

## Magnetic Hyperfine Interaction and Electronic Relaxation in Rare-Earth Ions in Europium Iron Garnet\*

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The attenuation and rotation of the integral angular correlation for the  $2^-(1409 \text{ keV})2^+(122 \text{ keV})0^+$   $\gamma$ - $\gamma$  cascade in  $\text{Sm}^{152}$  following  $K$  capture in  $\text{Eu}^{152}$  and of the  $1^-(1280 \text{ keV})2^+(123 \text{ keV})0^+$   $\gamma$ - $\gamma$  cascade in  $\text{Gd}^{154}$  following beta decay in  $\text{Eu}^{154}$  was measured in polycrystalline samples of europium iron garnet from  $-25^\circ\text{C}$  to above the Néel point with and without magnetizing field perpendicular to the counter plane. These data and differential angular correlation data, have been analyzed using an extension of the theory of Abragam and Pound to time-dependent magnetic hyperfine interactions in magnetic materials. Explicit formulas for the dependence of the angular correlation on the electronic relaxation time, the average effective field acting at the nucleus in the direction of the magnetizing field  $\langle H_{\text{int}}^z \rangle$ , and the mean square fluctuating field  $\langle H_{\text{int}}^2 \rangle$  are given. The sign, magnitude, and temperature dependence of  $\langle H_{\text{int}}^z \rangle$  in  $\text{Sm}^{152}$  were in excellent agreement with

the expectation value of  $H_{\text{int}}^z$  calculated from molecular field theory under the assumption that the electronic configuration following  $K$  capture in  $\text{Eu}^{152}$  is that of the  $\text{Sm}^{+3}$  ion. Crystalline field and quadrupole interaction effects have been neglected. The contribution of the magnetic hyperfine interaction arising from the exchange between the  $4f$  and inner core  $s$  electrons was small compared with that from the orbital and spin moments of the  $4f$  shell. The value of the root-mean square hyperfine field was found to be  $4.7 \times 10^6$  Oe and that of the average effective field was  $4 \times 10^6$  Oe at room temperature. The electronic relaxation time was  $4 \times 10^{-12}$  sec at room temperature and varied inversely with absolute temperature. The electronic state in  $\text{Gd}^{154}$  following beta decay in  $\text{Eu}^{154}$  has as yet not been determined.  $\langle H_{\text{int}}^z \rangle$  was found to be  $8 \times 10^4$  Oe at room temperature.

### I. INTRODUCTION

THE hyperfine interaction in atoms or ions in solids has been extensively studied by various techniques such as electron spin resonance and nuclear magnetic resonance. While the exchange interactions between spins in the ordered phase has rendered electron spin resonance determinations of hyperfine interactions in magnetic materials unfeasible, such studies have been carried out by nuclear magnetic resonance, nuclear alignment, and more recently Mössbauer techniques. The goal of some of these experiments has been to determine the magnitude and sign of the effective magnetic field,  $H_{\text{int}}$ , at the nucleus and applications have been made to various transition elements and some rare earths.

In this laboratory we have concentrated on the study of magnetic hyperfine interactions using the method of  $\gamma$ - $\gamma$  angular correlations. The application of the angular correlation technique to the study of magnetic materials has already been described by us.<sup>1,2</sup> It is the purpose of this paper to report in detail the results of such studies of the magnetic hyperfine interaction in some rare-earth nuclei in rare-earth iron garnets, from which we have been able to determine the magnitudes and signs of the magnetic hyperfine fields and the electronic relaxation times of the rare-earth ions over a wide range of temperatures.

### II. ANGULAR CORRELATION THEORY FOR MAGNETIC MATERIALS<sup>3</sup>

The angular correlation of successive nuclear gamma rays from a nucleus in free space depends only on the

angle between the directions of the emitted radiation  $\theta$ , and is usually written in terms of an expansion in Legendre polynomials, i.e.,

$$W(\theta) = 1 + \sum_L A_L P_L(\cos\theta). \quad (1)$$

A magnetic field  $H$ , applied perpendicular to the plane formed by the radioactive source and the two radiation detectors, causes a Larmor precession of the nuclear moment about the field axis; the precession angle being determined by the Larmor frequency  $\omega$  and the time  $t$  spent by the nucleus in the intermediate state before the emission of the second radiation. Thus, the angular correlation pattern is rotated through an angle  $\Delta\theta = \omega t$  and we have

$$W(\theta, t) = 1 + \sum_L A_L P_L[\cos(\theta + \omega t)], \quad (2)$$

with

$$\omega = (\mu_N/I)H/\hbar = g_N \mu_{nm} H/\hbar. \quad (3)$$

Here,  $\mu_N$  is the nuclear magnetic moment,  $\mu_{nm}$  the nuclear magneton,  $I$  the nuclear spin, and  $g_N = \mu_N/I\mu_{nm}$  the nuclear "g factor" of the intermediate state.

In the *differential* angular correlation measurement,  $W(\theta, t)$  is measured as a function of  $t$ . This form of the correlation can only be determined in an experiment in which the resolving time of the apparatus is less than the mean intermediate-state nuclear lifetime  $\tau_N$ .

In the *integral* correlation the resolving time of the apparatus is large compared with the lifetime  $\tau_N$  so that the expression (2) must be averaged over the distribution  $e^{-t/\tau_N}$ . For the special case where  $W(\theta, t) = 1 + A_2 P_2[\cos(\theta + \omega t)]$  (applicable to the cascades studied in this paper) this integration results in the form

$$W(\theta, t) = 1 + [3A_2/(4 + A_2)] \cos(2\Delta\theta) \cos 2(\theta + \Delta\theta), \quad (4)$$

effect of extranuclear fields on the correlation, see, for instance Rolf M. Steffen, *Phil. Mag.* **4**, 293 (1955); E. Heer and T. B. Novey, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1959), Vol. 9, p. 200.

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<sup>1</sup> M. E. Caspari, S. Frankel, and M. A. Gilileo, *J. Appl. Phys.* **31**, 320S (1960).

<sup>2</sup> M. E. Caspari, S. Frankel, D. Ray, and G. T. Wood, *Phys. Rev. Letters* **6**, 345 (1961).

<sup>3</sup> For an account of angular correlation measurements and the

where  $\Delta\theta$  is the mean precession angle given by

$$\Delta\theta = \frac{1}{2} \tan^{-1}(2\omega\tau_N). \quad (5)$$

The coefficient  $\cos 2\Delta\theta$  in expression (4) represents an "apparent" attenuation of the angular correlation coefficient, which arises physically from the fact that the nuclei live for different times in the applied field and hence exhibit different rotations.

Both differential and integral angular correlation measurements have been used in the past to study magnetic moments of excited nuclear states, and the angular correlation method accounts for almost all the determinations of excited state moments. Because easily obtainable applied fields of about 20 000 G have been used in the past for such measurements, this method has been restricted to states having lifetimes larger than about  $10^{-9}$  sec.

In practice the interactions of the nucleus with atomic fields complicate the simple picture. The anisotropy of the angular correlation is caused by differences in the population of the magnetic substates of the intermediate nuclear state following the emission of the first  $\gamma$  ray. The effect of time-dependent fluctuating fields which may arise from atomic interactions is to cause transitions among these nonuniformly populated magnetic substates of the intermediate nuclear state. If the fluctuating fields are sufficiently strong so that the magnetic substates become equally populated in a time less than the nuclear lifetime, the angular correlation can be completely destroyed.

If there is no preferred orientation of the random field and the characteristic frequencies of the fluctuating fields  $\nu_s = 1/\tau_s$  are large compared with  $\omega$  and  $1/\tau_N$ , the differential correlation can be shown to take the form

$$W(\theta, t, \lambda) = 1 + A_2 e^{-\lambda t} P_2[\cos(\theta + \omega t)]. \quad (6)$$

The integral correlation then becomes

$$W(\theta, \lambda) = 1 + [3A_2/(4\alpha + A_2)] \cos(2\Delta\theta') \cos(2\theta + 2\Delta\theta'),$$

where

$$\alpha = 1 + \lambda\tau_N \quad \text{and} \quad \Delta\theta' = \frac{1}{2} \tan^{-1} \beta = \frac{1}{2} \tan^{-1} \left( \frac{2\omega\tau_N}{1 + \lambda\tau_N} \right). \quad (7)$$

Abragam and Pound<sup>4</sup> have given the theoretical basis for Eq. (6) and have given explicit expressions for  $\lambda$  for time-dependent electric fields interacting with the nuclear quadrupole moment. Comparison with (4) shows that the essential effect of time dependent perturbations is to reduce both the amplitude and mean rotation by a factor of approximately  $(1 + \lambda\tau_N)^{-1}$  for small rotations.

In magnetic materials the situation is somewhat different largely because of the presence of magnetic hyperfine interactions arising from the interaction of the electrons in the incomplete shell (3d electrons in the

transitions elements, 4f electrons in the rare earths) with the nuclear magnetic moment. In solids the effect of the magnetic hyperfine interactions is usually described in terms of a magnetic hyperfine field  $\mathbf{H}_{\text{int}}$  acting at the nucleus.

We will first discuss the case where the hyperfine interaction can be considered to be static relative to the lifetime of the intermediate nuclear state. In a paramagnetic atom without an applied magnetic field the internal field averaged over all nuclei is then zero. In magnetic materials below the Curie or Néel temperature  $T_c$ , however, the electrons in the incomplete shell of the magnetic atoms or ions are exchange coupled and their spins or magnetic moments may be almost completely aligned. In ferro- or ferrimagnetic materials a magnetic field applied perpendicular to the measurement plane (z direction) can be used to orient the domains in the sample and hence the magnetic hyperfine field  $\mathbf{H}_{\text{int}}$ . The absolute values of  $\mathbf{H}_{\text{int}}$  are usually very large compared with the applied fields presently available. Thus, in the transition elements these fields are of the order of several hundred kilo-oersteds and in the rare earths (except for ions with  $L=0$ ) they are of the order of several million oersteds. If, in a ferro- or ferrimagnetic material, the spins of the magnetic atoms or ions are completely aligned and the domains are oriented in a direction perpendicular to the plane of the counters, the rotation of the angular correlation pattern is then governed by the large magnetic hyperfine field acting at the nucleus since the applied magnetizing field needed for saturation is almost always negligible compared with the hyperfine field. If there is no fluctuating component of the hyperfine field, expressions (2) and (3) still describe the rotation of the angular correlation patterns with  $H$  in expression (3) being replaced by  $H_{\text{int}}$ . This condition is achieved when the electronic relaxation time  $\tau_s$ , is greater than the nuclear lifetime  $\tau_N$ . Below  $T_c$ , this is the case in most magnetic materials since the exchange interaction greatly enhances the electronic relaxation time.

The situation in some ferrimagnetic materials differs from the simple case discussed above in the following significant respects: According to molecular field theory the exchange interaction between the various magnetic sublattices can be expressed by a magnetic exchange field  $H_{\text{exch}}$  which acts on the spin of an atom or ion on one sublattice and is proportional to the magnetization of the other sublattices as well as that of its own sublattice. In a structure which has three magnetic sublattices, it is possible that the exchange interaction between two of these sublattices is much stronger than any of the other exchange interactions present. It is then the interaction between these strongly interacting sublattices which determines the Néel temperature of the substance. The effect of the magnetic interactions on an atom or ion in the other sublattice is then similar to that of an external magnetic field on a paramagnetic atom or ion except in so far as  $H_{\text{exch}}$  acts

<sup>4</sup> A. Abragam and R. V. Pound, Phys. Rev. **92**, 943 (1953).

only on the electronic spin of the atom or ion while the applied field acts on the total magnetic moment. Complete alignment of the spin or magnetic moment of this atom or ion may then only occur at temperatures well below the Néel temperature. In addition, the electronic relaxation time of the magnetic atom or ion in this sublattice may be less than the mean lifetime of the intermediate nuclear state. As will be discussed later, this situation applies to the rare-earth ions (except for  $\text{Gd}^{3+}$ ) in ferrimagnetic rare-earth iron garnets which are the subject of the measurements to be discussed in this paper. Under these circumstances the rotation of the angular correlation is determined by the average magnetic hyperfine field  $\langle H_{\text{int}}^z \rangle$  acting at the nucleus in the direction of the applied field perpendicular to the counter planes used to orient the domains and hence,  $H_{\text{exch}}$ . The average magnetic hyperfine field is caused by the differences in the population among the various electronic magnetic sublevels of the atom or ion in the exchange field and has the same origin as the fluctuating field which induces transitions among the magnetic sublevels of the intermediate nuclear state and, hence, leads to an attenuation of the correlation, namely, the magnetic hyperfine field produced by the electrons. We have extended the investigation of Abragam and Pound<sup>4</sup> to include this situation. We define  $\langle H_{\text{int}}^z \rangle^{1/2}$  as the root-mean-square average of the time-varying magnetic field at the nucleus. As before,  $\langle H_{\text{int}}^z \rangle$  is the average value of the magnetic field at the nucleus in the direction determined by the (applied) magnetizing field.

Under the conditions  $\tau_s \ll \tau_N$ ,  $\tau_s \ll 1/\omega_m$  and  $\langle H_{\text{int}}^z \rangle \ll \langle H_{\text{int}}^2 \rangle^{1/2}$ , Eqs. (6) and (7) still apply and  $\lambda$  is given by

$$\lambda = -\frac{2\tau_s}{3\hbar^2} \langle H_{\text{int}}^2 \rangle g_N^2 \mu_{nm}^2 I(I+1) [1 - (2I+1)W(I12I|II)], \quad (8)$$

while

$$\omega = g_N \mu_{nm} \langle H_{\text{int}}^z \rangle / \hbar \quad \text{and} \quad \omega_m = g_N \mu_{nm} \langle H_{\text{int}}^2 \rangle^{1/2} / \hbar. \quad (9)$$

Here  $I$  is the spin of the intermediate state and  $W$  is the usual Racah coefficient. For the cascades studied in this paper,  $I=2$ , and

$$\lambda(I=2) = (2\tau_s/\hbar^2) \langle H_{\text{int}}^2 \rangle^{1/2} g_N^2 \mu_{nm}^2. \quad (10)$$

Eq. (8) is identical to that derived by Abragam and Pound<sup>4</sup> for the case of time-dependent randomly oriented magnetic hyperfine interaction and therefore applies strictly to magnetic materials only above the Curie or Néel temperature. Here  $\langle H_{\text{int}}^z \rangle = 0$  and hence there is an attenuation but no rotation of the correlation. In magnetic materials which can be described within the framework of the molecular field concept it is possible to show by perturbation theory that Eq. (8) also applies below the Curie or Néel temperature to the first order in the magnetic exchange field. Time-dependent quadrupole hyperfine interactions may of

course also lead to an attenuation of the correlation in magnetic materials. The development of the theory in terms of the parameter  $\lambda$  remains then unaltered but the explicit expression for  $\lambda$  in Eq. (8) applies to magnetic interactions only.

In the analysis of angular correlations in magnetic materials it is thus very important to establish whether time-dependent perturbations are present. For long lifetimes of the intermediate nuclear state the differential angular correlation measurement provides direct evidence for time-dependent perturbation because of the presence of the exponential damping factor  $e^{-\lambda t}$ , while the rotation in the hyperfine field appears in the separate oscillatory term  $P_2[\cos(\theta + \omega t)]$ . The differential correlation measurement for long lifetimes is therefore the most direct way of measuring the parameters  $\omega\tau_N$  and  $\lambda\tau_N$  since in the integral correlation experiment both the amplitude and rotation angle depend on these parameters in a complicated way. For intermediate states having mean lifetimes of the order of  $10^{-9}$  sec or less (this applies to cascades to be described in this paper), the resolving time of differential angular correlation measurements with the techniques presently available is such as to make such measurements quite inaccurate or even impossible. Even in the lifetime region of  $10^{-9}$  sec it may, however, still be profitable to use the differential angular correlation measurement to obtain direct evidence regarding the presence of time dependent perturbations. Once this is established the integral correlation will then give the most accurate values of the parameters  $\lambda\tau_N$  and  $\omega\tau_N$ .

Another type of experiment that can be performed consists of a measurement of the angular correlation below the Curie or Néel temperature but *without* an applied magnetic field. In this case  $\langle H_{\text{int}}^z \rangle$  of the different domains of a polycrystalline sample are randomly oriented. If Eq. (6) is integrated over the randomly distributed internal field directions as well as over the nuclear lifetime, we obtain

$$W(\theta, \lambda) = 1 + A_2 G_2 P_2(\cos\theta), \quad (11)$$

where

$$G_2 = \frac{1}{5\alpha} \left[ 1 + \frac{2}{1 + (\beta/2)^2} + \frac{2}{1 + \beta^2} \right]. \quad (12)$$

It is clear that it is advantageous to measure both the amplitude and rotation of the angular correlation in an applied field since these two parameters allow a determination of both  $\omega\tau_N$  and  $\lambda\tau_N$ . It is interesting to note, however, that the *attenuation* of the angular correlation in the applied field case is quite similar to that obtained in the field free case. We can rewrite Eq. (7) in terms of the Legendre polynomials as

$$W(\theta, \lambda) = 1 + A_2 G_2' P_2[\cos(\theta + \Delta\theta)] \quad (13)$$

where

$$G_2' = \left\{ \left[ 1 + \frac{A_2}{4\alpha} \left( 1 - \frac{1}{(1 + \beta^2)^{1/2}} \right) \right] [\alpha(1 + \beta^2)^{1/2}] \right\}^{-1}. \quad (14)$$

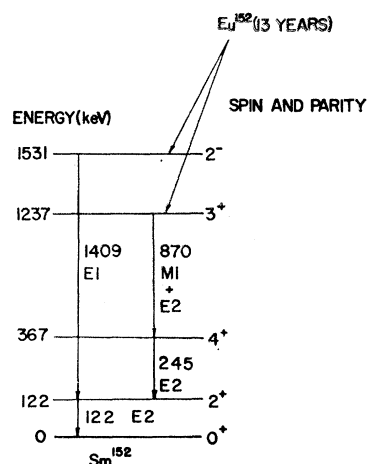


FIG. 1. Partial decay scheme of 13-yr  $\text{Eu}^{152}$   $K$ -capture decay to  $\text{Sm}^{152}$ .

For the conditions of our experiment,  $A_2/4\alpha \ll 1$  and  $\beta^2 < 1$ , we obtain

$$G_2' \cong \alpha^{-1}(1+\beta^2)^{-1/2} = \frac{1}{\alpha} \left[ 1 - \frac{1}{2}\beta^2 + (15/40)\beta^4 - \dots \right]. \quad (15)$$

Under the same assumptions,  $G_2$  of Eq. (11) can be rewritten as

$$G_2 = -\frac{1}{\alpha} \left[ 1 - \frac{1}{2}\beta^2 + (17/40)\beta^4 - \dots \right]. \quad (16)$$

Thus, we expect the amplitudes of the rotated pattern (with applied field) and of the unrotated pattern (without applied field) to be very much the same.

### III. STUDIES IN $\text{Sm}^{152}$ FOLLOWING $K$ CAPTURE DECAY OF $\text{Eu}^{152}$ IN EUROPIUM IRON GARNETS

Powdered europium iron garnet ( $\text{EuIG}$ ) enriched in  $\text{Eu}^{151}$  was synthesized and pressed in the form of cylindrical pellets approximately 1.5 mm in diam and 1.0 mm long. For the preparation of these samples we are indebted to Dr. M. A. Gilleo and his collaborators at the Bell Telephone Laboratories. The garnets were neutron irradiated in the facilities of the Oak Ridge National Laboratory. Although the garnets  $3\text{Eu}_2\text{O}_3 \cdot 5\text{Fe}_2\text{O}_3$  contain iron, the  $\text{Eu}^{151}$  slow neutron capture cross section is sufficiently large that no disturbance from iron activities was present in the source. The electronic magnetic moments were oriented below the Néel temperature by small permanent magnets incorporating the garnet sample between tapered soft iron pole tips.

#### (1) Integral Angular Correlation Measurements of 1409–122 keV $\gamma$ - $\gamma$ Cascade

**Apparatus:** For many of these measurements two  $1\frac{1}{2}$ -in. diam by 1-inch  $\text{NaI(Tl)}$  scintillation crystals were used as detectors together with a conventional fast-slow coincidence system (setup I). For other of

these measurements a three-counter system (setup II) was used utilizing a  $4\frac{1}{2}$ -in. diam by 6-in.  $\text{NaI(Tl)}$  crystal (counter 3) to detect the 1409-keV  $\gamma$  rays and two  $1\frac{1}{2}$ -in. diam by  $1\frac{1}{2}$ -in.  $\text{NaI(Tl)}$  crystals (counters 1 and 2) to detect the 122-keV  $\gamma$  rays. The latter system provided better efficiency and resolution for the detection of the high-energy  $\gamma$  rays. The use of two counters for the simultaneous measurement of the second cascade  $\gamma$  rays at two angles minimized electronic drift and doubled the counting rates. In the three-counter system one measures the ratio of the integral correlation functions  $W(\theta_{13})/W(\theta_{23})$ , where  $\theta_{13}$  and  $\theta_{23}$  represent the angles subtended at the source by the counter pairs 1-3 and 2-3, respectively. This ratio is given by the corresponding ratio of coincidence counting rates divided by the 1 to 2 ratio of singles counting rates. In order to cancel out any efficiency difference in the 1-3 and 2-3 coincidence circuits the ratio  $W(\theta_{23}')/W(\theta_{13}')$  was also measured where  $\theta_{23}' = 2\pi - \theta_{13}$  and  $\theta_{13}' = 2\pi - \theta_{23}$ . In experiments where there was an external magnetic field applied at the source perpendicular to the plane of the counters, the field direction was reversed when measuring at the primed angles. Thus, the two configurations were equivalent apart from any difference of the coincidence efficiency of the two coincidence circuits. The corrected ratio of integral correlation functions was obtained from the geometric mean ratio,

$$\{ [W(\theta_{13})/W(\theta_{23})][W(\theta_{23}')/W(\theta_{13}')] \}^{1/2}.$$

**Results:** Measurements of the 1409 to 122 keV angular correlations in  $\text{Sm}^{152}$  following the  $K$  capture of 13-yr  $\text{Eu}^{152}$  in polycrystalline samples of europium iron garnet were carried out from liquid nitrogen temperature to 700°C with and without applied magnetic field. A partial decay scheme showing the pertinent levels is shown in Fig. 1.<sup>5</sup> The first measurements were carried out at room temperature without applied

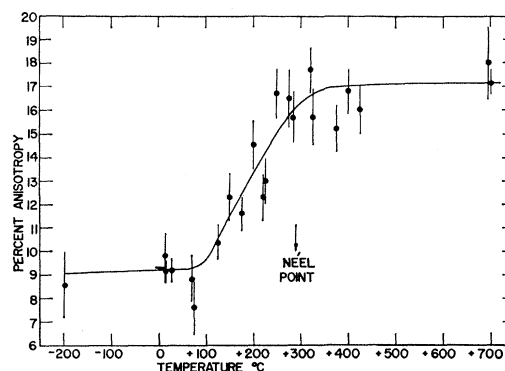


FIG. 2. Percent anisotropy as a function of temperature of 1409–122 keV cascade in  $\text{Sm}^{152}$  following  $K$  capture of  $\text{Eu}^{152}$  in polycrystalline samples of europium iron garnet without applied magnetic field.

<sup>5</sup> O. Nathan and S. Hultberg, *Nuclear Phys.* **10**, 118 (1959).

magnetic field using setup I. Some samples were annealed for several hours at  $700^\circ\text{C}$  in order to demagnetize the samples and anneal out any imperfections resulting from the slow-neutron irradiation. No differences in anisotropy [ $\alpha \equiv W(\pi)/W(\pi/2) - 1$ ] between the annealed or nonannealed samples were observed in measurements carried out a few weeks after the slow neutron irradiation.

The experimental anisotropies obtained in setup I as a function of temperature from liquid nitrogen temperature to  $700^\circ\text{C}$  without applied magnetic field are shown in Fig. 2. These data are not corrected for the finite size of the  $\gamma$ -ray detectors. The most precise data were obtained at room temperature and at  $700^\circ\text{C}$ . At these temperatures the experimental anisotropies were found to be  $\alpha(26^\circ\text{C}) = (9.6 \pm 0.4)\%$  and  $\alpha(700^\circ\text{C}) = (17.2 \pm 0.5)\%$ . In the same geometry the angular correlation coefficient was measured for a liquid source of europium chloride dissolved in dilute HCl. Under this condition we obtained  $\alpha = (27.3 \pm 0.7)\%$ .

When the angular correlation was measured with a magnetizing field applied perpendicular to the plane containing the counters, a rotation of the angular correlation pattern was observed below the Néel temperature. Representative plots of  $W(\theta) - 1$  as a function of  $\theta$  are shown in Fig. 3 for three different temperatures. These data were taken with setup II and represent the raw data uncorrected for detector resolution. Plots of the rotation  $\Delta\theta$  and the % anisotropy [ $W(\theta)_{\text{max}}/W(\theta)_{\text{min}} - 1$ ] taken from curves such as these at various temperatures from  $-25^\circ\text{C}$  to  $700^\circ\text{C}$  are shown in Figs. 4 and 5, respectively.

Measurements of the anisotropy without applied magnetic field were also taken with setup II to check on the earlier results with setup I and were found to yield identical values within statistics.

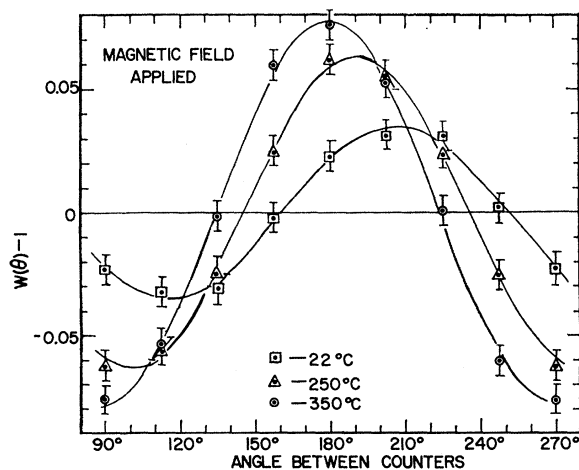


FIG. 3. Representative angular correlation patterns of the 1409-122 keV cascade in  $\text{Sm}^{152}$  following  $K$  capture of  $\text{Eu}^{152}$  in polycrystalline samples of europium iron garnet at various temperatures with magnetic field applied perpendicular to the plane of the counters.

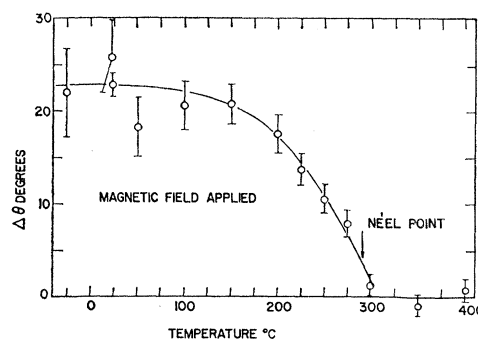


FIG. 4. Angle of rotation of angular correlation pattern of 1409-122 keV cascade in  $\text{Sm}^{152}$  following  $K$  capture of  $\text{Eu}^{152}$  in polycrystalline samples of europium iron garnet with applied magnetic field perpendicular to the plane of the counters. These data were obtained from the rotated angular correlation patterns as represented in Fig. 3.

## (2) Differential Angular Correlation Measurements of the 1409-122 keV Cascade

Differential angular correlation measurements were also carried out on the 1409-122 keV cascade in  $\text{Sm}^{152}$  following the decay of  $\text{Eu}^{152}$  in europium iron garnet at room temperature with a magnetizing field applied perpendicular to the plane of the counters.

**Apparatus:** The measurements were carried out using a fast time-to-amplitude converter coincidence circuit (TAC) together with energy pulse-height selection in a fast-slow system. The pulses from the TAC which carry the time information were analyzed on a 256-channel analyzer. The 1409-keV  $\gamma$  ray was selected in a  $1\frac{1}{2}$ -in. diam  $\times 1\frac{1}{2}$ -in. NaI(Tl) scintillation crystal. The 122-keV  $\gamma$  ray was detected in a lead-loaded (5% lead by weight) liquid scintillator. These scintillators were coupled to RCA 7746 photomultiplier tubes. In the lead-loaded liquid scintillator the 122-keV photopeak was not resolved but pulses resulting from 50- to 100-keV electrons in the liquid scintillator were selected. The time resolution of the system was measured using the 1.28-0.511 MeV prompt coincidence in  $\text{Na}^{22}$ . Here the same pulse-height selection as described above was used except the window level on the NaI(Tl) counter was lowered to the 1.28-MeV photopeak. The  $\text{Na}^{22}$  TAC coincidence spectrum had a width at half-maximum counting rate of 1.9 nsec. The pulse-height to time calibration was performed by measuring the number of channels shift in the TAC coincidence spectrum produced by the insertion of a known delay between one of the counters and its input to the TAC. Using close geometry and a "weak" source in order to make random background small the  $\text{Sm}^{152}$  TAC coincidence spectrum was measured for the 1409-122 keV cascade with the counters at an angle of  $180^\circ$  to each other. A pure exponential decay of the 122 keV state was observed over two decades corresponding to a half-life of  $1.39 \pm 0.05$  nsec or a mean lifetime of approximately 2.0 nsec in agreement with earlier meas-

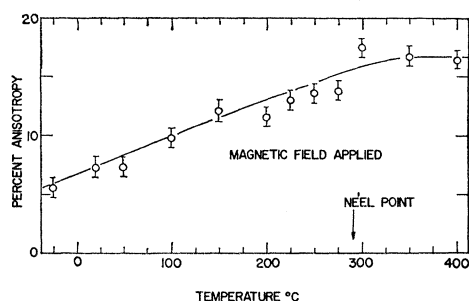


FIG. 5. Maximum to minimum percent anisotropy as a function of temperature of the 1409–122 keV cascade in  $\text{Sm}^{152}$  following  $K$  capture of  $\text{Eu}^{152}$  in polycrystalline samples of europium iron garnet with applied magnetic field perpendicular to the plane of the counters. This data was obtained from the rotated angular correlation patterns as represented in Fig. 3.

urements.<sup>6</sup> For the angular correlation measurements a stronger source was used and the random background at the peak of the TAC coincidence spectrum was approximately 3%.

**Results:** In taking these data the counters were kept at a fixed angle of  $135^\circ$  and the magnetic field perpendicular to the plane of the counters was reversed every 10 min by rotating the magnet through  $180^\circ$ . The apparatus was automatically controlled and the TAC spectra in which the north pole of the magnet was up and those in which the north pole was down were accumulated in the upper and lower memory halves of a 256-channel analyzer. All pulses emerging from the single-channel analyzer associated with each counter were accumulated simultaneously in scalars for each of the two positions of the magnet. The channels in each memory half were divided off into successive groups of three channels. In each “time” group the counts were summed and rates, normalized by dividing by the product of the corresponding single rates, were computed for each time group. We compute the ratio of normalized counting rates in the upper to lower memory halves of the analyzer for each time group. In this way a measurement of the ratio of the differential

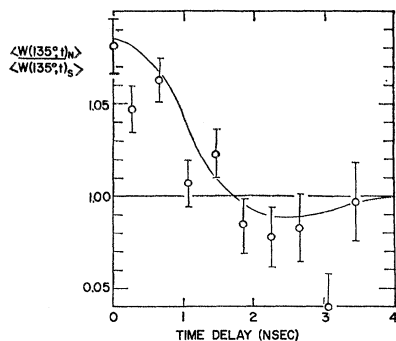


FIG. 6. Differential angular correlation results of 1409–122 keV cascade in  $\text{Sm}^{152}$  following  $K$  capture of  $\text{Eu}^{152}$  in polycrystalline samples of europium iron garnet with applied magnetic field perpendicular to the plane of the counters at room temperature.

<sup>6</sup> A. W. Sunyar, Phys. Rev. **98**, 653 (1955).

correlation functions averaged over the finite resolving time of the TAC,  $\langle W(135, t) \rangle_N / \langle W(135, t) \rangle_S$ , was obtained. Here  $t$  is taken as the time corresponding to the center channel of each time group and the subscripts N and S refer to the pole of the magnet which was up. These ratios are plotted in Fig. 6 together with a theoretical curve which is discussed in the section on evaluation of results.

#### IV. STUDIES IN $\text{Gd}^{154}$ FOLLOWING THE $\beta$ DECAY OF $\text{Eu}^{154}$ IN EUROPIUM IRON GARNET

##### (1) Integral Angular Correlation Measurements of the 1280–123 keV $\gamma$ - $\gamma$ Cascade

Europium iron garnet enriched in  $\text{Eu}^{153}$  was prepared and neutron irradiated as described before. A partial decay scheme for the decays of  $\text{Eu}^{154}$  to  $\text{Gd}^{154}$  is shown in Fig. 7.<sup>7</sup> Measurements of the angular correlation without an applied field were taken as a function of temperature. It was found, in contrast to the  $\text{Sm}^{152}$  results, that only a slight change in the angular correlation was obtained in a series of measurements from

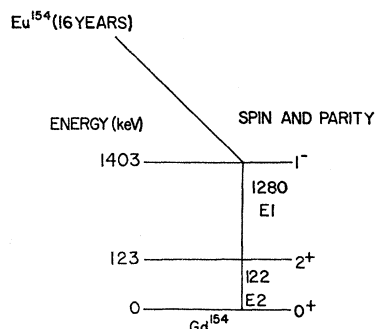


FIG. 7. Partial decay scheme of 16-yr  $\text{Eu}^{154}$   $\beta$  decay to  $\text{Gd}^{154}$ .

$25^\circ$  to  $400^\circ\text{C}$ . Most measurements therefore were taken at  $25^\circ\text{C}$  (below the Néel point) and at  $400^\circ\text{C}$  (above the Néel point) in order to establish the difference in the angular correlation. We obtain for the anisotropies  $\alpha(25^\circ\text{C}) = (14.4 \pm 0.3)\%$  and  $\alpha(400^\circ\text{C}) = (16.1 \pm 0.3)\%$ . The rotation  $\Delta\theta$  was measured at  $25^\circ\text{C}$  with an applied magnetic field. It was obtained from a least squares fit of measurements at angles of  $125^\circ$ ,  $135^\circ$ , and  $145^\circ$  between the 1280- and 123-keV detectors. These points are shown in Fig. 8 and give the result  $\Delta\theta = 5.7 \pm 0.8^\circ$ .

##### 2. Differential Angular Correlation Measurements of the 1280–123 keV Cascade

Measurements of the differential correlation were carried out without an applied magnetic field at  $25^\circ\text{C}$  and above the Néel temperature at  $400^\circ\text{C}$ . using the same apparatus as described before. In these measurements one counter was moved between positions of  $90^\circ$  and  $180^\circ$  with respect to the other counter every ten minutes. The average coincidence rates were collected

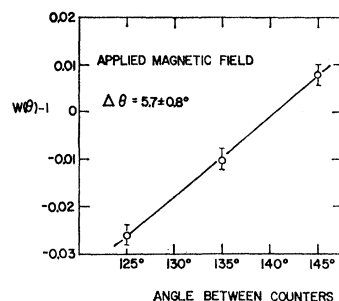
<sup>7</sup> O. Nathan and M. A. Waggoner, Nuclear Phys. **2**, 548 (1957).

and normalized as described before. The anisotropy,  $\langle W(180^\circ) \rangle / \langle W(90^\circ) \rangle - 1$ , is plotted as a function of time delay in Figs. 9 and 10.

### V. ANALYSIS OF RESULTS

We first consider the angular correlation measurement of the 1409-122 keV cascade in  $\text{Sm}^{152}$  using an aqueous solution of  $\text{EuCl}_3$ . We have converted the measured anisotropy to the angular correlation coefficient  $A_2$  and corrected for the finite resolution of our detectors. For the corrected result we obtain a value  $A_2 = 0.202 \pm 0.005$ . This is to be compared with the theoretical value for a  $2^-(E1)2^+(E2)0^+$  cascade, namely,  $A_2 = 0.250$ . If the angular correlation in the liquid were unperturbed by extranuclear fields we would conclude that the 1409 keV  $\gamma$ -ray must be a mixed transition of  $E1 + M2$ . This assumption is supported by other measurements. Ofer<sup>8</sup> has found  $A_2 = 0.21$  independent of the viscosity of the liquid source, while Goldring and Scharenberg<sup>9</sup> have Coulomb-excited the  $2^+$  state in  $\text{Sm}^{152}$  using a liquid target and find the theoretical unperturbed angular distribution of the emitted  $\gamma$  ray.

FIG. 8. Correlation functions  $W(\theta) - 1$  as a function of angle between counters for the 1280-123 keV angular correlation in  $\text{Gd}^{154}$  following the  $\beta$  decay of  $\text{Eu}^{154}$  in polycrystalline samples of europium iron garnet at room temperature with magnetizing field perpendicular to the plane of the counters.



Stiening and Deutsch<sup>10</sup> have measured the dependence of the 1409 to 122 keV angular correlation on the delay time using the differential method and find, for dissolved sources, no evidence for a time-dependent perturbation over a time twice the nuclear lifetime.

On the other hand the measurements of the angular correlation in the garnet above the Néel temperature at 400°C are below that observed in the liquid and correspond to a value  $G_2 = 0.65 \pm 0.03$  in the formula  $W(\theta) = 1 + A_2 G_2 P_2(\cos\theta)$ . Below the Néel point at 25°C our result is  $G_2 = 0.36 \pm 0.02$ . This attenuation above the Néel temperature we have attributed to the presence of time dependent perturbations and we have assumed throughout the analysis of the experimental results that the electronic relaxation time  $\tau_s$  of the rare-earth ions is smaller than the mean intermediate-state nuclear lifetime  $\tau_N$  over the entire temperature range studied in this paper. In fact, the existence of very short electronic relaxation times in the rare earth ions

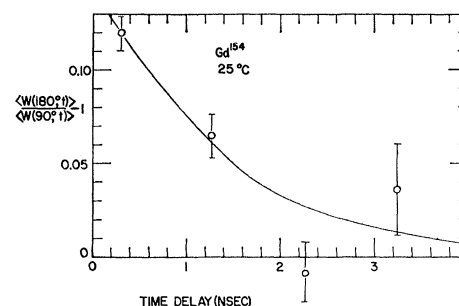


FIG. 9. Differential angular correlation results of 1280-123 keV cascade in  $\text{Gd}^{154}$  following  $\beta$  decay of  $\text{Eu}^{154}$  in polycrystalline samples of europium iron garnet without applied magnetic field at 25°C. Anisotropy between 90 and 180° is plotted vs the time delay.

(except for  $\text{Gd}^{3+}$ ) in rare-earth iron garnets has already been postulated to explain the results of ferrimagnetic resonance experiments.<sup>11</sup>

From these data alone one cannot determine whether the perturbations arise solely from interactions between the nuclear magnetic moment with fluctuating magnetic fields or whether there are in addition interactions between the nuclear electric quadrupole moment and fluctuating electric field gradients at the nucleus. We have, therefore, further assumed that time-dependent quadrupole interactions are negligible compared with the magnetic interactions within the accuracies of our work so that Eqs. (6) to (10) are applicable to our experimental observations. The justification of these assumptions is based upon the fact that it provides the most consistent and reasonable interpretation of all of our data.

To verify the presence of time-dependent perturbations we turn our attention to the measurements of the differential angular correlation. The data of Fig. 6 show the damping of the correlation coefficient with time. Without the exponential damping term of  $e^{-\lambda t}$  the correlation coefficient would be an oscillatory term of constant amplitude. These data, because of the poor statistics, cannot be used as proof for the presence of time-dependent perturbations. They are however not inconsistent with this view. The curve drawn in Fig. 6

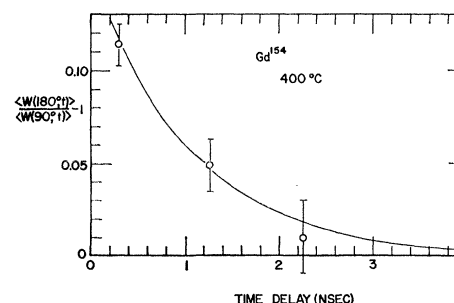


FIG. 10. Differential angular correlation results of 1280-123 keV cascade in  $\text{Gd}^{154}$  at 400°C.

<sup>8</sup> S. Ofer, Nuclear Phys. 4, 477 (1957).

<sup>9</sup> G. Goldring and R. P. Scharenberg, Phys. Rev. 110, 701 (1958).

<sup>10</sup> R. Stiening and M. Deutsch, Phys. Rev. 121, 1484 (1961).

<sup>11</sup> C. Kittel, Phys. Rev. 115, 1587 (1959).

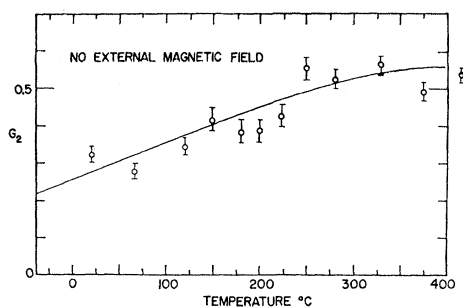


FIG. 11. Attenuation factor  $G_2$  as a function of temperature for the 1409-122 keV cascade in  $\text{Sm}^{152}$  following  $K$  capture of  $\text{Eu}^{152}$  in polycrystalline samples of europium iron garnet without applied magnetic field.

represents the correct functional form of the time-dependent correlation function. The parameters  $\omega$  and  $\lambda$  needed to construct this curve were obtained from the integral correlation data contained in Figs. 4 and 5 using Eqs. (7) and (15) and a value of  $2.0 \times 10^{-9}$  sec for the mean intermediate-state lifetime  $\tau_N$ .

As a further check of the internal consistency of our analysis we have plotted the attenuation factors  $G_2$  for no applied field and  $G_2'$  for the applied field case. In Figs. 11 and 12 we see, in agreement with the predictions of Eqs. (12) and (16), that the magnitude and temperature dependence of  $G_2$  and  $G_2'$  are the same within statistics.

In Fig. 13 we have plotted the parameter  $\omega\tau_N$  from the integral correlation data as a function of the temperature. The parameter  $\lambda\tau_N$  as a function of  $1/T$ , where  $T$  is the absolute temperature, is similarly plotted in Fig. 14. The scale of the ordinate on the right-hand side of the graph in Fig. 13 indicates the value of the magnetic hyperfine field  $\langle H_{\text{int}} \rangle$  which was calculated from  $\omega$  using Eq. 9 and the independently measured value of  $g_N = 0.351 \pm 0.03$  for the  $g$  factor of the intermediate nuclear state. The solid curve in Fig. 13 represents the results of a theoretical investigation which will be discussed in the next section.

No attempt was made to carry out numerous experiments with an applied field as a function of temperature for the cascade in  $\text{Gd}^{154}$  since the observed rotation was very small ( $5.7 \pm 0.8^\circ$ ). The difference in the anisotropies at  $25^\circ\text{C}$  and at  $400^\circ\text{C}$  was small in this case as would be expected from the small observed rotation. Thus we observe at  $400^\circ\text{C}$  an anisotropy  $\alpha = (16.1 \pm 0.3\%)$  while at  $25^\circ\text{C}$   $\alpha = (14.4 \pm 0.3\%)$ . Using a value of  $0.227 \pm 0.006$  for the unperturbed angular correlation coefficient  $A_2$  for the  $\text{Gd}^{154}$  cascade from the measurements of Stiening and Deutsch<sup>10</sup> in a molten salt at  $1000^\circ\text{C}$ , the attenuation factor  $G_2$  and hence the parameter  $\lambda\tau_N$  at  $400^\circ\text{C}$  can be calculated for this cascade. The values of  $\lambda\tau_N$  and  $\omega\tau_N$  at  $25^\circ\text{C}$  can be obtained similarly from the integral correlation data. We thus find at  $400^\circ\text{C}$ ,  $\lambda\tau_N = 1.23 \pm 0.08$  while

<sup>12</sup> R. W. Bauer and M. Deutsch, Bull. Am. Phys. Soc. **6**, 224 (1961).

at  $25^\circ\text{C}$ ,  $\lambda\tau_N = 1.44 \pm 0.08$  and  $\omega\tau_N = 0.25 \pm 0.04$ . The presence of time-dependent perturbations in the  $\text{Gd}^{154}$  cascade is shown most dramatically in the differential angular correlation measurements presented in Figs. 9 and 10. Here too it can be noted that  $\langle W(180^\circ, t) \rangle / \langle W(90^\circ, t) \rangle - 1$  does not change markedly from 25 to  $400^\circ\text{C}$ . The differential angular correlation curve at  $25^\circ\text{C}$  does not show the oscillatory behavior exhibited in Fig. 6 for  $\text{Sm}^{152}$ . This is because, during the time interval of measurement of the small rotation, the Legendre polynomial  $P_2[\cos(\theta + \omega t)]$  is approximately equal to  $P_2(\cos\theta)$ . The solid curves in Figs. 9 and 10 represent values calculated from the integral correlation. A value of  $1.73 \times 10^{-9}$  sec was used for the intermediate-state lifetime  $\tau_N$  to obtain the values of  $\lambda$  from the parameters  $\lambda\tau_N$  above. Good agreement between the integral and differential correlation measurements again demonstrates the consistency of our analysis. Using a value of  $0.36 \pm 0.06$  for the  $g$  factor of the  $2+$  state in  $\text{Gd}^{154}$ , the value of the magnetic hyperfine field at the nucleus is found to be approximately  $(8 \pm 2) \times 10^4$  Oe at room temperature.

## V. DISCUSSION

### 1. Introduction

As indicated in Sec. III, the evaluation of our results is carried out within the framework of the molecular field theory (Néel theory of ferrimagnetism). The application of the theory to rare earth-iron garnets<sup>13</sup> describes the influence of the antiferromagnetic exchange interaction between the rare-earth sublattice and the two  $\text{Fe}^{3+}$  sublattices on the electron configuration of the rare earth ions in terms of a magnetic exchange field,  $H_{\text{exch}}$ , which acts on the rare-earth ions and is proportional to the sublattice magnetization of the two  $\text{Fe}^{3+}$  sublattices (i.e.,  $H_{\text{exch}} = a_1 M_{\text{FeI}} + a_2 M_{\text{FeII}}$  where  $M_{\text{FeI}}$  and  $M_{\text{FeII}}$  are the sublattice magnetizations of the first and second  $\text{Fe}^{3+}$  sublattice, respectively). The antiferromagnetic exchange interaction between the two  $\text{Fe}^{3+}$  sublattices is much stronger than that between the  $\text{Fe}^{3+}$  sublattices and the rare-earth ion sub-

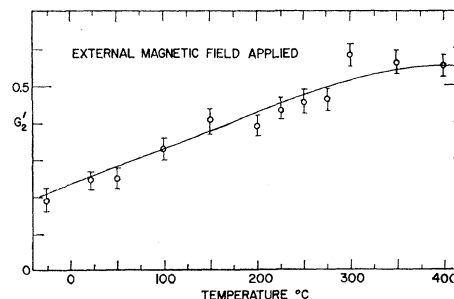


FIG. 12. Attenuation factor  $G_2'$  as a function of temperature for the 1409-122 keV cascade in  $\text{Sm}^{152}$  in polycrystalline samples of europium iron garnet with applied magnetic field perpendicular to the plane of counters.

<sup>13</sup> R. Pauthenet, Ann. phys. (Paris) **3**, 424 (1958).



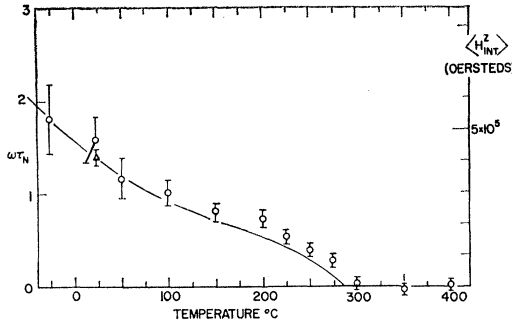


FIG. 13. The parameter  $\omega\tau_N$  and the average magnetic field  $\langle H_{\text{int}}^z \rangle$  acting at the  $\text{Sm}^{152}$  nuclei in the direction perpendicular to the plane of the counters as a function of temperature. The solid curve represents a theoretical relation of  $\langle H_{\text{int}}^z \rangle$  as a function of temperature as explained in the text.

lattice and in fact determines the Néel temperature of the crystals. However, there exists a net magnetization of the two  $\text{Fe}^{3+}$  sublattices because there are more ions per formula unit in one sublattice than in the other. The exchange interaction between the rare-earth ions themselves is small and can be neglected. The influence of the magnetic exchange interactions on the rare-earth ions in rare-earth iron garnets can therefore be described in terms of a magnetic exchange field acting on the rare earth ion which is proportional to the magnetization of the  $\text{Fe}^{3+}$  sublattices. The effect of the exchange field on the rare-earth ion is then analogous to that of an applied field on a paramagnetic ion except in so far as the interaction of the electronic magnetic moment with an applied field involves both the spin and orbital magnetic moments with their appropriate  $g$  factors while the interaction with the exchange field involves the spins only.<sup>14</sup>

The magnetic behavior of triply charged rare-earth ions has been extensively discussed by Van Vleck.<sup>15</sup> The ions obey Russell-Saunders coupling and the electronic states are described by the quantum numbers  $L$ ,  $S$ ,  $J$ , and  $M_J$ . The spin-orbit interaction energy is very large and, for an ion in a crystal, is larger than the crystalline electric field energy so that the orbital contribution to the magnetic moment is not appreciably quenched.

The molecular field theory has provided a consistent and fairly satisfactory description of the magnetic properties of all rare-earth iron garnets except  $\text{SmIG}$ . In particular, Wolf and Van Vleck,<sup>14</sup> neglecting crystalline field and saturation effects, have been able to deduce the temperature dependence of the saturation magnetization and the rare-earth ion sublattice magnetization in  $\text{EuIG}$ . The magnetic exchange field acting at the rare-earth ions in  $\text{EuIG}$  was taken to be proportional to the net magnetization of the two  $\text{Fe}^{3+}$  sublattices and its temperature dependence was ob-

tained from the saturation magnetization measurements in  $\text{YIG}$ . The constant of proportionality was chosen to fit the data of the measured saturation magnetization of  $\text{EuIG}$  at a single (room) temperature. This value of  $H_{\text{exch}}$  as a function of temperature for  $\text{EuIG}$  will be used in this paper. The value of  $H_{\text{exch}}$  at room temperature is  $25.8 \times 10^4$  Oe.

The measured sublattice magnetization of the  $\text{Sm}^{3+}$  ions in  $\text{SmIG}$  appears to be close to zero at all temperatures.<sup>13</sup> This fact has so far not been explained.<sup>16</sup>

## 2. Discussion of the Results of the 1409 to 122 keV Angular Correlation in $\text{Sm}^{152}$

The values of  $\langle H_{\text{int}}^z \rangle$  can be theoretically evaluated as a function of temperature under certain simplifying assumptions and may be compared with the experimental results. If one assumes that the electronic configuration in  $\text{Sm}^{152}$  following the  $K$  capture of  $\text{Eu}^{152}$  is that of the ground state of the  $\text{Sm}^{3+}$  ion, the expectation value of  $\langle H_{\text{int}}^z \rangle$ , neglecting crystalline field effects, can be calculated from standard perturbation theory to the first power in  $H_{\text{exch}}$ , within the framework of the molecular field approach.<sup>17</sup> Thus, the electronic configuration of the  $\text{Sm}^{3+}$  ion in the ground state (given by Russell-Saunders coupling) is perturbed by the magnetic exchange field in the direction of the applied magnetizing field ( $z$ -direction) with the perturbing Hamiltonian  $\mathcal{H}^{(1)} = 2S^z H_{\text{exch}}$ .

If one neglects the indirect contribution to the magnetic hyperfine interaction, arising from the contact interaction of inner-core  $s$  electrons which are exchange coupled to the uncompensated spins of the  $4f$  electrons, the magnetic hyperfine interaction Hamiltonian is<sup>18</sup>

$$\begin{aligned} \mathcal{H}_{\text{hf}} &= -\mu_N \mathbf{H}_{\text{int}} \cdot \mathbf{I} \\ &= 2\mu_B \mu_N \langle r^{-3} \rangle \{ \mathbf{L} \cdot \mathbf{I} + \xi L(L+1) \mathbf{S} \cdot \mathbf{I} \\ &\quad - \frac{3}{2} \xi [(\mathbf{L} \cdot \mathbf{S})(\mathbf{L} \cdot \mathbf{I}) + (\mathbf{L} \cdot \mathbf{I})(\mathbf{L} \cdot \mathbf{S})] \} \quad (17) \end{aligned}$$

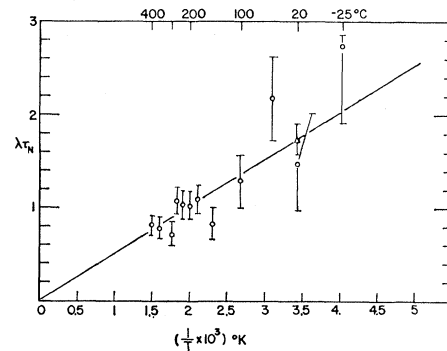


FIG. 14. The parameter  $\lambda\tau_N$  as a function of  $1/T$ , where  $T$  is the absolute temperature. The temperature dependence of the parameter  $\lambda\tau_N$  reflects primarily the temperature dependence of the electronic relaxation time.

<sup>14</sup> J. A. Wolf and J. H. Van Vleck, *Phys. Rev. Letters* **6**, 412 (1961).

<sup>17</sup> J. Kanamori and K. Sagimoto, *J. Phys. Soc. Japan* **13**, 754 (1958).

<sup>18</sup> A. Abragam and M. H. L. Pryce, *Proc. Roy. Soc. (London)* **A205**, 135 (1951).

<sup>14</sup> W. P. Wolf and J. H. Van Vleck, *Phys. Rev.* **118**, 1490 (1960).

<sup>15</sup> J. H. Van Vleck, *Theory of Electric and Magnetic Susceptibilities* (Clarendon Press, Oxford, 1932).

with

$$\xi = (2l+1-4S)/S(2l-1)(2l+3)(2L-1), \quad l=3.$$

In this equation,  $\mu_B$  is the Bohr magneton,  $k$  the Boltzmann constant, and  $\langle r^{-3} \rangle$  the average inverse cube radius of an electron in the 4f shell.

For  $\text{Sm}^{3+}$  we then calculate the expectation value of  $H_{\text{int}}^z$  in the  $JM$  representation of the wave functions perturbed by the exchange field. Taking into account the off-diagonal terms arising from the admixture of the first excited multiplet in  $\text{Sm}^{3+}$ ,<sup>14</sup> we obtain

$$\begin{aligned} \langle H_{\text{int}}^z \rangle &= \mu_B H_{\text{exch}} \left[ \sum_{JM} \{ \langle J^0 M^0 | H_{\text{int}}^z | J^0 M^0 \rangle 2(y_J - 1)M/kT \right. \\ &\quad + 2 \sum_{J'=J} \langle J^0 M^0 | H_{\text{int}}^z | J^0 M^0 \rangle \\ &\quad \times \langle J^0 M^0 | 2S^z | J^0 M^0 \rangle / (W_{J^0} - W_J) \} \\ &\quad \times \exp(-W_{JM}/kT) \bigg] / \sum_{JM} \exp(-W_{JM}/kT) \end{aligned} \quad (18)$$

where  $g_J$  is the Landé splitting factor,  $W_J^0$  the unperturbed energy levels of the  $\text{Sm}^{3+}$  ion, and  $J^0$  and  $M^0$  represent unperturbed wave functions.<sup>17</sup> Taking  $H_{\text{exch}}$  as a function of temperature for EuIG from the results of Wolf and Van Vleck<sup>14</sup> as explained above,  $W_{7/2}^0 - W_{5/2}^0 = 220/k$  from Van Vleck<sup>15</sup> and  $\langle r^{-3} \rangle = 51 \text{ \AA}^{-3}$  for  $\text{Sm}^{3+}$  from Elliott and Stevens,<sup>19</sup> one obtains  $\langle H_{\text{int}}^z \rangle$  as a function of temperature as indicated by the solid curve in Fig. 13.

The agreement between theory and experiment is seen to be very good. (The deviation at higher temperature is probably due to uncertainties in the determination of the sample temperature.) In addition, the calculated sign of  $\langle H_{\text{int}}^z \rangle$  also agrees with the observed sense of the rotation of the angular correlation.<sup>2</sup>

The root-mean square magnetic hyperfine field  $\langle H_{\text{int}}^2 \rangle^{1/2}$  was calculated from first order perturbation theory using the experimentally determined values of  $\langle H_{\text{int}}^z \rangle$ , but otherwise the same approximations as those used in the calculation for  $\langle H_{\text{int}}^z \rangle$ , were made. An independent knowledge of  $\langle r^{-3} \rangle$  and  $H_{\text{exch}}$  is not required for the determination of  $\langle H_{\text{int}}^2 \rangle^{1/2}$ . The value of  $\langle H_{\text{int}}^2 \rangle^{1/2}$  in  $\text{Sm}^{3+}$  was found to be  $4.7 \times 10^6$  Oe almost independent of temperature.

While the excellent agreement between theory and experiment may be partly fortuitous due to the uncertainties in the value of  $\langle r^{-3} \rangle$  and the neglect of the crystalline field in the calculation, it nevertheless lends experimental support to the following conclusions:

(1) The electronic configuration following the  $K$ -capture decay of  $\text{Eu}^{152}$  reaches that of the  $\text{Sm}^{3+}$  ground-state configuration within a time less than  $10^{-9}$  sec.

(2) Calculations based on the molecular field theory appear to adequately predict the value of the magnetic hyperfine field acting on the  $\text{Sm}^{3+}$  nucleus in EuIG. In contrast, the experimentally determined sublattice magnetization of the  $\text{Sm}^{3+}$  ion sublattice in SmIG

appears to be zero,<sup>13</sup> a fact which does not seem to be compatible with conclusions reached from molecular field calculations.<sup>16</sup>

(3) In contrast to the transition elements, the "indirect" contribution to the magnetic hyperfine interaction arising from the exchange interaction between the 4f electrons and inner-core  $s$  electrons in  $\text{Sm}^{3+}$  is small compared with the "direct" contribution.

(4) The presence of short electronic relaxation times ( $10^{-9}$  sec) in the rare-earth ions in rare-earth iron garnets, first postulated in order to explain the results of ferrimagnetic resonance experiments,<sup>11</sup> has received experimental confirmation.

Neglecting quadrupole interactions, the value of  $\tau_s$  can be calculated from Eq. (10). At  $400^\circ\text{C}$  we find  $\tau_s = 3.2 \times 10^{-12}$  sec, in good agreement with the value for  $\tau_s$  postulated by de Gennes, Kittel, and Portis<sup>20</sup> to explain the linewidth of ferrimagnetic resonance experiments. Since  $\langle H_{\text{int}}^z \rangle$  is almost independent of temperature, the temperature dependence of  $\lambda\tau_n$  in Fig. 14 represents that of the electronic relaxation time. Thus, within experimental accuracy,  $\tau_s$  was found to vary inversely with the absolute temperature over the temperature range investigated ( $-25$  to  $400^\circ\text{C}$ ).

### 3. Discussion of the Results of the 1280 to 123 keV Angular Correlation in $\text{Gd}^{154}$

The situation in  $\text{Gd}^{154}$  is not as clear as that in  $\text{Sm}^{152}$ . The presence of time-dependent perturbations has been established from the differential angular correlation measurements. In addition, there is a marked decrease in the anisotropy above the Néel temperature and this result can not be consistently interpreted in terms of static interactions. Since the relaxation time in  $\text{Gd}^{3+}$  is known to be larger than  $10^{-9}$  sec from ferrimagnetic resonance experiments, it is safe to state that the electronic configuration of the  $\text{Gd}^{154}$  following the  $\beta$  decay of  $\text{Eu}^{154}$  is not that of  $\text{Gd}^{3+}$ . Experiments on the angular correlation in  $\text{Dy}^{160}$  following the  $\beta$  decay of  $\text{Tb}^{160}$  indicate that in this case the electronic configuration of the ion is that of  $\text{Tb}^{3+}$ .<sup>21</sup> However, if it is assumed that the electronic configuration of the  $\text{Gd}^{154}$  following the  $\beta$  decay of  $\text{Eu}^{154}$  is that of  $\text{Eu}^{3+}$ , a calculation similar to that performed for the  $\text{Sm}^{152}$  case taking into account the off-diagonal matrix elements between the  $J=0$  and  $J=1$  multiplets, yields a value of the magnetic hyperfine field at room temperature which is approximately four times larger than the observed one. On the other hand, the calculated sign of the rotation agrees with experiment.<sup>2</sup> Taking into account the contribution of the exchange interaction between the uncompensated spins in the 4f shell and inner-core  $s$  electrons to the magnetic hyperfine field,

<sup>19</sup> R. J. Elliott and K. W. H. Stevens, Proc. Roy. Soc. (London) **A219**, 387 (1953).

<sup>20</sup> P. G. de Gennes, C. Kittel, and A. M. Portis, Phys. Rev. **116**, 323 (1959).

<sup>21</sup> M. E. Caspari, S. Frankel, and D. Ray (to be published).

only increases the magnitude of the calculated magnetic hyperfine field. No explanation has as yet been found for this discrepancy. It is possible that the electronic configuration of the ion following the  $\beta$  decay of  $\text{Eu}^{154}$  is neither that of the ground state of  $\text{Eu}^{3+}$  nor  $\text{Gd}^{3+}$ . Since the electronic configuration of the  $\text{Gd}^{154}$  ion is not known, the root-mean square value of the magnetic hyperfine field  $\langle H_{\text{int}}^2 \rangle^{1/2}$  and, hence, the magnitude of the electronic relaxation time  $\tau_s$ , could not be obtained in this case. From the values of

$\lambda\tau_N$  at 400 and 25°C we can deduce that the electronic relaxation time does not increase by more than 20% between room temperature and 400°C.

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## Electron Spin Resonance of $\text{Fe}^{3+}$ and $\text{Mn}^{2+}$ in Single Crystals of CaO

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Single crystals of CaO doped with  $\text{Mn}^{2+}$  and  $\text{Fe}^{3+}$  have been investigated by paramagnetic resonance at 9.5 kMc/sec. Both ions are found to go in substitutionally for the  $\text{Ca}^{2+}$  ion. The spectrum of each can be described by a spin Hamiltonian for an ion in a cubic field. The parameters determined for  $\text{Mn}^{2+}$  are  $g = 2.0009 \pm 0.0005$ ,  $a = (5.9 \pm 0.3) \times 10^{-4} \text{ cm}^{-1}$  and  $A = (-80.8 \pm 0.2) \times 10^{-4} \text{ cm}^{-1}$ . The  $\text{Fe}^{3+}$  parameters are  $g = 2.0052 \pm 0.0005$  and  $a = (63.8 \pm 0.3) \times 10^{-4} \text{ cm}^{-1}$ . The results are discussed in relationship to the Powell, Gabriel, and Johnston theory of the ground-state splitting of  $\text{Mn}^{2+}$  by cubic crystalline fields.

#### INTRODUCTION

THE partial splitting of the sixfold degeneracy of  $3d^5$ ,  $^6S$  ground-state ions by cubic crystalline fields has been a subject of considerable interest in recent years. The theory of Watanabe<sup>1</sup> predicts that the splitting between the doublet ( $\Gamma_7$ ) and the quartet ( $\Gamma_8$ ) levels is proportional to even powers of the crystal potential  $V$ , with  $V^2$  the dominant term. One consequence of this theory is that the sign of the cubic-field splitting parameter  $a$  is independent of the sign of the cubic potential which is dependent on whether the coordination is octahedral, tetrahedral, or fluorite. To date, all values of  $a$  have been found to be positive with one exception, that of  $\text{Mn}^{2+}$  in NaCl where Watkins<sup>2</sup> has tentatively assigned a negative value of  $a$  to explain the spectra observed.

Powell, Gabriel, and Johnston<sup>3</sup> have criticized Watanabe's arguments and pointed out that on going from a picture in terms of electrons to one in terms of holes that odd powers of  $V$  would also contribute. Calculations for  $\text{Mn}^{2+}$  based on this theory predict positive values for  $a$  with the exception of small  $Dq$  values ranging between 0 and 200  $\text{cm}^{-1}$ . The results of Watkins<sup>2</sup> are consistent with the theory of Powell *et al.*; but Geshwind<sup>4</sup> points out that the very small negative

value of  $a$  ( $10^{-4} \text{ cm}^{-1}$ ) could arise from excited configurations. Walsh<sup>5</sup> has studied the effects of hydrostatic pressure on the paramagnetic spectra of  $\text{Mn}^{2+}$  and  $\text{Fe}^{3+}$  in cubic MgO. The results of this study showed that the pressure dependencies of  $a$  for  $\text{Mn}^{2+}$  and  $\text{Fe}^{3+}$  are identical and are proportional to  $V^4$ . These results were found to be consistent with the calculations of Powell *et al.*<sup>3</sup> On the other hand, in a comparison of the cubic field splittings of  $\text{Fe}^{3+}$  occupying octahedral and tetrahedral sites in yttrium gallium garnet, Geschwind<sup>4</sup> found that the ratio of the two splittings was proportional to  $V^2$ .

More recently, Gabriel, Johnston, and Powell<sup>6</sup> have revised their calculation for  $\text{Mn}^{2+}$  in MgO and found that the predicted value for the cubic-field splitting using the Pratt and Coelho<sup>7</sup> optical data for MnO resulted in a value which was far too small. Among the possible causes for this discrepancy was the difference in lattice parameters between MgO and MnO affecting  $Dq$ .

Because of the general interest in  $^6S$  ions, the spectra of  $\text{Mn}^{2+}$  and  $\text{Fe}^{3+}$  have been investigated in CaO. This presents an opportunity to compare the cubic-field splittings in CaO with those observed in isomorphous MgO and a further comparison with the theory of Powell *et al.*,<sup>6</sup> especially with regard to the effect of a change in lattice parameter.

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