The full linewidth to half-power is ΔH:

$$\Delta H=2\,|\,\mathrm{Im}[\tfrac{1}{2}MR+\tfrac{1}{2}M\chi_{zz}(G_\perp\delta')^2]|. \qquad (19)$$

The above equations are actually applicable only for a system with one spin per cc. In order to apply to a sample containing N contributing sites, where N is expressed as a fraction of c sites, the equations should be multiplied by the factor $1.262\times10^{22}\,N$. This completes the formal problem of the coupling of the ferromagnetic resonance to the paramagnetic response of the rare-earth ion. In order to obtain numerical predictions for both the shift in the field for resonance and the linewidth, it is now necessary to specify the paramagnetic susceptibilities χ_{ij}.

First, consider the longitudinal contribution. If the longitudinal relaxation is taken to be governed by an equation of the form

$$dJ_z/dt=-[J_z-J_0(t)]/T_1, \qquad (20)$$

then the longitudinal susceptibility is found to be

$$\chi_{zz}=-\tfrac{1}{2}(2KT^{-1})\ \mathrm{sech}^2(G_\perp M\delta/2KT) \times[(1-i\omega T_1)/(1+\omega^2T_1^2)]. \qquad (21)$$

T_1 is the longitudinal relaxation time.

The contribution of longitudinal relaxation of a Kramers ion to the resonance properties of YIG has been discussed by Van Vleck and Orbach.[19] If the longitudinal relaxation time is short compared to the resonance frequency, then the shift in the field for resonance closely approximates the torque derivative. For the anomaly, however, the shift as measured at 1.5°K is far narrower in angular extent than the torque derivative. In fact, close analysis shows that unlike most other effects of rare-earth ions in YIG, this ytterbium anomaly is best considered under the assumption that longitudinal relaxation is too slow to be of significance, at least for the 1.5°K measurements. This is equivalent to setting the longitudinal relaxation time equal to some value greater than 10^{-10} sec. Although most previous considerations of rare-earth ion relaxation in YIG are not strictly applicable to the case at hand, it is still possible to conclude that such values of T_1 are not unreasonable for these low temperatures and small level splittings. Thus we will ignore terms involving χ_{zz}.

The bulk of the interesting detail in the resonance measurements arises from the frequency dependence of the transverse susceptibilities contained in the function designated R in Eq. (17). For example, consider the susceptibility of the rare earth as it would be derived from the Landau and Lifshitz model of a damped classical spin. The same form results, if it is assumed that the spin relaxes via short collisions.[23] The explicit form of this susceptibility is, for the case at hand,

$$\chi^{\pm}=\frac{J_0}{G_\perp M\delta}\,\frac{\pm G_\perp M\delta+(i\hbar/T)}{\pm G_\perp M\delta-\hbar\omega+(ih/T)}. \qquad (22)$$

Note that there is just one relaxation parameter which appears in this form. This parameter T would probably be some function of angle, temperature, and possibly even frequency. However, for the sake of clarity, I will consider here only the case where T is taken as constant. The basic conclusions are not substantially altered when this restriction is lifted.

Before comparing numerical predictions with the data, it should be remarked that it is the resonance denominator in Eq. (22) which is responsible for the double peaks. Recall, however, that the double peaks occur in the plot of linewidth or shift against angle of the magnetization, and thus it is the level splitting which is being swept past the resonance frequency. Along with the variation of angles comes a rather strong variation in the coupling factors in Eqs. (18) and (19), which will modify the effect of the resonance

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[23] R. Karplus and J. Schwinger, Phys. Rev. **73**, 1020 (1948).

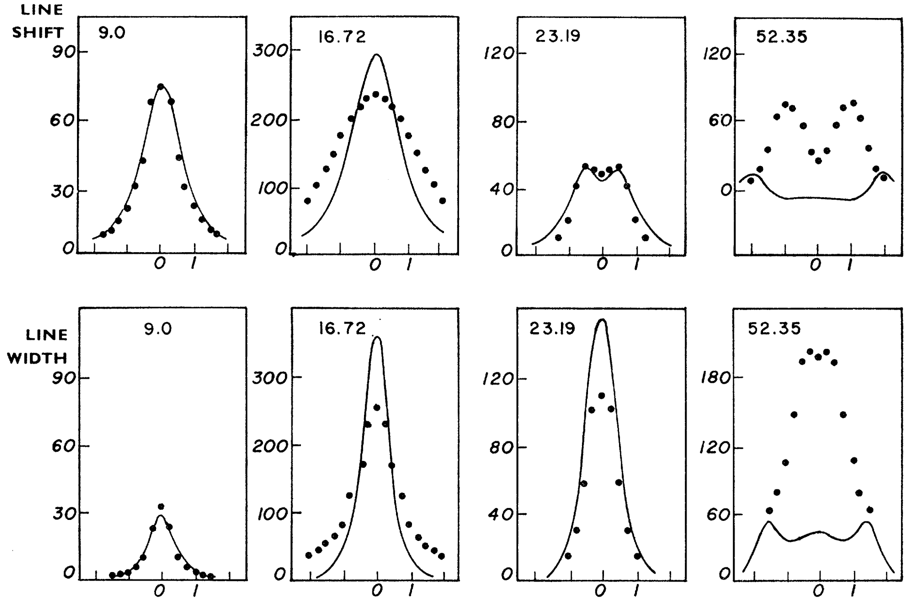

Fig. 7. Comparison for Landau and Lifshitz form for the susceptibility. This is a best fit which corresponds to the parameters $G_\perp M=22$ kMc/sec, $T=1.5\times10^{-11}$ sec, in Eq. (22). The 16-Gc/sec data were taken by B. Clarke on a 5.1%-doped sample at 4.2°K. All other data are by J. Dillon on a 0.1%-doped sample at 1.5°K. The "experimental points" shown above as circles are not actual data points, but rather a symmetrized summary of the results. The abscissa represents the angle from a ⟨112⟩-anomaly direction.

denominator considerably. In particular, for some choices of parameters, it is possible to pass through resonance without producing any double peaks at all (see Fig. 5). In summary, a large variety of curve shapes may be produced for different sets of parameters, and thus it is difficult to make brief statements regarding the general nature of the predictions. I will therefore only discuss the comparison with experiment.

C. Experiment

Experimental measurements of the resonance anomaly have been done by Dillon,[1] Clarke,[2] and Penney.[3] I will focus attention on the measurements of Dillon,[1] performed on a 0.1%-doped sample at 1.5°K, at frequencies of 9.0, 23.19, and 52.35 Gc/sec, and also on those performed by Clarke on a 5%-doped sample at 4.2°K, for a frequency of 16.7 Gc/sec.[24] I have estimated the anomalous contribution to the lineshifts by subtracting off a smooth background. No attempt was made to subtract off background effects for the linewidth.

The scale factor N, which gives the number of contributing anomalous ions, was estimated for the two samples as follows. Clarke's sample was presumed to be similar to the one used by Pearson, and for which an independent value of N was available from static-torque measurements. For Dillon's sample, no independent value of N was available, so N was chosen by arranging for the lineshift prediction for 9 Gc/sec, at the center of the anomaly to agree with experiment. This leaves just two free parameters in the equations. They are the minimum level separation $G_\perp$ and the relaxation time T.

Figure 7 represents a best fit, obtained principally by trial and error with these two parameters and the Landau and Lifshitz susceptibility. Particular emphasis was placed on fitting the lowest-frequency curves, and reasonable success was achieved. However, the disagreement for the 52 Gc/sec curve is quite serious. The theoretical prediction may generously be said to have some of the shape characteristics of the experimental measurements. However, it is a factor 5 or so too small in magnitude. There are modifications regarding the relaxation time which can provide a better fit to the shape, but if the agreement at low frequency is to remain acceptable,[25] it would seem that (for the assumed form of the susceptibility) the high-frequency curve cannot be made to agree. The trouble lies in the fact that if the double peak at 23 is to be reproduced, the minimum splitting cannot be assumed to be much higher than 23 Gc/sec; and, furthermore, the relaxation time must not be too short. However, if these conditions are satisfied, the absorption at the center of the anomaly should be smaller at 52 Gc/sec than at 23. In reality, the opposite is the case.

A considerable number of variations of the procedure leading to the above results have been considered. For example, the relaxation time was allowed to vary with angle and with frequency. Also the results for various parameters were averaged over angles to allow for some sort of gross crystal inhomogeneity. However, no significant improvement was achieved. The basic difficulty, which is an insufficient range in frequency for the strongly resonant behavior of the absorption or dispersion with angle, seems to be inexorably tied to the form which has been chosen for the susceptibility.

There is still another difficulty which is to be associ-

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[24] Note that there is some difference in the manner in which these authors defined the doping.

[25] Should the low-frequency data be ignored, it is quite simple to reproduce the 52-kMc/sec measurements.

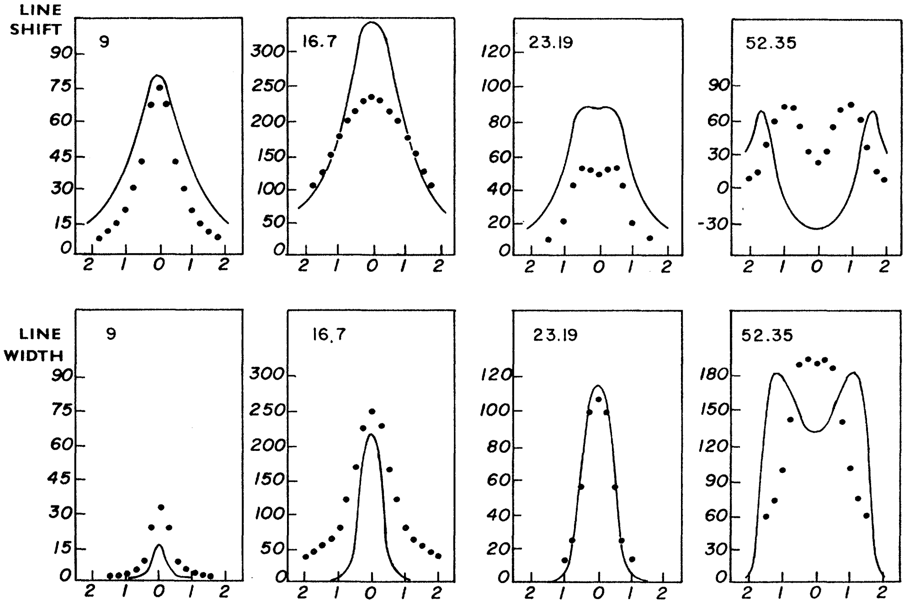

FIG. 8. Comparison for inhomogeneous broadening. A particularly simple form of inhomogeneous broadening, which corresponds to a radial Gaussian distribution of $G_{\perp}M$ about some most probable value, is shown. Here, the most probable value is taken as 25 kMc/sec, and the width of the distribution is 20 kMc/sec. As in Fig. 7, the abscissa represents the angle from a ⟨112⟩-anomaly direction.

ated with the rather short transverse (10^{-11} sec) relaxation time indicated by these results. Recall that the longitudinal relaxation time was found to be longer than 10^{-10} sec. On the other hand, the form of susceptibility which was chosen is based on a collision-type model which would imply longitudinal and transverse relaxation times of the same magnitude.

It might be noted at this point that an effort was made to compute the susceptibility associated with relaxation to magnons, since this process is fully parametrized by the magnetic coupling. A modification of the Green's procedure of Huber and Van Vleck[26] was applied to a Hamiltonian similar to Eq. (2), but extended to include spin-wave effects on the Fe magnetization. From the results, it is clear that this mechanism is far too weak to account for the short observed transverse relaxation time. Since this mechanism would be likely to contribute to longitudinal relaxation as well, it is not surprising, in view of the long longitudinal relation time, that this mechanism was found to be small.

Several attempts were made to fit the data with alternative forms for the susceptibility. The most promising of these is shown in Fig. 8. Here, the susceptibility is constructed by averaging over contributions for different values of $G_{\perp}$ with the relaxation time taken as infinite. The origin of this distribution is envisioned to be some sort of quasistatic broadening mechanism. Such a mechanism would not be expected to contribute to longitudinal relaxation,[27] and thus the rather broad resonance would not be inconsistent with the long assumed longitudinal relaxation time. The disagreement in the shapes of the curves can probably be remedied by a reasonable assumption regarding the change in the distribution with angle. However, the most serious problem here which would remain is that at the lower frequencies the linewidth is generally smaller than what is observed.

In this section, it has been shown that many features of the resonance data may be reproduced by the theory outlined. However, complete agreement for all frequencies has not been achieved. It should be noted, however, that the frequency range covered spans both above and below the assumed level-splitting frequency of the ion. Thus the predictions are quite sensitive to the exact form assumed for the rare-earth ion susceptibility and not just some limiting case of it, as, for example, has been applied by various authors in their discussions of the "fast-relaxation theory."[28] It is quite possible that some more appropriate assumptions regarding the susceptibility might yet bring about good agreement with experiment. However, until measurements are performed at a sufficiently high frequency so that the linewidth is clearly decreasing with successive increases in frequency, it is not possible to be confident about the form which such a susceptibility might take.

6. CONCLUSION

The theory of static-torque and ferromagnetic resonance for a magnetic moment coupled to an ion described by a Kramers doublet has been applied to the case of the (111) anomaly in ytterbium-doped YIG. The simple model is completely solvable in the context

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[26] D. Huber and J. H. Van Vleck, Rev. Mod. Phys. **38**, 187 (1966).

[27] R. Kubo, in *Lectures in Theoretical Physics*, edited by Brittin and Dunham (Interscience Publishers, Inc., New York, 1959), Vol. 1, p. 120.

[28] See M. Sparks, *Ferromagnetic Relaxation Theory* (McGraw-Hill Book Co., New York, 1964).

of a molecular-field approximation to the exchange interaction, and predictions for all relevant properties have been produced.

The theory for the static-torque anomaly can be made to agree with experiment, provided that $G_{||}M = 55$ cm^{-1}. The other parameter in the spin Hamiltonian is not determinable from the data which are available, and it would be useful in this regard if data at temperatures lower than about 0.5°K could be obtained.

The result of a comparison of the theory for ferromagnetic resonance with linewidth and lineshift measurements is encouraging. The resonance predictions depend sensitively on the exact form of the resonant susceptibility of the rare-earth ion. They thus have the potential of providing a deeper insight into this property than previous work on rare-earth-doped YIG.[17] However, it is also clear that the high-frequency behavior of the rare-earth susceptibility is still incompletely described, and it would seem that further experimental results at higher frequencies would be most valuable in resolving this point.

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Theory of Magnetically Induced Electric Field Gradients in Cubic Fe^{2+}†

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The detection of a nonvanishing quadrupole interaction in ferrous compounds in which the Fe^{2+} ion occupies a site of cubic symmetry has been achieved in several cases, using Mössbauer spectroscopy. In some cases, the onset of this interaction has been found to be simultaneous with the appearance of magnetic ordering. A detailed theory of this effect is presented, which applies where the magnetic ordering is spontaneous (magnetic phase transitions), as well as where it is obtained by applying external magnetic fields to a paramagnetic compound. It is shown that an electric field gradient is induced by the magnetic ordering via the spin-orbit coupling. Utilizing the crystal-field approach, the magnetic ordering is described by adding a magnetic term to the Hamiltonian, using the molecular-field approximation. For cases where the magnetic term can be treated as a perturbation—which requires that it should be small compared to the spin-orbit interaction—closed expressions are obtained for the induced electric field gradient and for the magnetic hyperfine field at the site of the nucleus. The procedure required for other cases is outlined. The form of the resulting Mössbauer spectrum is discussed. It is shown that the quadrupole interaction is positive if the magnetic axis is parallel to a ⟨111⟩ direction, and that is it of equal magnitude, but negative, when the axis is parallel to a ⟨100⟩ direction. This fact may be utilized to determine the direction of the magnetic axis from Mössbauer measurements on a powder sample. Experimental evidence and possible applications of the theory are discussed.

1. INTRODUCTION

In recent years Mössbauer spectroscopy has become an important tool for investigating hyperfine interactions between nuclei and their electronic environment.[1]

The quadrupole interaction, i.e., the interaction between the quadrupole moment of the nucleus and the electric field gradient (EFG) at the site of that nucleus, has been observed to contain very interesting information on the environment of the site, as well as on the electronic structure of the ion.

In the following discussion we shall be concerned with ferrous compounds, namely compounds containing the Fe^{2+} ion.

In paramagnetic ferrous compounds, the quadrupole interaction, which causes the splitting of the Mössbauer absorption line of the Fe^{57} nucleus (ΔE_Q), can be

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[1] G. K. Wertheim, *Mössbauer Effect: Principles and Applications* (Academic Press Inc., New York, 1964).