formed in the Ames Laboratory of the U. S. Atomic Energy Commission.

[1] T. P. Das and M. Pomerantz, Phys. Rev. 123, 2070 (1961).

[2] F. W. de Wette, Phys. Rev. 123, 103 (1961).

[3] R. M. Sternheimer, Phys. Rev. 84, 244 (1951); R. M. Sternheimer and D. Tycko, Phys. Rev. 93, 734 (1954); R. M. Sternheimer and H. Foley, Phys. Rev. 102, 731 (1956).

[4] M. Pomerantz and T. P. Das, Phys. Rev. 119, 70 (1960).

[5] W. W. Simmons and C. P. Slichter, Phys. Rev. 121, 1580 (1961).

[6] N. Bloembergen and T. J. Rowland, Acta Met. 1, 731 (1953).

[7] N. E. Alekseevskii, Pham Zuy Hien, V. G. Shapiro, and V. S. Shpinel, Zh. Eksperim. i Teor. Fiz. 43, 790 (1962) [translation: Soviet Phys.—JETP 16, 559 (1963)].

[8] A. J. F. Boyle, D. St. P. Bunbury, and C. Edwards, Proc. Phys. Soc. (London) 79, 416 (1962).

[9] G. Burns and E. G. Wikner, Phys. Rev. 121, 155 (1961).

[10] H. S. Khaikin, Zh. Eksperim. i Teor. Fiz. 39, 899 (1960) [translation: Soviet Phys.—JETP 12, 623 (1960)].

EFFECT OF THE Fe^{3+}-Tm^{3+} EXCHANGE INTERACTIONS ON THE PARAMAGNETIC RESONANCE AND RELAXATION OF IRON IMPURITIES IN THE THULIUM GARNETS

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(Received 22 January 1964)

In a recent Letter Hutchings and Wolf[1] have reported on the paramagnetic resonance of Yb^{3+} impurities in thulium aluminum (TmAlG) and thulium gallium (TmGaG) garnets. The Tm^{3+} ion's lowest multiplet, $4f^{12}\,{}^3H_6$, has in these crystals a singlet ground state[2] separated from the next excited state by 30 to 60 cm^{-1}. Therefore, at sufficiently low temperatures these two garnets will behave similarly to their diamagnetic counterparts, and permit the observation of paramagnetic resonance of other impurities. As indicated in reference 1, such resonances will exhibit effects due to exchange interactions between the impurity and the neighboring Tm^{3+} ions. The parameters of the spin Hamiltonian that describes the electron paramagnetic resonance (EPR) spectrum of the impurity will have contributions arising from the exchange interactions. The structure constants exhibit significant variations between the various garnets, and so do the spin-Hamiltonian parameters for most impurities. In reference 1 the exchange contribution to the g tensor of Yb^{3+} in the Tm garnets was isolated by comparing the g values measured in these with values obtained by interpolation for a hypothetical diamagnetic host with the same structure as the Tm garnet. Such a procedure gives acceptable results because the variations in the g values in the diamagnetic garnets are smooth functions of the structural parameters.

The ${}^6S$ ground state of Fe^{3+} has, in most diamagnetic hosts, an isotropic g tensor, with a g value essentially equal to that of a free spin. Any exchange contributions to it can therefore be immediately isolated. Exchange contributions to the other spin-Hamiltonian parameters of Fe^{3+} in the Tm garnets are also expected and may be isolated by the interpolation procedure of reference 1. In addition, the Fe^{3+}-Tm^{3+} exchange interactions may bring about[3] a two-phonon spin-lattice relaxation process for Fe^{3+} involving lattice oscillators with energy essentially equal to the Tm^{3+} crystal field splitting. This effect would appear as an exponential temperature dependence governing the Fe^{3+} relaxation, having an activation energy equal to the Tm^{3+} splitting.

A study of the Fe^{3+} EPR spectrum and relaxation in a series of garnet hosts has indeed revealed the presence of all above mentioned effects in TmGaG and TmAlG.

There are two chemically inequivalent sites available for the Fe^{3+} impurities. For dilute solutions in the gallium garnets a strong preferential substitution at the a (octahedral) sites is observed[4]; the concentrations of Fe^{3+} at the a and d (tetrahedral) sites are about equal in the Al garnets. Consequently, in TmGaG we were not able to detect any lines that could, with certainty, be ascribed to Fe^{3+} in d sites. A complete octahedral Fe^{3+} spectrum was observed in all crystals. It is qualitatively similar for all samples including that of the Tm garnets. Complete tetrahedral spectra were only found (with the available frequencies and field range) in the diamagnetic hosts. However, we did observe a set of lines in TmAlG which exhibit tetrahedral

Table I. Experimentally determined spin-Hamiltonian parameters of the Fe^{3+} ground state in various garnet hosts.

Host	Site	Lattice constant[b] (Å)	O^2 parameter[b] $y \times 10^4$	$g_\parallel$	$g_\perp$	D (cm^{-1})	$a - F$ (cm^{-1})	$\lvert a \rvert$ (cm^{-1})	α (degrees)[e]	
									$a > 0$	$a < 0$
YAlG	*a*	12.00	512	2.0015	2.0015	-0.1053	0.0178	0.0205	27.5	32.5
TmAlG	*a*	11.96	523	1.985	1.931	-0.1287	0.0214	0.0227	29	31
LuAlG	*a*	11.906	536	2.001	2.001	-0.0935	0.0228	0.0292	27.5	32.5
YGaG[a]	*a*	12.28	562	2.003	2.003	-0.1320	0.0142	0.0189	28	32
TmGaG	*a*	12.23	564	2.175	2.123	-0.1572	0.0185	0.0239	30	30
LuGaG	*a*	12.178	566	2.001	2.001	-0.1290	0.0217	0.0174	28	32
YAlG	*d*	12.00		2.004	2.004	-0.1028				
TmAlG	*d*	11.96		1.235	1.755[c]	(0.2)				
				1.23	1.72[d]					
LuAlG	*d*	11.906		2.004	2.004	-0.1249				

[a] Spin Hamiltonian parameters in YGaG are from reference 4; those in the other crystals are from the present work.

[b] F. Euler (private communication).

[c] At 35 Gc/sec.

[d] At 16 Gc/sec.

[e] As discussed in reference 4, the resonance data yield the absolute value of a and two possible values for the angle α; $a \gtrless 0$ according as $\alpha \lessgtr 30°$.

symmetry and which may, with reasonable certainty, be identified with the central $(\frac{1}{2} \rightarrow -\frac{1}{2})$ transition of tetrahedral iron.

The experimentally determined spin-Hamiltonian parameters are shown in Table I. The symbols are those given in reference 4, and the parameters were obtained using the techniques discussed therein. Spectra were taken at 16 and 35 Gc/sec. For the tetrahedral spectrum in TmAlG we give the effective g values as obtained at the two frequencies. The small variation of these g values with frequency is indicative that we are indeed dealing with the central transition. Intensity considerations exclude the possibility that these lines are due to other iron group impurities. The observed angular dependence eliminates the possibility that the lines are due to rare earth impurities which would enter the lattice substitutionally for Tm^{3+}. D, for tetrahedral Fe^{3+}, was estimated from the frequency variation of $g_\perp$.

The lattice constant and the same oxygen coordinate y used in reference 1 were used as parameters to interpolate the magnetic contribution to D and a. Such interpolation permits quite satisfactory determination of the exchange contribution, δD, for both Tm garnets; however, only for TmGaG could δa be determined well. The large variation of the cubic field parameter between YAlG and LuAlG did not permit determination of a meaningful δa for TmAlG. The exchange contributions for the various parameters are given in Table II.

Relaxation measurements were performed at X band by the "transient recovery from saturation" technique.[5] At the lowest temperature, i.e., direct process region, marked concentration effects were observed which will be dealt with in later publications. However, for both TmAlG and TmGaG, there was quite a large temperature range over which the Fe^{3+} relaxation

Table II. Exchange contributions to the spin-Hamiltonian parameters of the Fe^{3+} ground state in the Tm garnets.

Host	Site	$\delta g_\parallel$	$\delta g_\perp$	$\langle \delta g \rangle = \frac{1}{3}(\delta g_\parallel + 2\delta g_\perp)$	δD (cm^{-1})	δa (cm^{-1})
TmGaG	*a*	+0.175	+0.122	+0.140	-0.030	0.005
TmAlG	*a*	-0.016	-0.069	-0.051	-0.025	
TmAlG	*a*	-0.770	-0.245	-0.42	(~-0.1)	

Table III. Expressions for T_1^{-1} ($\sec^{-1}$) obtained by fitting the experimental data of the temperature dependence of the spin-lattice relaxation time for Fe^{3+} in various garnet hosts. (T in degrees Kelvin.)

Sample	Site	Transition	$1/T_1$ ($\sec^{-1}$)	Temperature range (°K)
TmAlG, 0.1% Fe	*a*	$5/2 \rightarrow 3/2$	$5 \times 10^2 T + 10^{10} \exp(-55/T)$	$1.9 \leq T \leq 5$
TmAlG, 0.1% Fe	*d*	$1/2 \rightarrow -1/2$	$1.96 \times 10^2 T + 6.5 \times 10^8 \exp(-57/T)$	$1.9 \leq T \leq 8$
TmGaG, 0.1% Fe	*a*	$5/2 \rightarrow 3/2$	$7.8 \times 10^2 T + 3.47 \times 10^8 \exp(-82/T)$	$3 \leq T \leq 10$
TmGaG, 0.1% Fe	*a*	$3/2 \rightarrow 1/2$	$0.574 \times 10^2 T + 2.2 \times 10^8 \exp(-84/T)$	$3 \leq T \leq 11$
YGaG, ~1% Fe	*a*	$5/2 \rightarrow 3/2$	$1.4 \times 10^4 T$	$1.9 \leq T \leq 15$
LuAlG (<0.1%) Fe (trace impurity)	*a*	$5/2 \rightarrow 3/2$	$1.08 \times 10^2 T$	$1.9 \leq T \leq 30$

times followed an exponential law. This exponential temperature dependence was conspicuously absent in the diamagnetic garnets. The fits of the relaxation time, T_1, as a function of the temperature for some of the transitions are given in Table III. From these data we derive the following values for the splitting between the ground and first excited states of Tm^{3+}: $\Delta = 58 \pm 5\ \mathrm{cm}^{-1}$ in TmGaG and $\Delta = 39 \pm 5\ \mathrm{cm}^{-1}$ in TmAlG. These measurements indicate unequivocally the presence of the Fe^{3+}-Tm^{3+} interaction effects. They do not, however, unambiguously show whether the dynamic effect necessary to bring about relaxation comes from thermal modulation of the crystal potential, acting on the Tm^{3+}, or from the time-dependent part of the Fe^{3+}-Tm^{3+} exchange interaction.

Let us now turn our attention to the salient features of the data, namely, the change in sign of δg for *a* sites between TmGaG and TmAlG, the different variations of δD and δg when these two hosts are compared, and finally the relatively large value of $\langle \delta g \rangle$ for *d* sites in TmAlG. Consider first the octahedral sites: A purely isotropic interaction could only explain the change in sign of the *g* shift between the two crystals if its sign is assumed to change. This is unlikely. Generally, in addition to an isotropic term $J_0 \vec{S}_{Fe} \cdot \vec{S}_{Tm}$, one has to consider at least an antisymmetric interaction[6] $\vec{J}_1 \times \vec{S}_{Fe} \cdot \vec{S}_{Tm}$ and a pseudodipolar term $J_2[\vec{S}_{Fe} \cdot \vec{S}_{Tm} - 3(\vec{S}_{Fe} \cdot \hat{r})(\vec{S}_{Tm} \cdot \hat{r})]$. Spectroscopy of rare earths, e.g., Dy^{3+} and Er^{3+},[2] indicates considerable differences in strength and symmetry of the crystal field between Al and Ga garnets. The presence of similar variations for Tm^{3+}, together with anisotropic exchange, may account for the observed change in sign of the δg.

The perturbation expressions of reference 1 enable one to write the magnetic contributions to *g* and *D* as $\langle \delta g \rangle = J_g/\Delta$ and $\delta D = -J_D^2/\Delta$. The J_g and J_D are thus defined as effective exchange constants involving matrix elements of $\vec{S}_{Tm}$ summed over all neighbors considered. For the *a* sites one would expect $J_g \neq J_D$ since the antisymmetric term which appears linearly in the expression for δg will give no net contribution to J_g because the *a* site's point group includes the inversion operator. δD, however, is quadratic in the interaction and consequently J_D includes a net contribution from the antisymmetric exchange.

The tetrahedral point group does not include the inversion operator and therefore the J_g for Fe^{3+} at *d* sites will contain a contribution from the antisymmetric term. In addition, the *d* site has two rare-earth nearest neighbors at a distance[7] $(4/5)^{1/2}$ less than the six nearest-neighbor rare earths of an *a* site. These considerations could explain the much larger δg found for the *d* sites as compared to the δg of the *a* sites.

The following values for the effective exchange constants are obtained from the data presented in Table II and splittings, Δ, derived from relaxation measurements: For *a* sites, in TmGaG, $J_g = 8\ \mathrm{cm}^{-1}$, $|J_D| = 1.4\ \mathrm{cm}^{-1}$; in TmAlG, $J_g = -2\ \mathrm{cm}^{-1}$, $|J_D| = 1\ \mathrm{cm}^{-1}$; and for *d* sites, in TmAlG, $J_g = -16\ \mathrm{cm}^{-1}$. Due to the lack of knowledge of the matrix elements of S_{Tm}, the preceding values indicate only the order of magnitude of the interaction constants involved (J_1 is not present in all cases).

We are not aware of other direct measurements of Tm-Fe interactions. However, we have available for comparison the exchange splittings observed in the optical spectrum of Yb^{3+} in YbIG.[8] These splittings are expressible as functions of exchange constants, as is J_g, and the measured values are in the order of $25\ \mathrm{cm}^{-1}$. The major contribution to such exchange splittings probably comes from the (rare earth)-Fe^{3+} *d*-site interaction[7] which is consistent with the present results. The actual quantitative differences between the two results may be due to differences in rare earth spin matrix elements and to structural variations between the hosts.

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[1] M. T. Hutchings and W. P. Wolf, Phys. Rev. Letters 11, 187 (1963).

[2] W. P. Wolf, M. Ball, M. T. Hutchings, M. J. M. Leask, and A. F. G. Wyatt, J. Phys. Soc. Japan 17, Suppl. B-1, 443 (1962).

[3] R. Orbach, Proc. Roy. Soc. (London), A264, 458 (1961).

[4] S. Geschwind, Phys. Rev. 121, 363 (1961).

[5] Bierig, Weber, and Warschaw (to be published).

[6] T. Moriya, Phys. Rev. 120, 91 (1960).

[7] S. Geller and M. A. Gilleo, J. Phys. Chem. Solids 3, 30 (1957).

[8] K. A. Wickersheim, in Magnetism, edited by G. T. Rado and H. Suhl, (Academic Press, New York, 1963), Vol. 1, p. 269.

MODE COMPETITION AND COMBINATION TONES IN A GAS LASER

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(Received 10 February 1964)

This Letter presents the results of an investigation on the occurrence and on the behavior of a few laser modes of various order with equal frequency spacing during tuning of the laser over half a wavelength.

The laser line is the $2s_2$ - $2p_4$ Ne transition (Paschen notation) with a wavelength of 1.153 microns, with a Doppler width at half-maximum intensity of 800 Mc/sec and with an estimated natural linewidth of about 30 Mc/sec at the working pressure.

The measurements were carried out on a short gas laser, described elsewhere,[1] with a mirror separation $L = 12$ cm, giving a longitudinal mode separation of 1250 Mc/sec. Thermal expansion of the laser[2] shows a periodic series of far-field patterns, apparently corresponding to modes whose L/λ value is an increasing function, although this increase is not necessarily monotonic.

However, such a simple tuning experiment does not reveal the exact values of frequency and intensity of these modes; each of the observed far-field patterns is in fact a superposition of more than one. Therefore it seemed of interest to us to determine these frequencies. To this end an optical method was used, not only giving exactly the relative frequency values, but simultaneously displaying the corresponding far-field patterns (see Fig. 5 of de Lang and Bouwhuis[3]). Figure 1 shows schematically the arrangement. As an optical analyzer a one-meter confocal interferometer is used, with a measured "finesse" of 150, corresponding to an instrumental broadening of 0.5 Mc/sec and a resolving power of 6×10^8 at

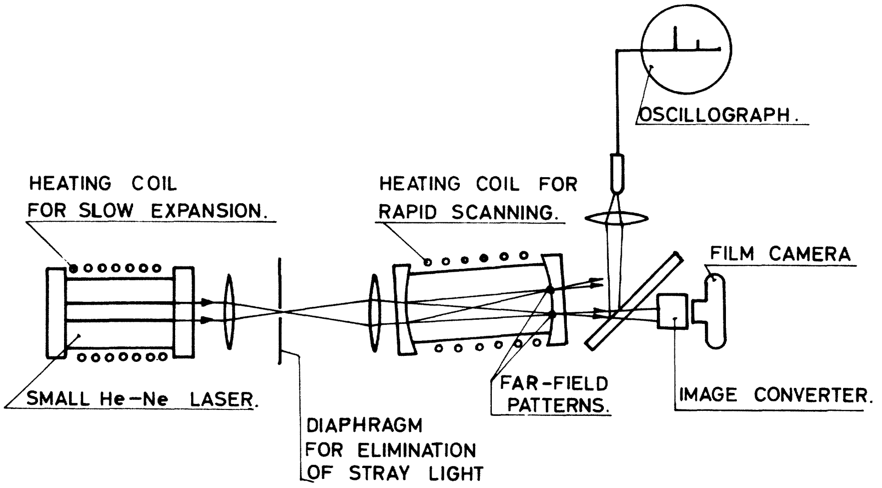

FIG. 1. Experimental arrangement of the optical frequency analysis.