Hyperfine Structure of Fe^{57} in Yttrium-Iron Garnet from the Mössbauer Effect*

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The hyperfine structure of Fe^{57} in yttrium-iron garnet [$Y_3Fe_2(FeO_4)_3$] has been obtained through the Mössbauer effect. A 0.002-in. thick slice of a single crystal of yttrium-iron garnet, cut normal to a [110] direction, was used as an absorber of recoil-free gamma rays emitted by a stainless steel source. The iron in yttrium-iron garnet is located in two nonequivalent sites, tetrahedral and octahedral, each of which has an axially symmetric electric field gradient. Data were taken with the magnetization aligned in a [111] and in a [100] direction in order to produce the simplest absorption pattern. For each direction of magnetization, the absorption lines of Fe^{57} at both sites have been resolved. The magnetic field at an Fe^{57} nucleus has been found to be 3.9×10^5 oe at a tetrahedral site and 4.7×10^5 oe at an octahedral site when the crystal is at room temperature (~300°K). The quadrupole coupling was found to be 7.5×10^{-8} ev in the tetrahedral site and 9.0×10^{-8} ev in the octahedral site.

INTRODUCTION

THE yttrium-iron garnet, $Y_3Fe_2(FeO_4)_3$, although a recent discovery, has already become one of the most thoroughly studied magnetic materials. The temperature dependence of the bulk magnetization of yttrium-iron garnet and of substituted garnets has been extensively studied[1] and provides an important experimental verification of the theory of ferrimagnetism.[2] One feature which has up to now remained unknown is the actual value of the magnetic field at the iron nuclei in this material. It would be of particular interest to obtain the temperature dependence of the field at iron nuclei in both the tetrahedral and octahedral sites since measurements of the bulk mangetization give no direct information on these two types of iron separately. In iron metal, it has been shown with the Mössbauer effect[3] that the field at the nucleus and the magnetization have the same temperature dependence.[4] The same tool appears particularly well suited for a study of the iron garnets. In addition to the magnetic field at the nuclei in the two types of sites, the electric quadrupole coupling may also be obtained.

The Fe^{57} Mössbauer effect[5] utilizes the gamma-ray transition between the ground and first excited states of the nucleus and requires a source containing radioactive Co^{57} and an absorber containing stable Fe^{57}. Any naturally iron-bearing substance may be used as an absorber since the natural abundance of Fe^{57} is 2.14%. The Co^{57} in the source decays by electron capture with a half-life of 270 days to an excited state of Fe^{57}. This state decays in part directly to the ground state of stable Fe^{57} and in part to the spin $\frac{3}{2}$ first excited state. This level is located 14.4 kev above the ground state and has a half-life of 10^{-7} sec.

The hyperfine structure of the 14.4-kev transition between the ground and first excited states can be resolved with the Mössbauer effect. The nuclear magnetic moments of the spin $\frac{1}{2}$ ground state and of the spin $\frac{3}{2}$ first excited states are known as the result of resonance[6] and Mössbauer experiments,[7] respectively. The quadrupole moment of the first excited state is known to be large and negative.[8] In the general case where the magnetic field at the nucleus is in an arbitrary direction and in which the electric field gradient (EFG) is not restricted by symmetry considerations, the hyperfine splitting of the excited state is difficult to obtain. The situation is considerably simplified when the EFG tensor has axial symmetry as it does in the present case. The energy of the magnetic sublevels can then be expressed in terms of two parameters, (1) the angle θ between the direction of the magnetic field H and the axis of the field gradient and (2) the ratio λ of quadrupole to magnetic hyperfine coupling. The requisite numerical calculations have been done by Parker.[9]

Yttrium-iron garnet is a cubic ferrimagnetic crystal, containing trivalent iron, in which there are eight formula units in a unit cell. Iron nuclei occupy two types of sites, tetrahedral and octahedral, which are present in a ratio of 3:2. Neither the tetrahedral nor the octahedral site has cubic symmetry, although the crystal as a whole is cubic. However, each site has sufficient symmetry to insure that the EFG tensor at the iron nucleus is axially symmetric. In the tetrahedral site, the iron nucleus is equidistant from four oxygen ions placed at the corners of a distorted tetrahedron as shown in Fig. 1. This tetrahedral figure has a fourfold rotary inversion axis in a [100] direction, which is consequently the axis of symmetry of the EFG tensor at

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TABLE I. Characteristics of iron sites in yttrium-iron garnet for the two cases used in the experiment.

Iron site	Field direction 111 Angle[a]	111 Intensity[b]	100 Angle[a]	100 Intensity[b]
Tetrahedral	54°44′	6	90°	4
			0°	2
Octahedral	70°32′	3	0°	4
	0°	1	54°44′	

[a] Angle between direction of magnetization and axis of electric field gradient tensor.
[b] Relative number of iron atoms occupying sites characterized by the given angle.

the tetrahedral site. In the octahedral site, the iron nucleus is equidistant from six oxygen ions placed at the corners of a distorted octahedron, as shown in Fig. 2. This octahedral figure has a threefold axis of rotation in a [111] direction, which is similarly the axis of symmetry of the EFG tensor at the octahedral site. Since

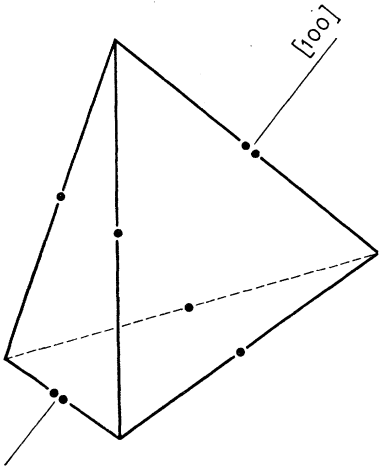

FIG. 1. Oxygen atom location around tetrahedral iron site. The symmetry axis of the tetrahedron (and of the crystal as a whole) lies in a [100] direction. Dots indicate lines of equal length.

there are four [111] directions and three [100] directions, there are seven different angles θ when H is taken in an arbitrary direction. In this case, the absorption spectrum would be particularly difficult to analyze, since it would consist of a superposition of seven distinct six-line absorption spectra, due to Fe^{57} nuclei in seven nonequivalent sites.

In order to produce the simplest absorption spectra, the direction of magnetization in the crystal (which may be determined by an external magnetic field) was chosen to minimize the number of values of θ. There are two particularly advantageous cases: H in the [100] or [111] direction. When the magnetic field is in a [100] direction, all symmetry axes of the octahedral sites, which are the [111] directions, make an angle of 55° with it. For the tetrahedral sites, there are two values

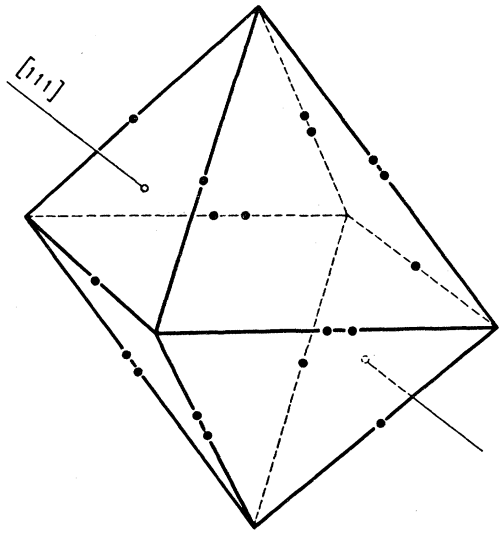

FIG. 2. Oxygen atom location around octahedral iron site. The symmetry axis of the octahedron lies in a [111] direction.

of θ, 90° and 0°, with the former occurring twice as often as the latter. When the magnetic field is in a [111] direction, all symmetry axes of the tetrahedral sites, which are the [100] directions, make an angle of 55° with it. For the octahedral site, the values are 70° and 0°, with the former occurring three times as often as the latter (see Table I).

EXPERIMENTAL

A diagram of the experimental equipment is shown in Fig. 3. The source was Co^{57} diffused into type 310 stainless steel, in which the 14.4-kev gamma-ray line is unsplit.[10] The source was mounted on a loudspeaker which was driven by a symmetric sawtooth voltage motion. The absorber was a 0.002-in. thick, (110) slice of a single crystal of yttrium-iron garnet. It was mechanically polished according to the method described by Dillon and Earl,[11] but was not etched. The crystal-

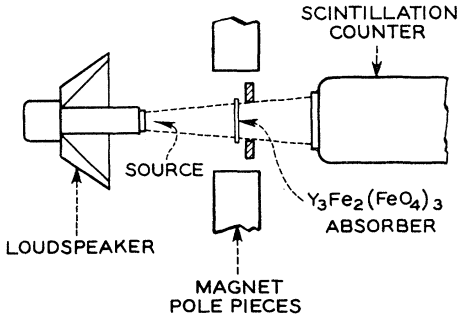

FIG. 3. Experimental equipment.

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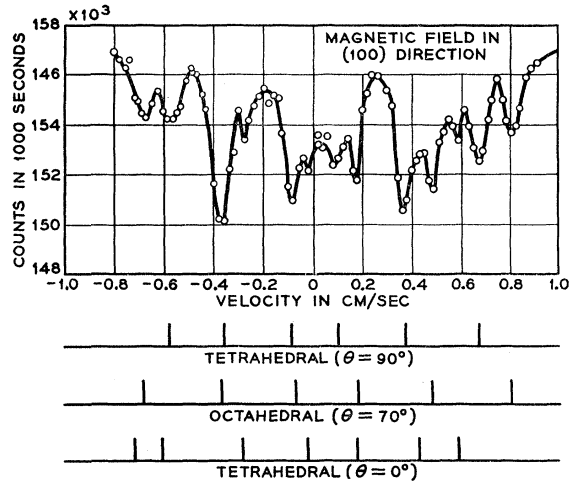

FIG. 4. Resonant absorption of 14.4-kev Fe^{57} gamma ray in yttrium-iron garnet magnetized in [100] direction.

lographic orientation of the crystal slice was determined by x-ray diffraction.[12] The plane of the absorber was chosen normal to a [110] direction since this plane contains the required [111] and [100] directions. The direction of magnetization in the absorber was determined by application of an external magnetic field of 500 oe parallel to the plane of the absorber. Data were taken at room temperature (~300°K) with the magnetic field in a [111] and a [100] direction. The 14.4-kev gamma rays transmitted by the absorber were detected with a conventional thallium-activated sodium iodide scintillation counter spectrometer, set for an energy interval of from 10 to 20 kev. Absorption spectra were obtained by recording counts for equal intervals of time at each velocity. Counts corresponding to positive and negative velocities were recorded separately.

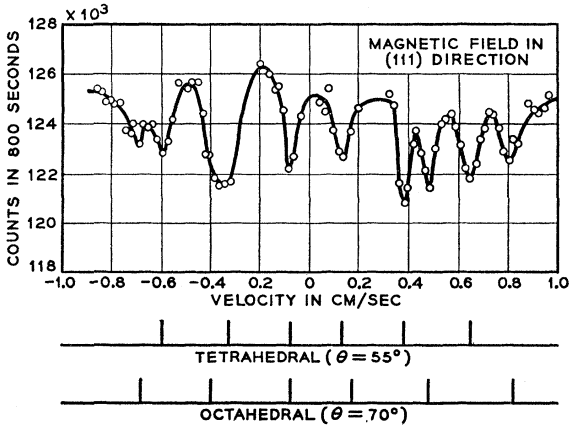

FIG. 5. Resonant absorption of 14.4-kev Fe^{57} gamma ray in yttrium-iron garnet magnetized in [111] direction.

[12] The crystal was oriented by Mrs. M. H. Read.

RESULTS AND DISCUSSION

The data obtained are shown in Figs. 4 and 5. When the field is in a [100] direction, three sets of lines due to Fe^{57} in the three nonequivalent sites are found. These are an octahedral site in which $\theta=55°$, a tetrahedral site in which $\theta=90°$, and a tetrahedral site in which $\theta=0°$. As expected, the last set of lines is weaker than the other two. When the field is in a [111] direction, only two sets of lines are found, corresponding to the tetrahedral sites in which $\theta=55°$, and the octahedral sites in which $\theta=70°$. The octahedral sites for which $\theta=0°$ have not been resolved. This is in accord with their very low intensity.

The hyperfine patterns for $\theta=0°$, 55°, 70°, and 90° were computed for a range of values of λ using the nuclear magnetic moments of the ground and excited states and the calculations of Parker. The first step in the data analysis was to separate the lines due to nuclei in octahedral sites from those due to nuclei in tetrahedral sites by comparing the experimentally obtained absorption patterns with those computed. After this separation was made, the magnetic field at each site was obtained from the ground-state splitting, which is given by the separation of lines 2 and 4, and lines 3 and 5. Since there were two sets of data, two independent determinations were made. When the magnetization was in a [100] direction, the magnetic field at the site of the iron nuclei was found to be 3.90×10^5 oe for the tetrahedral site and 4.67×10^5 oe for the octahedral site. When the magnetization was in a [111] direction, the values obtained are 3.94×10^5 oe for the tetrahedral site and 4.81×10^5 oe for the octahedral site. The agreement between the two determinations was satisfactory. The average values obtained are $(3.92\pm0.05)\times10^5$ oe for the tetrahedral site and $(4.74\pm0.07)\times10^5$ oe for the octahedral site. The latter value is comparable to other measured magnetic fields at trivalent iron sites; e.g., Kistner and Sunyar[13] have found the field at the iron nucleus in Fe_2O_3 to be 5.15×10^5 oe at room temperature. It should be pointed out that although the bulk magnetization of yttrium-iron garnet as a function of temperature is known, the magnetic fields of the tetrahedral and octahedral sites cannot be extrapolated to 0°K since the temperature dependence of the two sites is not known. Further measurements at low temperatures are needed to determine the temperature dependence of the two sites.

By comparing the relative positions of the six lines composing each spectrum with the calculated relative positions, the ratio of the quadrupolar to magnetic hyperfine coupling, $\lambda=eqQ/4\mu H$, was found to be 0.10 ± 0.02 for both tetrahedral and octahedral sites. The error in λ is large, because the splitting of the excited state is particularly insensitive to λ in the region

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$\theta=55°$ and $\lambda=0.1$, where the strongest absorption spectra were obtained. The value of λ obtained corresponds to a quadrupole interaction $eqQ=(7.5\pm1.5)\times10^{-8}$ ev for the tetrahedral site and $eqQ=(9.0\pm1.8)\times10^{-8}$ ev for the octahedral site. A better value of eqQ could be obtained above the Curie temperature (272°C) where the splitting of the $I=\frac{3}{2}$ state would be purely quadrupolar.

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Magnetic Susceptibility of Cerous Magnesium Nitrate

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The most striking features of the behavior of cerous magnesium nitrate at liquid helium temperatures—extremely anisotropic susceptibility with $g_{\parallel}\approx0$, a large temperature-independent term in $\chi_{\perp}$, the spin-lattice relaxation time varying as the twelfth or higher power of T in the region of 2°K—have until very recently received no detailed explanation. A measurement of $\chi_{\perp}$ between 4° and 300°K was undertaken to elicit information on the energies of the excited doublets within the $J=\frac{5}{2}$ ground multiplet, and thus to provide a guide for the reassessment of the crystal field parameters. We find δ_1 and δ_2 to be 30 and (roughly) 200 cm^{-1}, respectively, in contrast to the 113 and 150 cm^{-1} of existing theory. The results are at variance with the published data for $\chi_{\perp}$ above 85°K, but are in fairly good agreement with the recent findings of Leask and Wolf at low temperatures.

I. INTRODUCTION

THE salt cerous magnesium nitrate (CMN), $Ce_2Mg_3(NO_3)_{12}\cdot24H_2O$, exhibits interesting and unusual features in its behavior at low temperatures. Its paramagnetism arises from the Ce^{3+} ion. Its $^2F_{\frac{5}{2}}$ ground state is split by the crystalline electric field into three Kramers doublets characterized roughly by $J_Z=\pm\frac{1}{2}, \pm\frac{3}{2}, \pm\frac{5}{2}$.[1] In the liquid-helium region, the salt obeys the Curie law very accurately, the two highest doublets being essentially unoccupied; the effective spin is $\frac{1}{2}$ and the g factor is extremely anisotropic[2]: $g_{\parallel}\leqslant0.05$,[3,4] and $g_{\perp}\approx1.84$.[2] The interactions which cause deviations from Curie's law at very low temperatures are extremely small and their effect upon the susceptibility does not become significant until 0.01°K or lower.[4,5] This feature and the concomitant one of very small specific heat below 1°K have already been made use of quite extensively in low temperature thermometric and magnetic cooling applications.[6] Finally, the spin-lattice relaxation time τ is strongly temperature dependent in the liquid helium region,[2] and in the customary Casimir-DuPré type of investigation one finds that τ increases from immeasurably small ($<10^{-4}$ sec) to immeasurably large ($>10^{-2}$ sec) in lowering the temperature from 2.2° to 1.7°K. This type of behavior was confirmed by us in a series of relaxation-time measurements[4,7] undertaken mainly to derive an independent estimate of the magnetic contribution to the specific heat as a check upon adiabatic demagnetization data.

To improve the understanding of the behavior of CMN and, in particular, to seek information on the splittings in the ground state, we decided to study the departures from Curie law behavior which set in at higher temperatures as the populations of the excited levels become significant. While this work was in progress, we learned that Wolf and collaborators were

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