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

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[12] J. H. Van Vleck, Phys. Rev. **57**, 426 (1940).

[13] T. Maiman, *Quantum Electronics* (Columbia University Press, New York, 1960), p. 324.

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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 $5\,Fe_2O_3\cdot 3\,Eu_2O_3$ is lower than that of an iron garnet such as $5\,Fe_2O_3\cdot 3\,Y_2O_3$ 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.

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 Eu^{+++} ion is given in Van Vleck's book.[1] 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

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

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 O_2 atoms, rather

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[1] 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).

than the Zener-Ruderman-Kittel-Yosida mechanism operative in metallic europium. The molecular-field approximation, which we use throughout and which works very well in the garnets, consists in taking the exchange potential to be

$$2\beta \mathbf{H}_{\text{ex}}\cdot \mathbf{S}_i, \quad \text{where} \quad \beta \mathbf{H}_{\text{ex}} = -\langle \textstyle\sum_j J_{ij}\mathbf{S}_j\rangle_{\text{av}}.$$

The Hamiltonian function then reduces to that of a one-atom problem and becomes

$$\mathcal{H} = A\,\mathbf{L}\cdot\mathbf{S}+\beta[2(\mathbf{H}_{\text{ex}}+\mathbf{H}_0)\cdot\mathbf{S}+\mathbf{H}_0\cdot\mathbf{L}].$$

It is particularly to be noted that the exchange field acts only on the spin. The standard formulas for the matrix elements of Eu^{+++} can readily be adapted to include the exchange field in addition to the applied field H_0. We have only to replace H by $H_0+2(g_J-1)H_{\text{ex}}/g_J$ and by H_0+2H_{ex}, respectively, in the diagonal and off-diagonal elements of the magnetic potential [Eq. (98), p. 173 of reference 1] and correspondingly in the first- and second-order Zeeman energies [Eq. (99) of ibid.]. For purposes of the present paper, saturation effects can be neglected without much error (about 2% at the lowest temperature), so that the development of the energy need not be carried beyond squares of the effective field. The moment, which is obtained in the usual way by averaging over all the various multiplet and Zeeman states weighted by the Boltzmann factor, is then linear in the applied and exchange fields, and is given by

$$M_{\text{Eu}} = \frac{8N\beta^2}{E_1(1+3e^{-E_1/kT})}\Bigg\{(H_0+2H_{\text{ex}}) \times\left[1+\left(\frac{15}{8}\frac{E_1}{E_2-E_1}-1\right)e^{-E_1/kT}\right] +\frac{3E_1}{16kT}(3H_0+2H_{\text{ex}})e^{-E_1/kT}\Bigg]\Bigg\} \tag{1}$$

instead of Eq. (23) of p. 248 of reference 1. Here 0, E_1, and E_2 are, respectively, the energies of the states $J=0$, 1, and 2. It is known from spectroscopy that the energy levels of the free ions are $E_i/k=0$, 480°, and 1330°, and these values are probably not appreciably changed in the solid compounds.[2] For our work the population of levels above $J=1$ can be neglected.

Because the $4f$ electrons are deeply sequestered, the strongest exchange interaction to which the europium ions are subject in the garnet is that with the iron atoms rather than with other europium ions. The couplings, in descending orders of magnitude, are thus Fe-Fe, Fe-Eu, Eu-Eu. We will make the approximation of assuming that the back reaction of the europium on the iron alignment is of minor consequence. Thereby a major simplification is made in the theory. The total field acting on the europium ion can then be considered as the sum of the applied field and a molecular field proportional to the magnetization M_{Fe} measured in yttrium iron garnet, where Eu^{+++} is replaced by a diamagnetic "rare earth." Actually, there are two types of Fe^{+++} ions, with spins oppositely directed, at different distances from a Eu^{+++} ion, and their magnetizations $\mathbf{M}_1$, $\mathbf{M}_2$ may not have the same temperature dependence so that the exchange field $a_1\mathbf{M}_1+a_2\mathbf{M}_2$ is not proportional to $\mathbf{M}_1+\mathbf{M}_2$. Existing experimental data, however, do not permit taking this refinement into account. We therefore take $H_{\text{ex}}=aM_{\text{Fe}}$, where a is constant. We thereby assume the exchange coupling between the Eu^{+++} ions is of minor importance, which is quite reasonable since this type of coupling is known to be fairly small in the other rare earth garnets, and it will be even smaller for Eu^{+++} because of its low magnetic moment.

We can now use our formula to calculate the magnetization of europium iron garnet in the absence of an applied field H_0. The iron atoms are ferrimagnetic, and so give an exchange field even when $H_0=0$. The total magnetization is the sum (numerically the difference) of the moments of the europium and iron ions. The iron part is known from measurements made on yttrium iron garnet, in which diamagnetic Y^{+++} ions replace Eu^{+++}. There is only one constant at our disposal, viz. the proportionality constant a in the exchange field. This can be obtained by fitting the observed magnetization at $T=0$. The magnetization per Eu ion at $T=0$ is 0.81β[3] and this requires $aM_{\text{Fe}}/k=24$°K.

After the value of a is fixed by the experimental data at $T=0$, the curve for the reduction in moment as a function of temperature is completely determined. The results are shown and compared with Pauthenet's measurements in Fig. 1. Pauthenet's data indicate a small impurity in his yttrium garnet sample and we consequently use his smooth fitted curve, given by $6I_d-4I_a$ in his notation. The agreement between our theory and experiment is excellent.

The susceptibility $\chi_{\text{Eu}}=\partial M_{\text{Eu}}/\partial H_0$ in an externally applied field H_0 can immediately be obtained from Eq. (1). Its maximum value, achieved near $T=0$, is $1.12N\beta \times 10^{-6}$. Thus an appreciable change in M_{Eu} would be observed only for fields above about 10^5 oersted.

It is of interest to compare the size of the exchange field exerted by the iron in europium garnet with that in the other rare earth iron garnets. In this connection a word should be said on how this comparison should be made.[4] It is important to take account of the fact

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[2] The multiplet intervals are not observed directly in gaseous Eu^{+++}, but are obtained by a minor extrapolation from Sm^{+++}. See J. H. Van Vleck, Ann. inst Henri Poincaré **10**, 80 (1947). The interval 480° is also reported by Gobrecht in solid $\text{Eu}_2(\text{SO}_4)_3\cdot 8\text{H}_2\text{O}$ Ann. Physik **28**, 673 (1937).

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

[4] R. Brout and H. Suhl, Phys. Rev. Letters **2**, 388 (1959) give the impression that the elements of the exchange coupling which are diagonal and nondiagonal in J differ mainly in being of long and short range, respectively, when the Z-R-K-Y model applies. Actually in the rare earths other than Eu and Sm, the nondiagonal elements are unimportant simply because the multiplet intervals are so wide. On the other hand, the interaction which we use in Eu is almost entirely of the type $\Delta J=\pm 1$.

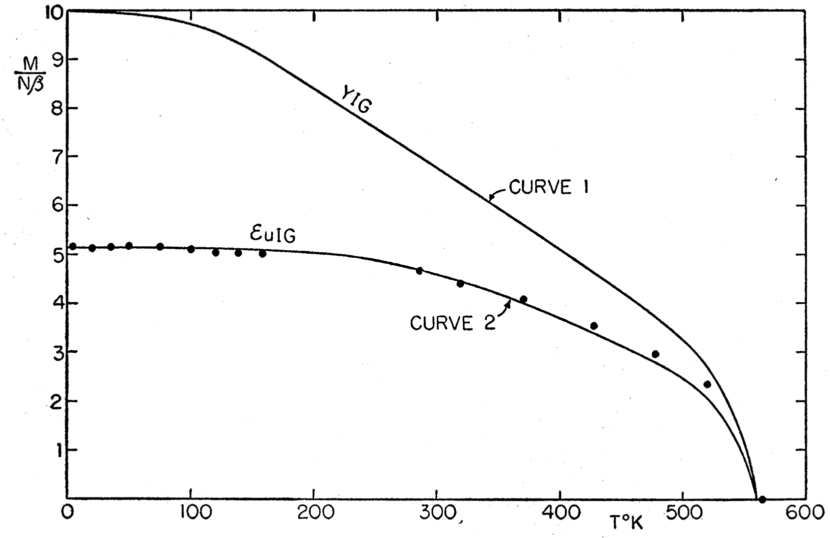

FIG. 1. Curve 1. Empirical variation of magnetization of yttrium iron garnet $3Y_2O_3 \cdot 5Fe_2O_3$, taken from Pauthenet's smoothed values of $6I_d - 4I_a$, see reference 3, curve 2. Theoretical variation of magnetization of europium iron garnet calculated from $M(\text{YIG}) - M_{\text{Eu}}$ [Eq. (1)], with $M(\text{YIG})$ obtained from curve 1. The constant of proportionality in the exchange field is determined so as to give agreement with experiment for $T=0$. Experimental values, see reference 3, are indicated by ●.

that exchange coupling acts not on the total but only on the spin angular momentum, and consequently, in suitable units, the appropriate comparison of exchange parameters is that given in Table IX of Pauthenet's[3] article rather than in Table I of his later paper.[5] The comparison is conveniently made in terms of the parameter $\beta H_{\text{ex}}/k = \beta a M_{\text{Fe}}/k$ which should be the same for all the rare earths if the exchange field from the iron atoms is uninfluenced by which rare earth atom is substituted.[6] The result is as follows:

Eu	Gd	Tb	Dy	Ho	Er	Tm
24°	25°	20°	22°	16°	16°	14°.

The value for Eu is obtained in the present paper; the values for the other ions are those found by Pauthenet. Only qualitative significance should be attached to the comparison other than between Eu and Gd, as in the other cases corrections for the effect of the crystalline field have not been made. A correction should also be applied to all the values to allow for the fact that the susceptibility, as measured by Pauthenet and used by him to calculate the molecular field coefficient n, is not quite equal to $M_{\text{RE}}/H_{c(ad)}$ due to the effect of saturation. In the Gd compound, for which $(M_{\text{Gd}})_{T=290°\text{K}} \approx \frac{1}{6}(M_{\text{Gd}})_{T=0}$ this effect introduces an error of about 3%, increasing the estimated value of n. Part of this error will have been offset by allowing for the deviation from Curie's law, which had been attributed to rare earth-rare earth interactions, but which in fact is mainly due to this effect, in agreement with paramagnetic measurements on rare earth gallium garnets.[5] But for the saturation correction it would be possible to use the relation

$$\chi_{\text{RE}} = M_{\text{RE}}/H_{c(ad)}$$

to estimate $H_{c(ad)}$ at all temperatures, without any effect from crystal fields, since χ and M will both be affected equally. However as M_{RE} begins to saturate this is no longer true. The values of n for the higher rare earths should therefore be treated with some caution, since for these the estimate was made at low temperatures, where the *combined* effect of saturation and crystal fields will be big.

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[5] R. Pauthenet, J. phys. radium **20**, 388 (1959).

[6] The conversion of Pauthenet's[3] molecular field parameters, n, n' to effective fields, $H_{c(ad)}$, has been discussed by de Gennes, Kittel, and Portis, Phys. Rev. **116**, 323 (1959), who show that at $T=0°\text{K}$

$$H_{c(ad)} = \tfrac{5}{8} N\beta \times n,$$

where N is Avogadro's number. This field acts on the magnetic moment and is related to the exchange field H_{ex} which acts on the spin by the equation

$$2\beta H_{\text{ex}} S_{\text{RE}} = H_{c(ad)} M_{\text{RE}},$$

where S_{RE} is the rare earth spin (in units of $h/2\pi$) and M_{RE} is the magnetic moment. In terms of the total angular momentum J per atom $M_{\text{RE}} = g_J \beta J$ and $S_{\text{RE}} = (g_J - 1)J$. Therefore in units of °K

$$\frac{\beta}{k}(H_{\text{ex}})_{T=0} = \frac{\beta}{k}\frac{5N\beta}{16} \times \frac{g_J}{g_J - 1} \times n = \frac{0.117 g_J}{g_J - 1} \times n = 0.234n',$$

where $H_{\text{ex}} = aM_{\text{Fe}}$ in our notation.