

## Electron Paramagnetic Resonance of Fe<sup>3+</sup> in TiO<sub>2</sub> (Rutile)\*†

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Paramagnetic resonance has been observed from 2 kMc/sec to 110 kMc/sec in Fe<sup>3+</sup>-doped single crystals of rutile at 78°K, 4.2°K, and 1.4°K. The rather large zero field splittings measured between the three doublets are 43.3±0.1 kMc/sec and 81.3±0.1 kMc/sec. The derived constants for the spin Hamiltonian

$$\mathcal{H} = g\beta\mathbf{H}\cdot\mathbf{S} + D(S_z^2 - 35/12) + E(S_x^2 - S_y^2) + (a/6)(S_x^4 + S_y^4 + S_z^4 - 707/16) + (7/36)F[S_z^4 - (95/14)S_x^2 + 81/16].$$

are  $D = 20.35 \pm 0.1$  kMc/sec,  $E = 2.21 \pm 0.07$  kMc/sec,  $a = 1.1 \pm 0.2$  kMc/sec,  $F = -0.5 \pm 0.3$  kMc/sec,  $D = 20.35 \pm 0.1$  kMc/sec,  $E = 2.21 \pm 0.07$  kMc/sec,  $a = 1.1 \pm 0.2$  kMc/sec,  $F = -0.5 \pm 0.3$  kMc/sec,  $g = 2.000 \pm 0.005$ . The average line width is 35 Mc/sec for  $2 \times 10^{19}$  spins per cm<sup>3</sup>, and the average spin-lattice relaxation time  $T_1$  at  $T = 1.4^\circ\text{K}$  is 4 msec.  $T_1$  still has a very slow inverse temperature dependence even at  $T = 78^\circ\text{K}$ . An increase in sensitivity over metal walled cavity spectrometers was achieved by using the pieces of Fe-doped rutile as the microwave resonators.

### A. INTRODUCTION

THE free ion Fe<sup>3+</sup> has the configuration  $3d^5$ ,  $^6S_5$ . In an orthorhombic crystalline field the six-fold degenerate state splits into three Kramers doublets which are further split when a constant magnetic field is applied.<sup>1-3</sup>

Many examples of Fe<sup>3+</sup> in crystalline surroundings have been discussed in the literature.<sup>4-6</sup> The motive of our research was to find a material which has large zero field splittings in the microwave range, narrow, homogeneously broadened lines and long spin-lattice relaxation times for use in a millimeter wave maser. Fe<sup>3+</sup> in rutile satisfies the foregoing requirements although the spin-lattice relaxation time  $T_1$  at 1.4°K is an order of magnitude shorter than maser materials presently employed. However, a slow temperature variation of  $T_1$  for temperatures as high as 78°K was observed.

Experiments were performed on artificially produced boules of Fe<sup>3+</sup> in TiO<sub>2</sub> (rutile) made by the Linde Company. Chemical analysis showed that Fe was present in amounts of approximately  $2 \times 10^{19}$  per cm<sup>3</sup>. The crystal structure of rutile is such that there are two equivalent sites per unit cell.<sup>7</sup> The local symmetry of each site is  $D_{2h}$  and the local symmetry axes of the two sites are mutually perpendicular and also perpendicular to the optic axis of the crystal. This con-

figuration gives rise to a 90° period in spin resonances for the field perpendicular to the optic axis. The symmetry observed in our experiments leads us to believe that Fe<sup>3+</sup> substitutes for Ti<sup>4+</sup> in the rutile lattice.

### B. SPIN HAMILTONIAN

The spin Hamiltonian used to describe the observed spectra is (see reference 5)

$$\mathcal{H} = g\beta\mathbf{H}\cdot\mathbf{S} + D(S_z^2 - 35/12) + E(S_x^2 - S_y^2) + (a/6)(S_x^4 + S_y^4 + S_z^4 - 707/16) + (7/36)F[S_z^4 - (95/14)S_x^2 + 81/16].$$

The axes for the spin Hamiltonian relative to the crystal directions are given in Table I. The values of the derived constants are:

$$D = 20.35 \pm 0.1 \text{ kMc/sec}, \quad E = 2.21 \pm 0.07 \text{ kMc/sec}, \\ a = 1.1 \pm 0.2 \text{ kMc/sec}, \quad F = -0.5 \pm 0.3 \text{ kMc/sec}, \\ g = 2.000 \pm 0.005.$$

Using the derived constants in  $\mathcal{H}$  the energy levels for magnetic field parallel to  $z$  and parallel to  $x$  for a single site were plotted as illustrated in Figs. 1 and 2, respectively. ( $\theta$  is the angle between  $\mathbf{H}$  and the  $z$  axis and  $\phi$  is the angle between the projection of  $\mathbf{H}$  on the  $x$ - $y$  plane and the  $x$  axis.) Figures 1 and 2 taken together represent the levels for both sites combined when  $\mathbf{H}$

TABLE I. Direction of axes in the crystal.

|         | Hamiltonian axis | Direction in crystal |
|---------|------------------|----------------------|
| Site I  | $x$              | [ $\bar{1}10$ ]      |
|         | $y$              | [001]                |
|         | $z$              | [110]                |
| Site II | $x$              | [ $\bar{1}10$ ]      |
|         | $y$              | [001]                |
|         | $z$              | [ $\bar{1}10$ ]      |

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† A brief review of this work has been given in *Quantum Electronics* (Columbia University Press, 1960), p. 389.

<sup>1</sup> J. H. Van Vleck and W. G. Penney, *Phil. Mag.* **17**, 961 (1934).

<sup>2</sup> H. A. Bethe, *Ann. Physik* **3**, 139 (1929).

<sup>3</sup> A. Abragam and M. Pryce, *Proc. Roy. Soc. (London)* **A205**, 135 (1951).

<sup>4</sup> K. A. Mueller, *Helv. Phys. Acta* **31**, 173 (1958).

<sup>5</sup> B. Bleaney and R. S. Trenam, *Proc. Roy. Soc. (London)* **A223**, 1 (1954).

<sup>6</sup> M. M. Zaripov and Iu Ia Shamonin, *Izvest. Akad. Nauk. (S.S.S.R.) Ser. Fiz.* **20**, 1224 (1956) [translation: *Bull. Acad. Sciences (U.S.S.R.)* **20**, No. 11, 1114 (1956)].

<sup>7</sup> F. A. Grant, *Revs. Modern Phys.* **31**, 646 (1959).

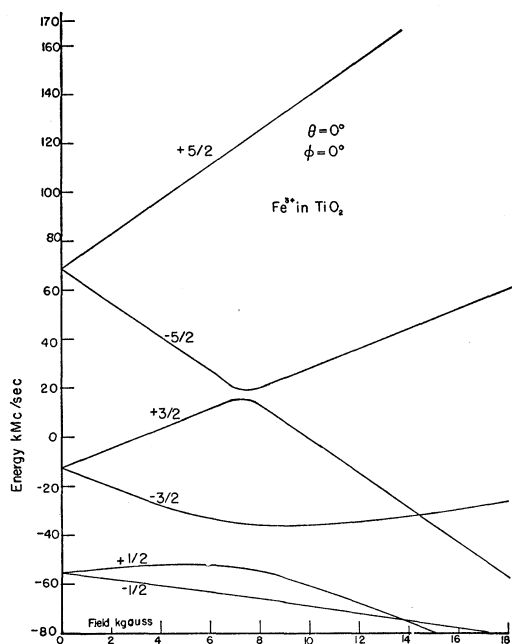


FIG. 1. Calculated energy levels as a function of field strength for the field in the  $z$  direction ( $\theta=0$ ,  $\phi=0^\circ$ ). The numbers on the levels are for identification.

points in the  $[110]$  or  $[\bar{1}10]$  direction. Energy levels for other various angles have been given elsewhere.<sup>8</sup>

### C. APPARATUS

The paramagnetic resonances were observed from 2 kMc/sec to 110 kMc/sec and from zero to 14 kilogauss using simple video type reflection spectrometers.

Most of the spectra were observed at 78°K but some measurements were made at 4.2°K and 1.4°K. The sensitivity of the spectrometer is quite high at these low temperatures even though moderate sensitivity electronic circuits are employed with the crystal detector. This sensitivity is derived mainly from the extremely high  $Q$  values and 100% filling factors obtained when one uses the  $\text{Fe}^{3+}$  doped rutile as the microwave resonator rather than a metal walled cavity.

For the millimeter wave spectra a sample of rutile having a volume of 0.016  $\text{cm}^3$  was placed at the bottom of a shorted RG98/U waveguide in the cryostat. The crystal was oriented accurately by three thin positioning rods, via observations of the angle periodicity of the magnetic resonances mentioned in Sec. A. The preliminary orientations were made using x ray and polarizing microscope techniques. The orientation was accurate to  $\pm 0.25^\circ$ . The piece of rutile was large enough so that the lowest mode resonance frequency was much lower than any operating frequency. Many microwave resonances occurred close together in frequency and one could always pick, from the many

<sup>8</sup> Columbia Radiation Laboratory Quarterly Report, September 15, 1959 to December 15, 1959 (unpublished).

microwave resonances near a desired frequency, those which had high  $Q$ 's and strong coupling to the magnetic spin resonances. Pieces of rutile were considered too large if most of the modes overlapped.

The above system was used from 50 kMc/sec to 110 kMc/sec. Typical loaded  $Q$  values for this range of frequencies are  $\sim 5000$  at 78°K and approximately a factor of two larger at 1.4°K. Power was supplied by: QK294 and QK295 klystrons from 45 kMc/sec to 60 kMc/sec; by the second harmonics of an R9521 klystron from 65 kMc/sec to 80 kMc/sec; and by the third harmonics of QK290 and R9521 klystron from 80 kMc/sec to 110 kMc/sec. It was possible to detect magnetic resonance at these higher frequencies using only a few  $\mu\text{watts}$  of power by employing a demountable differential screw type crystal detector and an oscilloscope which had a sensitivity of 200  $\mu\text{v/cm}$ .

A similar system using a piece of  $\text{Fe}^{3+}$  doped rutile having a volume of 0.12  $\text{cm}^3$  and X-band guide was used from 7 kMc/sec to 49 kMc/sec. A third system having a coaxial line input and a piece of  $\text{Fe}^{3+}$  doped rutile 0.8  $\text{cm}^3$  in volume was used from 1.5 kMc/sec to 7 kMc/sec. In the latter case the sample was placed in a metal chamber 5.5  $\text{cm}^3$  in volume and supported by polyfoam to keep it away from the chamber walls. The chamber was vacuum tight to avoid condensation of nitrogen and water. With this system loaded  $Q$ 's  $\approx 85,000$  at 78°K were obtained.

### D. SPECTROMETER SENSITIVITY

A detailed explanation of the characteristics of the rutile resonator and of high dielectric low loss resonators in general will be published elsewhere. The loss of the resonator is due mainly to the internal dielectric loss and there is no significant contribution from current losses on the crystal surfaces.

Consider the following system shown in Fig. 3. We have  $1/Q_0 = 1/Q_a + 1/Q_m$ , where  $Q_0$  is the  $Q$  of the reso-

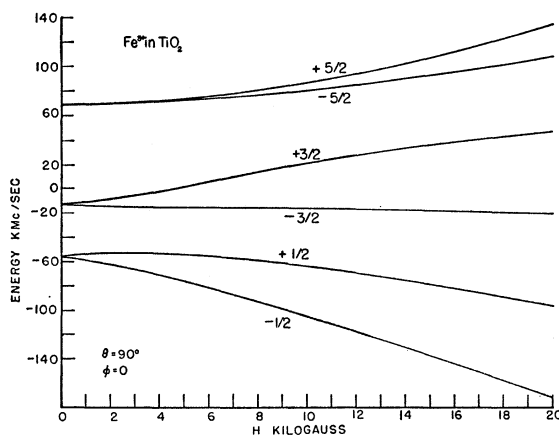


FIG. 2. Calculated energy levels as a function of field strength for the field in the  $x$  direction ( $\theta=90^\circ$ ,  $\phi=0$ ). The numbers on the levels are for identification.

nator with no external coupling and 1/Q<sub>d</sub> describes losses due to intrinsic resonator absorption. Absorption by the sample due to magnetic resonance is described by

$$1/Q_m = 4\pi\chi''\eta,$$

where η is the usual filling factor and is unity in this case and χ'' is the imaginary part of the magnetic susceptibility. If we assume 4πχ'' ≪ 1/Q<sub>d</sub> we obtain

$$Q_0 = Q_d(1 - 4\pi\chi''Q_d).$$

With a swept klystron one observes changes in the reflected power with a change in Q<sub>0</sub> due to magnetic resonance. This change is

$$\Delta Q_0 = 4\pi\chi''Q_d^2$$

to first order in χ''. One seeks to maximize the change in the reflection coefficient r = P<sub>r</sub>/P<sub>i</sub>, where P<sub>r</sub> and P<sub>i</sub> are, respectively, the reflected and incident powers for the resonator. One can write

$$r = (1 - \beta)^2 / (1 + \beta)^2,$$

where β = Q<sub>ex</sub>/Q<sub>0</sub> and Q<sub>ex</sub> describes the coupling to the resonator. The change in r for a change in the resonator is

$$\Delta r = 4\beta(1 - \beta)\Delta Q_0 / [(1 + \beta)^3 Q_0].$$

For a maximum Δr we must have d(Δr)/dβ = 0. The result is that Δr is maximum for β = 2 ± √3. Then

$$\Delta r / r = \Delta P_r / P_r = 4\beta\Delta Q_0 / (1 - \beta^2)Q_0 = 16\pi\beta\chi''Q_d / (1 - \beta^2),$$

since Q<sub>d</sub>/Q<sub>0</sub> ≈ 1; and for β = 0.27 = 2 - √3 (undercoupled case)

$$\Delta P_r / P_r = 14.6\chi''Q_d.$$

The signal to noise ratio of the crystal detector is S/N = MP<sub>r</sub> / (4kTΔν)<sup>1/2</sup> where M is the figure of merit of the crystal and Δν is the acceptance bandwidth of

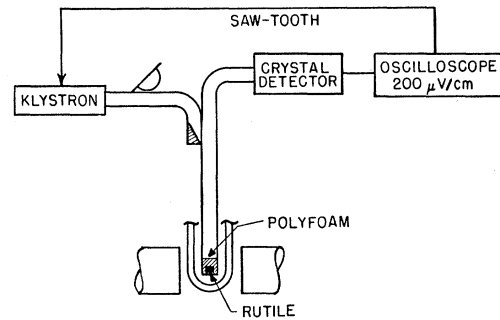


FIG. 3. Schematic diagram of the spectrometer.

the receiver system. If one sets ΔP<sub>r</sub>/P<sub>r</sub> = N/S as the minimum detectable change in power then

$$\chi_{\min}'' = (4kT\Delta\nu)^{1/2} / 14.6Q_dMP_r.$$

For an MA408B crystal at X-band, the parameters are: M = 220(w)<sup>-1/2</sup>, P<sub>r</sub> = 1 mw, T = 300°K, Q<sub>d</sub> = 85 000, Δν = 10 kc/sec. This gives χ<sub>min</sub>'' ≈ 1 × 10<sup>-13</sup> which corresponds to detecting about 10<sup>10</sup> spins/cm<sup>3</sup>. This minimum number of detectable spins has been decreased by using a fixed frequency klystron, magnetic modulation and a narrow band lock-in detector. Another sizeable increase in sensitivity can be achieved using a superheterodyne receiver to reduce the noise input.

In order to appreciate the sensitivity afforded in this particular instance let us make a comparison of our situation (1) with the usual case (2) of a low dielectric sample in a metal walled cavity. If n is the minimum number of detectable spins per unit volume, then the ratio of the minimum number of detectable spins, N, in the two cases is

$$N_1/N_2 = n_1V_1/n_2V_2,$$

where V is the volume of the sample. Since n ∝ χ<sub>min</sub>''

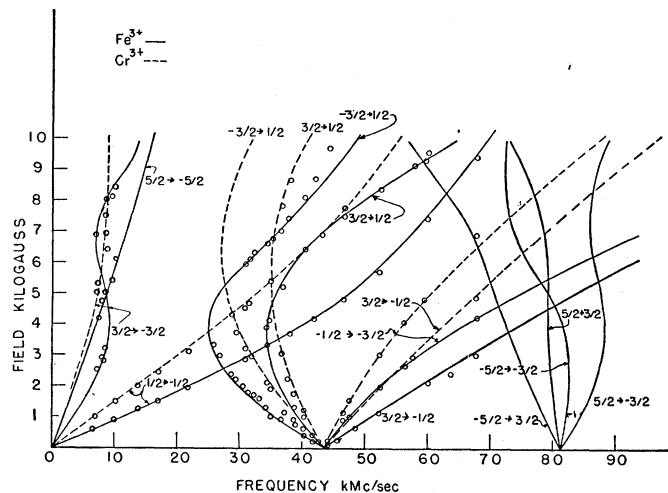


FIG. 4. Comparison of calculated and experimental values of magnetic field for resonance as a function of frequency, for a fixed orientation.

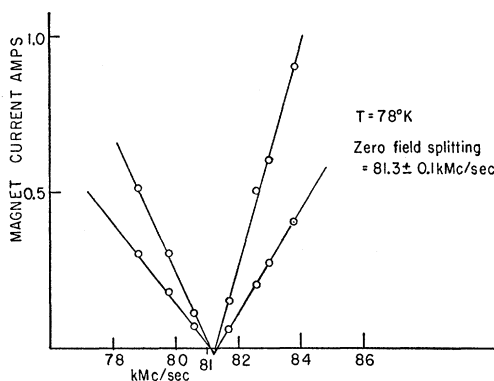


FIG. 5. Extrapolation of experimental resonance points to zero magnetic field at 81.3 kMc/sec (There is a small residual field for zero current in the electromagnet coils).

and  $\chi_{\min}''(1)/\chi_{\min}''(2) = Q_2\eta_2/Q_1\eta_1$  (assuming no saturation and the same power input), we have

$$N_1/N_2 = Q_2\eta_2V_1/Q_1\eta_1V_2.$$

Since both cases (1) and (2) are compared for the same frequency, the case (1) (dielectric) requires a smaller volume to support a microwave mode. If we consider the usual case of a small filling factor then  $\eta_2 \cong V_2/V_{2c}$  where  $V_{2c}$  is the volume of the metal walled cavity. In this case

$$N_1/N_2 = Q_2V_2V_1/Q_1V_{2c}V_2 = Q_2V_1/Q_1V_{2c}.$$

For the lowest dielectric mode  $V_1/V_{2c} = \epsilon_1^{*-1}$ , where  $\epsilon_1^*$  is the apparent dielectric constant.<sup>9</sup> For the higher dielectric resonator modes actually used  $V_1/V_{2c} = \epsilon_1^{*-1/2}$ . In this case

$$N_1/N_2 = Q_2/\epsilon_1^{*1/2}Q_1.$$

For rutile  $Q_1 \cong 85\,000$ ,  $\epsilon_1^* \cong 40$ . For case (2)  $Q_2 \cong 8500$ . The ratio of the minimum number of detectable spins is<sup>9</sup> then  $N_1/N_2 \cong 4 \times 10^{-4}$ .

### E. RESULTS OF SPECTROSCOPY

Two kinds of spectra were taken with the spectrometers described in Sec. C. The first was a survey over a large range of frequencies (7 kMc/sec to 110 kMc/sec) and magnetic fields (0–10 kgauss) at a fixed orientation of magnetic field in order to see the general characteristics of the spectra. In this way the two zero field splittings were determined. They are  $43.3 \pm 0.1$  kMc/sec and  $81.3 \pm 0.1$  kMc/sec. The frequency shifts of the zero field splittings as the temperature was changed from 78°K to 1.4°K were less than 0.5%. The results are shown in Fig. 4. Actually the sample for the spectrum of Fig. 4 was a mixture of 0.03% Fe and 0.04% Cr by weight. In this case the  $\text{Cr}^{3+}$  spectrum was fitted using the spin Hamiltonian of Gerritsen, Harrison, Lewis, and Wittke.<sup>10</sup> It is interesting to note

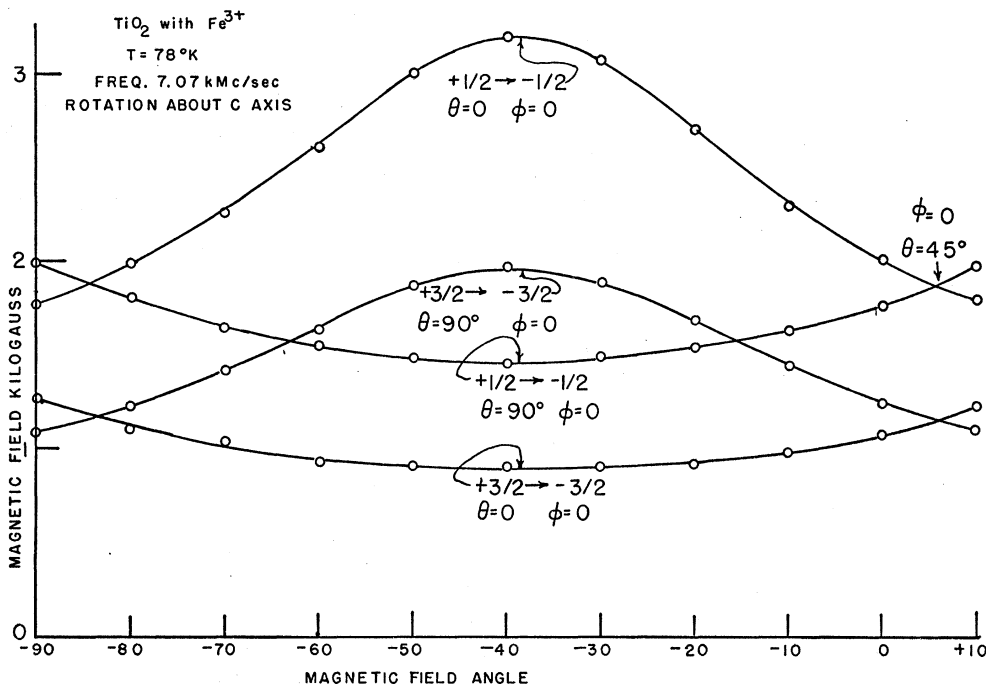
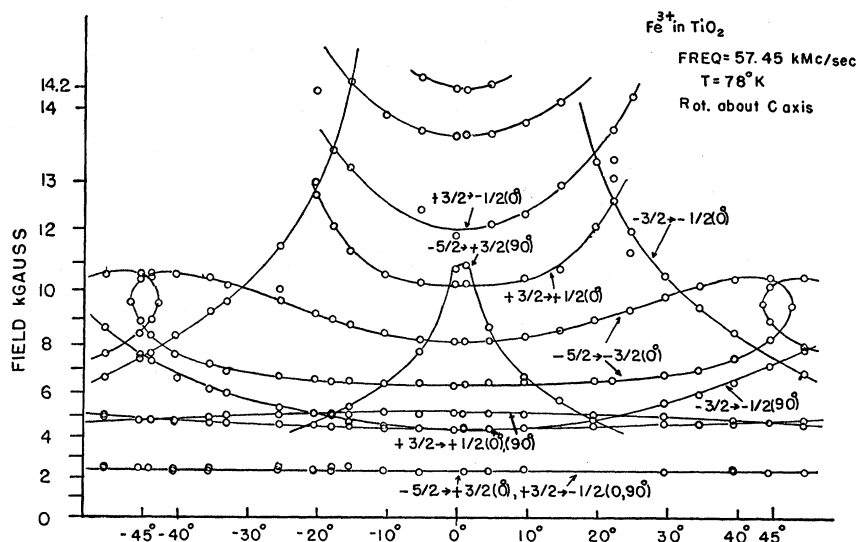


FIG. 6. Experimental values of magnetic field for resonance as a function of angle in the (001) plane for a fixed frequency of 7.07 kMc/sec.

<sup>9</sup> The physical meaning of using this apparent dielectric constant rather than the real dielectric constant ( $\sim 100$ ) will be explained in a later publication.

<sup>10</sup> H. J. Gerritsen, S. E. Harrison, H. R. Lewis, and J. P. Wittke, Phys. Rev. Letters 2, 153 (1959).

FIG. 7. Experimental values of magnetic field for resonance as a function of angle in the (001) plane for a fixed frequency of 57.45 kMc/sec.



that the  $\text{Cr}^{3+}$  zero field splitting coincides with the first zero field splitting of the  $\text{Fe}^{3+}$  within our experimental error. The orientation of the magnetic field for this spectrum was  $\theta = 83^\circ$ ,  $\phi = 83^\circ$ . For this orientation both sites I and II are equivalent and exhibit the same spectra.

For frequencies higher than 70 kMc/sec, experimental points do not fit the solid curves because the crystal orientation was changed and was not determined in that frequency region. In Fig. 5 the extrapolation to the second zero field splitting is shown. In this case the angles are undetermined. (The values of the zero field splittings are independent of orientation.) The other spectra taken were for fixed frequencies, variable magnetic field and variable field orientations. Constants for a spin Hamiltonian were adjusted to fit to these data. The experiments were done at 7.07 kMc/sec and 57.45 kMc/sec and  $T = 78^\circ\text{K}$  for rotations about the  $c$  axis of the crystal. Magnetic fields were measured with a proton and lithium nuclear probe. The experimental results are illustrated in Figs. 6 and 7. The angular part of the identification,  $\theta$ , of the transitions shown in parentheses in Fig. 7 refers to zero degrees on the abscissa of that figure. An accurate measurement of the constant  $a$  was made by observing the transition  $-\frac{5}{2} \rightarrow +\frac{3}{2}$  at  $\theta = \phi = 0^\circ$  and  $H = 7.5$  kgauss. At this point according to Fig. 1, the  $-\frac{5}{2} \rightarrow +\frac{3}{2}$  transition frequency is  $\sim 3.5$  kMc/sec and

is most sensitive to terms in the Hamiltonian which connect states having  $\Delta M_s = \pm 4$ . This measurement affords an almost independent determination of the constant  $a$ . The signs of the parameters in our Hamiltonian are consistent with intensity measurements obtained as the temperature was lowered from  $4.2^\circ\text{K}$  to  $1.4^\circ\text{K}$  and with the best possible fit of the experimental frequencies.

#### F. SPIN LATTICE RELAXATION TIMES AND LINE WIDTHS

Two methods were used for the determination of spin-lattice relaxation times. If the relaxation times were longer than 1 msec, then a stabilized klystron was used to saturate a desired magnetic resonance, while a low power klystron was continually swept over the microwave resonance which was displayed on an oscilloscope. The stabilized klystron was then shut off in approximately 1 msec and the oscilloscope trace was photographed with a continuous strip film which moved at 1.5 mm per msec. For times too short for the pulse-decay system, conventional cw methods were used.<sup>11</sup> The results are summarized in Table II. Not listed in the table is a strong transition at  $\nu = 25$  kMc/sec and  $T = 1.4^\circ\text{K}$ , which had an estimated  $T_1$  of  $\sim 1$  msec. This may indicate a  $1/\nu^2$  dependence; but more work is needed to establish this point. The value  $T_1 = 0.1$  msec at  $78^\circ\text{K}$  and  $\nu = 7.1$  kMc/sec given in

TABLE II. Line widths and spin lattice relaxation times.

| Transition                              |                 | $\Delta\nu$ | $T_1$                 | Temp                | Frequency    |
|---|-----------------|-------------|-----------------------|---------------------|--------------|
| $+\frac{3}{2} \rightarrow -\frac{1}{2}$ | $H \parallel Z$ | 34.5 Mc/sec | 4 msec                | $1.4^\circ\text{K}$ | 8.55 kMc/sec |
| $+\frac{3}{2} \rightarrow -\frac{1}{2}$ | $H \parallel X$ | 33.0 Mc/sec | 4.5 msec              | $1.4^\circ\text{K}$ | 8.55 kMc/sec |
| $+\frac{1}{2} \rightarrow -\frac{3}{2}$ | $H \parallel X$ | 50 Mc/sec   | 4.5 msec              | $1.4^\circ\text{K}$ | 8.55 kMc/sec |
| $+\frac{1}{2} \rightarrow -\frac{3}{2}$ | $H \parallel Z$ | 27 Mc/sec   | 4 msec                | $1.4^\circ\text{K}$ | 8.55 kMc/sec |
| $+\frac{1}{2} \rightarrow -\frac{3}{2}$ | $H \parallel Z$ | 34.5 Mc/sec | 0.1 msec <sup>a</sup> | $78^\circ\text{K}$  | 7.1 kMc/sec  |

<sup>a</sup> Calculated using c.w. methods.

<sup>11</sup> A. H. Eschenfelder and R. T. Weidner, Phys. Rev. **92**, 869 (1953).

Table II was calculated for  $Q=40\,000$ , input power  $=100\ \mu\text{w}$ ,  $\Delta\nu=34.5\ \text{Mc/sec}$ , matrix element  $\sim 1$  Bohr magneton and degree of saturation  $\sim 70\%$ . This value of  $T_1$  indicates that Raman processes are probably not dominant at  $T=78^\circ\text{K}$ .<sup>12</sup> This is also the case for ruby where saturation and subsequent maser action have been reported at temperatures as high as  $195^\circ\text{K}$ .<sup>13</sup>

#### G. ACKNOWLEDGMENTS

The authors would like thank Professor C. H. Townes for suggesting the investigation of this material, and for

<sup>12</sup> J. H. Van Vleck, *Phys. Rev.* **57**, 426 (1940).

<sup>13</sup> T. Maiman, *Quantum Electronics* (Columbia University Press, New York, 1960), p. 324.

many helpful discussions. We express our special thanks to F. R. Nash who worked in the early stages of the research and made the relaxation measurements. We are also indebted to Y. Okaya for the x-ray analysis; to D. Tycko and K. King for their help with the IBM 650; to N. Chang for help with various calculations; and to the Machine Shop of the Columbia Radiation Laboratory for their close cooperation.

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## Magnetism of Europium Garnet\*

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The theoretical expressions for the magnetic moment of a trivalent europium ion in a molecular field arising from exchange are applied to Pauthenet's measurements on europium iron garnet. It is a good approximation to assume that the exchange interaction stems entirely from the coupling with the iron atoms, which greatly simplifies the theory since the molecular field on the europium is then an impressed one and does not have to be determined self-consistently. The calculated variation of the magnetization with temperature is in excellent accord with experiment. The magnitude of the exchange interaction is compared with that in the other rare earth iron garnets; it is almost exactly the same as in gadolinium iron garnet.

THE magnetic moment of  $5\ \text{Fe}_2\text{O}_3 \cdot 3\ \text{Eu}_2\text{O}_3$  is lower than that of an iron garnet such as  $5\ \text{Fe}_2\text{O}_3 \cdot 3\ \text{Y}_2\text{O}_3$  in which the europium atoms are replaced by a diamagnetic ingredient. This fact shows that the coupling between the europium and iron atoms is antiferromagnetic in the sense that the magnetic moment of the europium is oppositely directed from the resultant moment of the ferrimagnetic iron lattices. It is the purpose of the present paper to discuss this reduction in moment on the basis of quantum mechanics, and especially to predict how it should vary with temperature.

$\text{Eu}^{+++}$  differs from the other trivalent rare earth ions in having a rather unusual type of magnetic behavior. Its ground state has  $J=0$ , but nevertheless is paramagnetic because of the induced magnetic moment associated with the second-order Zeeman effect. It is possible for the magnetic moment to have matrix elements which are nondiagonal in  $J$  because it is proportional to  $L+2S$  which, unlike  $L+S$ , is not a constant of the

motion. These off-diagonal elements parallel to the applied field are of the form  $\langle J|S_z|J\pm 1\rangle = -\langle J|L_z|J\pm 1\rangle$ . The theory of the magnetic susceptibility of a free  $\text{Eu}^{+++}$  ion is given in Van Vleck's book.<sup>1</sup> Some modification, however, is required for the application to europium garnet. We can safely neglect crystalline field effects in the solid, as the field is nearly cubic, and both the ground state and the first-excited state  $J=1$  are unaffected by a cubic field. The exchange coupling between a given ion  $i$  and the other paramagnetic ions  $j$  we represent by the usual exchange potential

$$-2\sum_j J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j,$$

where  $J_{ij}$  is the exchange integral connecting atoms  $i$  and  $j$ . This expression is rigorous only if the orbital charge clouds are centro-symmetric but is probably often a good approximation even in other than  $S$  states because of the small radii of the  $4f$  electrons. Since the garnets are nonconductors, the coupling is presumably indirect, of the Kramers type via the  $\text{O}_2$  atoms, rather

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<sup>1</sup> J. H. Van Vleck, *Electric and Magnetic Susceptibilities* (Oxford University Press, New York, 1932), p. 245 ff. See also A. Frank, *Phys. Rev.* **39**, 119 (1932); **48**, 765 (1935).