Theory of Ferromagnetic Resonance in Rare Earth Garnets. III. Giant Anisotropy Anomalies*

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The giant sharp anisotropy anomalies in YIG discovered by Dillon and attributed to rare earth ions are explained in terms of the crossovers or, most probably, near crossovers of the energy levels of the rare earth ions in the combined crystal and exchange fields. The central consequence deduced by the theory, independent of the detailed behavior of the energy levels, is that $-H_\alpha(\Delta\theta_{\frac{1}{2}})^2 \approx kTN'/M$, where H_α is the anisotropy field; $\Delta\theta_{\frac{1}{2}}$ the angular width of the peak; N' the concentration of rare earth ions at the crossover; M is the total magnetization; the result assumes $kT \gg$ level splitting at apparent crossover. This and other results appear to be in satisfactory agreement with the available experimental data. Crystals with giant anomalies have useful properties for adiabatic demagnetization experiments—the ferric-rare earth exchange field of 100 koe can be effectively turned on or off by rotation of the magnetic moment of the crystal. In an appendix we examine the validity of the molecular field approximation to the ferric-rare earth ion interaction, and we find that the approximation is excellent. A further appendix discusses the question of crossing or noncrossing of energy levels in static fields.

THE earlier papers in this series on ferromagnetic resonance in rare earth garnets dealt with g-values[1] and line widths[2] in rare earth garnets under conditions dominated by the rapid relaxation of the magnetic moments of the rare earth ions. The present paper[3] is concerned with an effect which appears at the lowest temperatures, where the magnetic relaxation of the rare earth ion is of secondary interest: at helium temperatures giant peaks appear (over narrow angular ranges) in the value of the static magnetic field required to produce ferromagnetic resonance. In one published experiment the substitution of only 0.1 at. % paramagnetic terbium for diamagnetic yttrium in yttrium iron garnet led at 1.5°K to a number of peaks in the resonance field at 23 Kmc, some as high as 5000 oersteds, over an angular range of a few degrees in the rotation plane. The effect was discovered by Dillon[4] and investigated further by Dillon and Nielsen,[5] whose results for YIG-0.1% Tb are reproduced in Fig. 1. The height of the peaks decreases and their width increases as the temperature is raised. Results for pure rare earth garnets are not presently available but a simple linear extrapolation should not be too wide of the mark, as we indicate below. Thus one would perhaps expect in pure terbium iron garnet to find peaks up to 5×10^6 oersteds in height.

The magnitude of this somewhat hypothetical number is quite surprising, because the exchange interaction between the rare earth and ferric lattices is equivalent to a magnetic field of only about 10^5 oersteds acting on the rare earth ions, and it may seem difficult to get an anisotropy 50 times stronger than the total coupling. Further, the narrowness and the sporadic location of the peaks defy plausible analysis in cubic harmonics of orders associated with the angular momenta $J=8$, 15/2, 6, $\frac{7}{2}$, and $\frac{5}{2}$ of the relevant rare earth ions.

It is essential to realize that the actual observation is of an anomaly in the resonance field, $H_{\rm res}$, defined by

$$\omega=\gamma H_{\rm res}; \quad \gamma=ge/2mc; \tag{1}$$

and not necessarily in the anisotropy energy itself. Let E denote the magnetocrystalline anisotropy energy per unit volume; consider the work done ΔE in a small deflection $\Delta\theta_\alpha$ of the magnetization from the direction of static equilibrium. Then

$$\begin{aligned}\Delta E&=\frac{\partial E}{\partial\theta_\alpha}\Delta\theta_\alpha+\frac{1}{2}\frac{\partial^2 E}{\partial\theta_\alpha{}^2}(\Delta\theta_\alpha)^2+\cdots\\&=T_\alpha\Delta\theta_\alpha+\frac{1}{2}\frac{\partial T_\alpha}{\partial\theta_\alpha}(\Delta\theta_\alpha)^2+\cdots,\end{aligned} \tag{2}$$

where T_α is the torque component normal to the plane defined by the initial and final directions of the magnetization $\mathbf{M}$. We always suppose here that the axis α is a principal axis of the local anisotropy surface, so that $\partial^2E/\partial\theta_\alpha\partial\theta_\beta=0$. Because the magnetization in the initial direction was in static equilibrium, $\partial E/\partial\theta_\alpha$ and T_α are identically zero. The initial direction is not necessarily precisely the direction of the external magnetic field. From (2) we have

$$\partial T_\alpha/\partial\theta_\alpha=\partial^2E/\partial\theta_\alpha{}^2. \tag{3}$$

It is usual and convenient, for small deflections, to discuss the anisotropy torque in terms of an effective field component H_α defined by

$$T_\alpha=MH_\alpha\Delta\theta_\alpha, \tag{4}$$

* Supported by the National Science Foundation.
[1] C. Kittel, Phys. Rev. **115**, 1587 (1959).
[2] de Gennes, Kittel, and Portis, Phys. Rev. **116**, 323 (1959).
[3] The central argument of the present paper was noted in C. Kittel, Phys. Rev. Letters **3**, 169 (1959).
[4] J. F. Dillon, Jr., Phys. Rev. **111**, 1476 (1958).
[5] J. F. Dillon, Jr., and J. W. Nielsen, Phys. Rev. Letters **3**, 30 (1959).

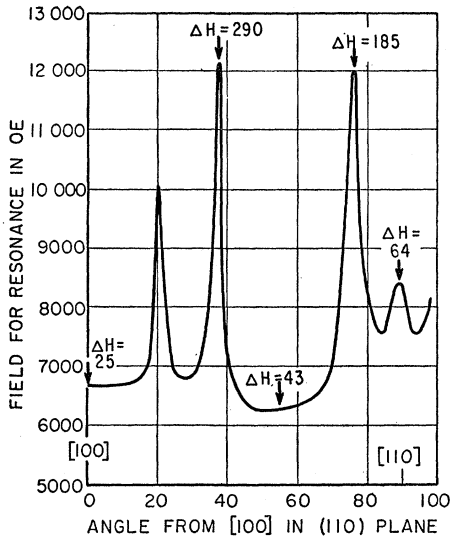

FIG. 1. Field for resonance at 1.5°K, 22 990 Mc/sec for YIG doped with 0.1% terbium, after Dillon and Nielsen.

where M is the saturation magnetization, so that

$$\partial T_\alpha/\partial\theta_\alpha = MH_\alpha = \partial^2 E/\partial\theta_\alpha{}^2. \tag{5}$$

Thus

$$H_\alpha = (1/M)(\partial^2 E/\partial\theta_\alpha{}^2). \tag{6}$$

This is a standard result in ferromagnetic resonance theory. Further, if $\Delta\theta_\alpha$, $\Delta\theta_\beta$ are perpendicular deflections along principal axes of the anisotropy surface, the resonance field is given by[6]

$$\omega/\gamma = [(H_{\rm res}+H_\alpha)(H_{\rm res}+H_\beta)]^{\frac{1}{2}}, \tag{7}$$

for a sphere, assuming the magnetization lies parallel to the applied field. For other geometries the usual demagnetization corrections apply. Static torque anisotropy determinations should show discontinuities in torque at each crossover orientation.

We see from (6) and (7) that a local large negative value of $\partial^2 E/\partial\theta_\alpha{}^2$ or $\partial^2 E/\partial\theta_\beta{}^2$, or both, will appear as a large peak in the resonance field. Thus a strict crossover, as in Fig. 2, of the ground-state energy level of a rare earth ion as a function of the angle θ will give at absolute zero a delta-function type singularity in $H_{\rm res}$ at θ_0. This is essentially the explanation of the anisotropy anomalies. The angle θ characteristically may measure the angle between an axis of the local crystal field and the direction of the molecular field, which is parallel to **M**. The crossover angle θ_0 need not in general coincide with a simple crystal direction; the singular derivative $\partial^2 E/\partial\theta^2$ will be negative at the crossover, so that the giant anomaly in $H_{\rm res}$ will be positive. Both these conclusions agree with the experimental evidence.

We propose then that the anisotropy anomalies occur at crossovers or near-crossovers in the ground-state energy of the rare earth ions, as a function of the direction of the magnetization of the ferric ion lattice. It is most probable that the levels with which we are concerned do not actually crossover, but are split at the apparent crossover. The high curvature at such points then gives the anisotropy peaks. There are a number of questions which must now be treated.

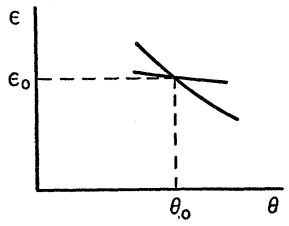

FIG. 2. Schematic crossover.

One central question concerns the validity of the picture of the energy levels of a single rare earth ion split by an exchange interaction acting just like a large magnetic field. This picture is used implicitly in the early discussions[7] of the temperature dependence of the saturation magnetization of rare earth garnets, but perhaps not in quite as sensitive a way as we use it here and as it has been used by Ayant and Thomas[8]; White and Andelin[9]; and Wolf[10] in treating the magnetic state of the rare earth ions in garnets at low temperatures. In Appendix A we examine the validity of the model by calculating (for low concentrations of rare earth ions) the second order correction to the energy, for an isotropic exchange interaction. We find the very useful result that the energy in the molecular field approximation is expected to be accurate to about 1% for low concentrations of rare earth ions in YIG. In fact, whenever the ferric ion-rare earth ion interaction is very much weaker than the ferric-ferric interaction, then the molecular field approach is valid. The argument should go through similarly for anisotropic exchange interactions in the sense that the eigenvalues in the above limit should be given quite accurately by expectation values of the actual interaction over the state in which the ferric-rare earth exchange is switched off. The crystal field part of the splitting of Tb^{+++} in YIG has not been determined; Baker and Bleaney[11] give the over-all crystal field splitting of Tb^{+++} in yttrium ethyl sulfate as 56 cm^{-1}. We should mention that unpublished calculations by L. Walker show that one can find a crystal potential for Tb^{+++} which will show near crossovers at the observed orientations.

We next calculate the anisotropy field H_α for ground-state energy levels which actually cross at the angle θ_0 in the plane under consideration. We take as before the axis α to be a principal axis of the local energy surface.

[6] C. Kittel, Phys. Rev. **73**, 155 (1948).

[7] R. Pauthenet, Ann. phys. **3**, 424 (1958).

[8] M. Y. Ayant and J. Thomas, Compt. rend. **248**, 387, 1955 (1959).

[9] R. L. White and J. P. Andelin, Jr., Phys. Rev. **115**, 1435 (1959).

[10] W. P. Wolf, Proc. Phys. Soc. (London) (to be published).

[11] J. M. Baker and B. Bleaney, Proc. Roy. Soc. (London) **A245**, 156 (1958).

For intersecting levels we have to make at this stage the assumption that the system always remains in thermal equilibrium, even at microwave frequencies. When the crossing is only apparent this assumption can be dropped, which will be a great improvement. We write

$$\epsilon_1 = -m_1 H_{ex} \Delta\theta; \quad \epsilon_2 = -m_2 H_{ex} \Delta\theta, \tag{8}$$

for the energy of the two levels for small angles $\Delta\theta$ from θ_0; the zero of energy is taken at θ_0. We neglect for the present the shift of θ_0 itself with applied magnetic field.

In thermal equilibrium ($\beta = 1/kT$) we have for the free energy

$$F = -(1/\beta) \ln(e^{-\epsilon_1\beta} + e^{-\epsilon_2\beta}), \tag{9}$$

so that

$$\partial^2 F/\partial(\Delta\theta)^2 \cong -H_{ex}^2 (m_1 - m_2)^2/4kT, \tag{10}$$

for

$$|m_1 - m_2| H_{ex}/kT \ll 1. \tag{11}$$

From (6) and (10) we have at the peak

$$H_\alpha = -(m_1 - m_2)^2 N' H_{ex}^2/4MkT, \tag{12}$$

where N' is the concentration of rare earth ions having crossovers at θ_0 and M is the total magnetization.

Now $|m_1 - m_2|$ for Tb^{+++} may plausibly be of the order 2 to 10 Bohr magnetons, so we may estimate the value of $|m_1 - m_2| N'/M$ as f, the fraction of yttrium sites occupied by rare earth ions. For a magnetic field in a general direction there are six magnetically-inequivalent rare earth sites. Roughly

$$H_\alpha \sim -f\mu_0 H_{ex}^2/kT. \tag{13}$$

Using, as for the example quoted at the beginning of this paper, $f \approx 10^{-3}$; $\mu_0 \approx 10^{-19}$ to 10^{-20}; $H_{ex} \approx 1.4 \times 10^5$; $T \approx 1.5°K$; we find $H_\alpha \approx -10^3$ to -10^4 oe, according to the value adopted for $|m_1 - m_2|$. This estimate has the correct order of magnitude and the correct sign, as the peak in H_{res} will be positive, according to (7). It is to be hoped that eventually the crystal field splitting of Tb^{+++} and other ions in the garnet structure will be well enough known to permit the calculation of the near crossovers θ_0 and of the factors $|m_1 - m_2|$ near the crossovers. We see from (13) that the height of the anisotropy peak is expected to be directly proportional to the concentration of rare earth ions and inversely proportional to the temperature. Both these relations will be modified at temperatures below those defined by the rare earth-rare earth exchange and dipolar interactions. In TbIG the molecular field between rare earth ions is expected to be less than 10^4 oe, corresponding to approximately 1°K.

We see that the total angular width at one-half the maximum anisotropy field is approximately

$$\Delta\theta_{\frac{1}{2}} \approx \frac{2kT}{|m_1 - m_2| H_{ex}} \approx (0.03 \text{ to } 0.3) T \text{ radian}. \tag{14}$$

The angular width observed by Dillon and Nielsen is at the lower end of this range, at 1.5°K. We may combine (12) and (14) to get an interesting expression which has a remarkable property: it is independent of $|m_1 - m_2|$ and of H_{ex}. We have

$$-H_\alpha (\Delta\theta_{\frac{1}{2}})^2 \cong kTN'/M. \tag{15}$$

We note from (2) that (15) may be expressed as

$$-\Delta E = N'kT. \tag{16}$$

This result assumes that kT is large in comparison with the minimum separation of the levels. In the work of Dillon and Nielsen[5] shown in our Fig. 1, the total concentration of Tb ions was 1.2×10^{19} cm^{-3}. In the (110) plane there are four magnetically-inequivalent rare earth sites, two having statistical weight $\frac{1}{3}$ and two having statistical weight $\frac{1}{6}$. The former will give stronger anomalies. For these at 1.5°K,

$$kTN'/M \cong (2 \times 10^{-16})(4 \times 10^{18})/185 \cong 4 \text{ oe}. \tag{17}$$

This relates to Eq. (15b) for an adiabatic process. It is difficult to obtain an accurate value for $\Delta\theta_{\frac{1}{2}}$ from the published curves, but we estimate crudely for the peak at $\theta_0 = 38°$ in Fig. 1 that $\Delta\theta_{\frac{1}{2}} \approx 0.05$ radian and $-H_\alpha \approx 8$ koe for a peak in H_{res} of 5 koe, on the assumption $H_\beta = 0$. Then

$$-H_\alpha (\Delta\theta_{\frac{1}{2}})^2 \approx 20 \text{ oe}, \tag{18}$$

of the same order as (17), bearing in mind that (18) may be an overestimate because we do not really know that the (110) plane contains a principal axis of the local anisotropy surface.[11a]

It is difficult to make a specific prediction about the number of peaks to be expected from a given rare earth element without knowing the details of the energy level diagram. If each nonequivalent site has a single closed curve as locus of crossover angles θ_0 in a hemisphere, then it is possible as one solution to get four anisotropy peaks in the (110) plane between [100] and [011]; two of these peaks may have about twice the strength of the two others, measured in terms of $H_\alpha (\Delta\theta_{\frac{1}{2}})^2$. This possibility is perhaps not inconsistent with the results in Fig. 1.

We should note that the position θ_0 of a crossover will depend somewhat on the static magnetic field intensity H, because the energy levels are displaced at different rates by the application of a magnetic field. Suppose that for θ near the crossover we can write

$$\begin{aligned} \epsilon_1 &= c_1 - m_1 H_t \theta; \\ \epsilon_2 &= c_2 - m_2 H_t \theta, \end{aligned} \tag{19}$$

[11a] Dr. J. F. Dillon, Jr., has kindly replotted on an expanded scale his data from which Fig. 1 was drawn. The experimental values of the product $\Delta H_{res}(\Delta\theta_{\frac{1}{2}})^2$ are approximately 3.8, 10.2, and 21.5 oersteds, respectively, for the peaks at 20°, 38°, and 76° from the [100] direction; here ΔH_{res} is the height of the anomaly above the estimated baseline at the appropriate angle. Results on HoIG and DyIG, in agreement with our model, will appear in a paper by J. F. Dillon, Jr., and J. W. Nielsen, J. Appl. Phys. **31** (1960), to be published.

where H_t is the total field, exchange plus magnetic, acting on an ion. The crossover θ_c is then given by

$$\theta_c = -\frac{c_2 - c_1}{m_2 - m_1}\frac{1}{H_t}; \tag{20}$$

this is what we have written as θ_0 for $H_t = H_{ex}$. Thus

$$\delta\theta/\theta_0 \cong -H_{mag}/H_{ex}. \tag{21}$$

For $H_{mag} \cong 10$ koe; $H_{ex} \approx 100$ koe; $\theta_0 \approx 1$ radian; we have $\delta\theta \approx 0.1$ radian. This is not a negligible shift in position and should be easily detectable. It is further possible, when the line shift is comparable with or greater than the width $\Delta\theta_{\frac{1}{2}}$, that the anisotropy peak will change shape according to whether it is explored from lower or higher values of θ.

If we were to take the crossover model literally in the sense of supposing that the levels actually crossover and the ground-state changes discontinuously at θ_0, then we would need a relaxation process to keep the system always with an excess population in the ground state. Otherwise the anisotropy anomaly will not appear. We would require that even for deflections at microwave frequencies the system remain essentially in thermal equilibrium at all stages of the motion. The fractional width of the resonance line at θ_0 from such a relaxation process alone will be $\Delta H/H \sim \omega\tau$, where τ is the relaxation time. If $\Delta H/H$ is 10^{-2} for $\omega \sim 10^{11}$, τ must be $\sim 10^{-13}$ sec. This time seems unreasonably short, even for a spin-spin process. This apparent difficulty is removed if the levels do not actually crossover, but are split. Such a situation is discussed next, and it is shown that the need for rapid relaxation can be removed without losing any of the essential results derived above for the crossover model. It seems rather unlikely that strict crossovers can actually occur, but we will continue to use the word, for convenience.

Suppose that two levels which seem destined to crossover do not, being repelled by a weak perturbation, as in Fig. 3. The perturbation may arise from terms in the crystal field, from imperfections, or from the time-dependent parts of the exchange and magnetic fields.[12] For small angles $\Delta\theta$ from the apparent crossover position θ_0 the secular equation for one ion may be written in schematic form as

$$\begin{vmatrix} p_1\Delta\theta - \epsilon & \delta \\ \delta & p_2\Delta\theta - \epsilon \end{vmatrix} = 0, \tag{22}$$

where δ is the matrix element of the perturbation between the unperturbed states 1 and 2, and p_1, p_2 are the slopes of the unperturbed levels in the neighborhood of θ_0. Then, at $\Delta\theta = 0$, we have

$$\partial^2\epsilon/\partial(\Delta\theta)^2 = -(p_1 - p_2)^2/4\delta. \tag{23}$$

[12] M. H. L. Pryce, Phys. Rev. **77**, 136 (1950).

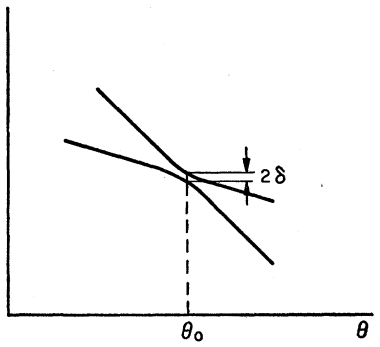

FIG. 3. Repulsion of energy levels at θ_0 because of perturbation.

At θ_0 the anisotropy field at absolute zero is

$$-H_\alpha = N'(p_1 - p_2)^2/4\delta M, \tag{24}$$

where N' is the concentration of rare earth ions having an approximate crossover at θ_0. Now $p_1 - p_2$ will be of the order of $-\mu_0 H_{ex}$, so that

$$-H_\alpha \approx N'\mu_0^2 H_{ex}^2/4\delta M, \tag{25}$$

where μ_0 is the moment of a rare earth ion. If $N' \approx 3 \times 10^{18}$ cm^{-3}; $\delta \sim 0.1$ cm^{-1}; $\mu_0 H_{ex} \sim 50$ cm^{-1}; we have for the anomalous anisotropy

$$-H_\alpha \sim 30 \text{ koe}. \tag{26}$$

Baker and Bleaney[11] suggest that the imperfections in Tb^{+++} in yttrium ethyl sulfate give a contribution of ~ 0.4 cm^{-1} to the zero field splitting. A spread in δ will give a contribution to the line width.

If the lowest energy levels are repelled in this way, not crossing, then it is not necessary to have relaxation processes between the levels in order to have an anomalous anisotropy. Rather, the ions will naturally tend to remain in their original states. Any thermalization or redistribution of population between the two states, in the course of a resonance experiment, will lead to energy losses. The losses vanish in the limit of very rapid or very slow relaxation.

If the system is equilibrated at θ_0 and makes small deflections $\Delta\theta$ about θ_0 without further population redistribution, then in the limit $kT \gg \delta$ we have

$$\partial^2\epsilon/\partial\theta^2 \cong -(p_1 - p_2)^2/4kT, \tag{27}$$

the same result as (10). Here relaxation processes will again contribute to the line width, with $\Delta H/H \sim 1/\omega\tau$. The line widths at the anomaly peaks require $\tau \sim 10^{-9}$ sec. This contains contributions from spin-spin processes, indirect exchange, and perturbation by impurities.

We have limited our calculation specifically to the vicinity of crossover orientations and we have not entered into the more conventional anisotropy present at other orientations. One may ask why it is that the crossovers do not make themselves evident in the calculations[13] on ferrites by Wolf and by Yosida and

[13] W. P. Wolf, Phys. Rev. **108**, 1152 (1957); K. Yosida and M. Tachiki, Progr. Theoret. Phys. (Kyoto) **17**, 331 (1957).

Tachiki. It appears that by assuming the crystal field energy is small in comparison with the exchange energy these workers have eliminated the possibility of crossovers. To obtain the present effects it is essential to include the crystal potential in the unperturbed problem. One gets simple and rapidly convergent expressions for the anisotropy energy in terms of cubic or spherical harmonics only when the crystal potential can be treated as a small perturbation on the relevant exchange interactions. We may note in passing that $\int H_\alpha d\theta = 0$ around a closed path or the equivalent.

MAGNETIC COOLING

It seems possible that the "crossover effect" in rare earth garnets or in similar ferromagnetic systems may find application in magnetic cooling apparatus in which the demagnetization stage of the cooling process is simulated by rotating the magnetization of a single crystal from an orientation well away from a crossover to an orientation at a crossover of ground-state energy levels. The magnetization rotation could be caused by rotating the crystal relative to an external magnet which produces a field adequate to cause saturation in the directions selected—that is, stronger than the anisotropy and demagnetization fields. In a suitably shaped YIG crystal doped with 0.1% rare earth impurity, a field of the order of 5 koe should suffice. We would then have in principle a situation where an effective magnetic field of 50 to 100 koe—of the order of the ferric-rare earth molecular field—could be turned on and off by rotation of a 5 koe real magnetic field. The advantage of this system over anisotropic paramagnetic systems lies just in the exchange field—the poor man's magnet.

The rare earth-rare earth coupling provided by the indirect exchange, dipolar, and superexchange interactions would limit the lowest temperature reached, but these interactions are reduced in the usual way by dilution and are quite weak even in the concentrated rare earth garnets.

The phonon and magnon contributions to the entropy at low temperatures are not important. According to the measurements of Edmonds and Petersen[14] the entropy of YIG in the liquid helium range is

$$S = 45.9T^{\frac{3}{2}} + 9.8T^3 \text{ erg/cm}^3\text{-deg K}. \quad (28)$$

At 1.5°K, $S = 103 + 34 = 137$ erg/cm³-deg K, which is comparable with the free spin entropy of 0.01% impurities in YIG, or 10^{18} spins/cm³. Thus a concentration of 0.1% rare earth ions should suffice for cooling the lattice and spin wave systems from an initial temperature of 1.5°K.

We must also consider the contribution to the entropy from those rare earth ions in sites not participating in the crossover at a particular θ_0. Most of the rare earth ions will not participate. As long as these have (at both the initial and final orientations of the crystal) large splittings between the ground state and next higher state, large in comparison with T_i, these ions will not contribute in a major way to the entropy. For two states separated by ϵ, the entropy is

$$S \cong Nk(\epsilon/2kT)e^{-\epsilon/kT}, \quad (29)$$

for $\epsilon \gg kT$. For $\epsilon = 10kT$, and $N = 10^{19}$ cm^{-3}, we have $S \sim 0.2$ erg/cm³-deg K, which is insignificant.

The final temperature T_f reached in cooling from an initial temperature $T_i = 1.5$°K is given by $T_f \approx T_i(H_f/H_i)$, where the initial effective field H_i is perhaps ~ 50 koe and the final field H_f represents the total effect of the perturbations at the crossover, perhaps 1 koe; thus $T_f \sim 0.04$°K.

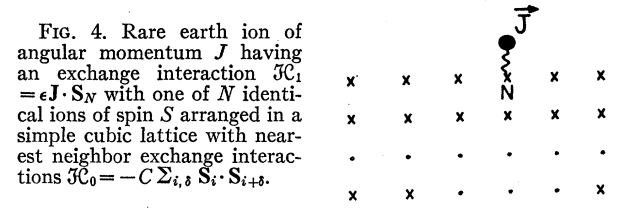

FIG. 4. Rare earth ion of angular momentum J having an exchange interaction $\mathcal{H}_1 = \epsilon \mathbf{J} \cdot \mathbf{S}_N$ with one of N identical ions of spin S arranged in a simple cubic lattice with nearest neighbor exchange interactions $\mathcal{H}_0 = -C \Sigma_{i,\delta} \mathbf{S}_i \cdot \mathbf{S}_{i+\delta}$.

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I am indebted to Dr. P.-G. de Gennes, Dr. Robert L. White, Professor W. A. Nierenberg, Dr. J. Smit, and Mr. M. Sparks for helpful discussions, and to Mr. Philip Pincus for checking the calculations.

APPENDIX A. LIMITS OF VALIDITY OF THE MOLECULAR FIELD APPROXIMATION TO THE FERRIC-RARE EARTH ION INTERACTION

We consider a simple model which contains the essential features of the problem for isotropic interactions. We consider as in Fig. 4 a simple cubic lattice of lattice constant a with N ions each of spin S connected together by an isotropic exchange interaction between nearest neighbors:

$$\mathcal{H}_0 = -C \sum_{i\delta} \mathbf{S}_i \cdot \mathbf{S}_{i+\delta}, \quad (A.1)$$

where $i+\delta$ is a nearest neighbor site to i. We connect a single rare earth ion of angular momentum $\mathbf{J}$ to the lattice by an isotropic exchange interaction

$$\mathcal{H}_1 = \epsilon \mathbf{J} \cdot \mathbf{S}_N, \quad (A.2)$$

if the connection is made only at the Nth ion of the host lattice. We assume that only the manifold J of the states of the rare earth ion need be considered, the other states taken to be at much higher energies. The nonadditive effects of several rare earth ions are considered separately.

The first-order energy when the host lattice is in the ground state and magnetized in the z-direction is just

[14] D. T. Edmonds and R. G. Petersen, Phys. Rev. Letters 2, 499 (1959).

the energy in the molecular field approximation:

$$E_0^{(1)}=E_0+\epsilon\langle Sm|J_zS_z|Sm\rangle=E_0+\epsilon Sm, \quad \text{(A.3)}$$

where m is the expectation value of J_z. We might have added the crystal field energy to the *unperturbed* problem, but it is not illuminating to our present purpose, although in an actual calculation the crystal potential must be included in $\mathcal{H}_0$.

We now estimate the second-order correction to the energy:

$$\Delta E=-\frac{\epsilon^2}{4}\sum_{\mathbf{k}}\frac{|\langle 1_{\mathbf{k}};m+1|J^+S_N^-|0_{\mathbf{k}};m\rangle|^2}{E_{\mathbf{k}}}, \quad \text{(A.4)}$$

where $1_{\mathbf{k}}$ denotes the spin wave $\mathbf{k}$ of the host lattice in the first excited state and

$$E_{\mathbf{k}}\cong CSa^2k^2 \quad \text{(A.5)}$$

is the spin wave energy. It is convenient to use (A.5) instead of the exact dispersion relation, and the approximation is satisfactory for purpose of an estimate. The spin functions for the states $1_{\mathbf{k}}$ are the sum of N terms each with one different spin reversed, so that

$$|\langle 1_{\mathbf{k}};m+1|J^+S_N^-|0_{\mathbf{k}};m\rangle|^2 =2S(J-m)(J+m+1)/N, \quad \text{(A.6)}$$

independent of $\mathbf{k}$. We need the sum

$$\sum_{\mathbf{k}}k^{-2}=\frac{Vk_m}{2\pi^2}=\frac{6^{\frac{1}{3}}V(N/V)^{\frac{1}{3}}}{2\pi^{\frac{4}{3}}}, \quad \text{(A.7)}$$

so that, with $a^2=(V/N)^{\frac{2}{3}}$,

$$\Delta E\cong-(6^{\frac{1}{3}}/4\pi^{\frac{4}{3}})(\epsilon^2/C)(J-m)(J+m+1). \quad \text{(A.8)}$$

The *maximum* correction occurs for the transition from $m=J$ to $m=J-1$, where the fractional correction is

$$\frac{\Delta E(M=J)-\Delta E(M=J-1)}{\epsilon S}\approx\frac{J}{5S}\frac{\epsilon}{C}\approx 0.01, \quad \text{(A.9)}$$

as ϵ/C in the garnets is of the order of 1/50. Thus the molecular field approximation appears to be excellent as applied to a rare earth ion in an iron garnet and in fact whenever the isotropic exchange interaction of an impurity ion with a host lattice is weak in comparison with the exchange interactions within the host lattice.

It may be noted that (A.8) is, apart from a minor numerical difference, identical with a result obtained by Suhl[15] for the contact hyperfine contribution to the self-energy of a nuclear moment in a ferromagnet. The calculation of the indirect interaction of two rare earth ions via the spin wave field is identical with the calculation of the indirect interaction of two nuclear moments in a ferromagnet, a problem already worked out by Suhl. The indirect interaction between two ions is of the order of $(\epsilon^2/C)J_n^+J_m^-$ times a range function. This additional perturbation on the molecular field approximation is of the order of (A.8), but vanishes as the concentration of rare earth ions goes to zero.

We must remember that the question of selection rules for magnetic dipole transitions between the levels we have calculated contains one trap. If the g-value of the rare earth ion should be equal to the g-value of the ferric ions, then the transition is forbidden. The transition is allowed, however, for unlike g-values, which is certainly the usual situation. At low concentrations the transitions among the levels of the rare earth ions are essentially the exchange frequency transitions[16]; in the concentrated rare earth garnets the frequency will be shifted because the ferric lattice will now be significantly perturbed and thus participates in the resonance. At elevated temperatures the rapid relaxation of the rare earth ions will change the character of the resonance, as discussed in reference 1.

APPENDIX B. REPULSION OF LEVELS AT APPARENT CROSSOVERS

In general, energy levels in combined crystalline and magnetic fields will not crossover, except in special symmetry conditions or by accident. A sufficient condition for accidental crossover is that the eigenstates of the total Hamiltonian

$$\mathcal{H}=\mathcal{H}_{\text{cryst}}+\mathcal{H}_{\text{mag}} \quad \text{(B.1)}$$

should be eigenstates separately of $\mathcal{H}_{\text{cryst}}$ and of $\mathcal{H}_{\text{mag}}$. The simplest example occurs for $S=1$ with the spin Hamiltonian

$$\mathcal{H}=S_z^2+HS_z, \quad \text{(B.2)}$$

which has the eigenvalues $1+H$, $1-H$, and 0, belonging, respectively, to the eigenstates $|1\rangle$, $|-1\rangle$, and $|0\rangle$ of S_z. The crossover of $|-1\rangle$ and $|0\rangle$ is accidental and is at $H=1$. The crossing levels do not belong to the same irreducible representation of the group of rotations about the z axis.

If we add a magnetic field component H_x perpendicular to the z axis the levels no longer cross, but are repelled by the perturbation $\mathcal{H}'=H_xS_x$, which has off-diagonal matrix elements connecting $|0\rangle$ with the other states. Near the former crossover we may carry out a perturbation calculation in the subspace of the two states concerned, $|-1\rangle$ and $|0\rangle$. Letting $\xi=H-1$, the secular equation is

$$\epsilon=-\tfrac{1}{2}\xi\pm(\tfrac{1}{4}\xi^2+\tfrac{1}{2}H_x^2)^{\frac{1}{2}}. \quad \text{(B.3)}$$

At $\xi=0$, the levels are separated by $2^{\frac{1}{2}}|H_x|$. The separation at general ξ is $(\xi^2+2H_x^2)^{\frac{1}{2}}$, always positive. If there are no crossovers in ϵ *vs* $\mathbf{H}$ at any angle θ, there can be no crossover in ϵ *vs* θ at any H. In the present problem there is of course the crossover at $H_x=0$ for $H=1$. At $H\gg 1$ the eigenvalues of (B.3) are approximately 0 and $1-H$, as in the unperturbed problem.

[15] H. Suhl, *Proceedings of the Grenoble Magnetism Conference*, 1958, p. 269 [Suppl. J. phys. radium **20**, Nos. 2–3 (1959)]; see also the appendix to W. Marshall, Phys. Rev. **110**, 1280 (1958).

[16] J. Kaplan and C. Kittel, J. Chem. Phys. **21**, 760 (1953).

In the general case one may argue that there will be no degeneracy (except accidental) if there is no symmetry in the problem. We are vitally concerned, however, with the order of magnitude of the splitting at near misses, because a splitting greater than the order of 1 cm^{-1} might be incompatible with the angular width of the anomalous anisotropy in the experiment of Dillon and Nielsen. This limit is to be compared with pure crystal field splittings presumed for Tb^{+++} to be of the order of 10 cm^{-1} between levels. The magnitude of the repulsive splitting may be reduced for high J values. Consider again the Hamiltonian (B.2), now for $J=S=6$. Crossovers occur for H parallel to the axis and the degeneracies are lifted when a perpendicular field component is applied. The matrix elements of S_xH_x between the crossing levels may be considerably reduced below the example for $S=1$. If two levels having $\Delta m \neq \pm 1$ cross for H parallel to the axis, then a perpendicular component H_x will not split the crossing in second order of perturbation theory. To take a fairly extreme case, consider a crossing between the levels $m_J=J$ and $m_J=0$, for $J=6$. If we rotate axes to $\theta=30°$ the mixture of the amplitude of $|0\rangle$ into the state originally $|6\rangle$ is about 0.01, using the Wigner rotation coefficients. The amplitude of $|1\rangle$ will be of the same order, so that for this angle the splitting at a crossover is of the order $0.01H$, or ~ 0.1 cm^{-1} in a rare earth iron garnet.

One would not expect examples as favorable as this—that is, with as small splittings as 0.1 cm^{-1}, to arise very frequently. We should remember, however, that an anisotropy peak which does not increase or sharpen below 4°K only requires a splitting of the order of 3 cm^{-1}, and such a splitting may not be a rare event.

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Recombination and Trapping in Tellurium

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Photoconductive decay in nearly perfect Te crystals shows a lifetime of up to 50 μsec at 300°K. The temperature dependence does not support previous suggestions of radiative recombination; at temperatures below 150°K marked trapping of excess minority electrons occurs, and at higher temperatures also the results suggest the activity of levels within the gap. Probably chemical impurities behave as recombination centers, and dislocations certainly act in this capacity (lifetime is reduced to ~1 μsec when 10^6 dislocations/cm^2 are introduced).

THE semiconducting properties of tellurium have been studied for some years, but many early results suffered from the unavailability of good single crystals. Crystals of high perfection are now available,[1] and a more realistic appraisal of the properties is possible, including carrier lifetime τ_T as a function of temperature T(°K).

Moss[2] estimated $\tau_{90}\sim 400$ μsec for evaporated Te layers and concluded that τ_{300} was some 10^4 times smaller. de Carvalho[3] also reported $\tau_{300}\sim 10^{-8}$ sec from P.E.M. measurements. Redfield[4] measured $\tau_{100}\sim 20$–50 μsec using photoconductive techniques; he concluded that lifetime must be very short at 300°K since he could not detect any photoconductance there. The same author suggested[5] that direct optical recombination should be more important than Shockley-Read decay in tellurium. But since Moss[6] calculates an optical lifetime of order 30 μsec at 300°K and 300 msec at 77°K, it is evident that other processes must have controlled Redfield's tellurium. There is a better chance that optical recombination could make a significant contribution in some tellurium we have been studying, since our samples yield τ_{300} as large as 50 μsec.

Redistillation and zone refinement are helpful up to a point in increasing τ_{300} for tellurium, but the benefits of purification can only be realized if the dislocation density is kept small. A standard etch readily exposes dislocation etch pits on the $10\bar{1}0$ face[7]; these pits have an asymmetric form which suggests that the dislocations themselves may run along $10\bar{2}0$ directions. We have examined crystals with dislocation densities $N_D<10^4$ cm^{-2}, yet since tellurium deforms plastically very easily, a density of 10^6 cm^{-2} or more can be introduced under a relatively small stress (such as that involved in lapping one face, or in dropping a sample onto a table). When N_D is large enough to dominate the lifetime, $\tau_{300}\sim(1.3/$

[1] T. J. Davies, J. Appl. Phys. **28**, 1217 (1957).
[2] T. S. Moss, *Photoconductivity in the Elements* (Butterworths Scientific Publications, London, 1952), pp. 208–216.
[3] A. P. de Carvalho, Compt. rend. **242**, 745 (1956).
[4] D. Redfield, in *Proceedings of the Conference on Photoconductivity, Atlantic City, 1954*, edited by R. G. Breckenridge, *et al.* (John Wiley and Sons, Inc., New York, 1956), p. 566.
[5] D. Redfield, Phys. Rev. **100**, 1094 (1955).
[6] T. S. Moss, *Optical Properties of Semiconductors* (Academic Press, Inc., New York, 1959), p. 178.
[7] Preferably a slow acting etch such as hot sulfuric acid.