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Spin-Lattice Relaxation of Al^{27} in Thulium Aluminum Garnet*

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The Al^{27} spin-lattice relaxation time T_1 has been measured between 127 and 425 °K at 8 and 14 MHz for the aluminum a and d sites in thulium aluminum garnet. Both sites exhibit T_1 dips at 275 °K which are attributed to Al^{27}-Tm^{169} cross relaxation. Below 190 °K the a-site T_1 magnitudes and approximately ω^{-2} frequency dependence are explained by magnetic field fluctuations caused by the Tm^{3+} ion making transitions between its two lowest crystal-field levels with a correlation time near 4×10^{-12} sec.

I. INTRODUCTION

In a previous study[1] (herein referred to as SJ) of the Tm^{169} and Al^{27} nuclear-magnetic-resonance (NMR) spectra in thulium aluminum garnet (TmAlG), the Tm^{169} NMR showed that the Tm^{3+}-ion magnetic-susceptibility tensor is very anisotropic, much more so than in thulium gallium garnet (TmGaG).[2] The paramagnetic shifts at the Al^{27} a and d sites at 1.5 °K agreed within about 10% with shifts calculated for dipolar fields from point dipoles at the Tm^{3+} sites. Above approximately 20 °K the Tm^{169} resonance was not observed because of line broadening from large fluctuating fields caused by transitions of the Tm^{3+} ions. The Al^{27} paramagnetic shifts at 27, 76, 192, 232, and 297 °K were used to infer values for the magnetic-susceptibility tensor (for a particular Tm^{3+} site) $\{\chi\}$ at these temperatures on the assumption that the fields at the Al^{27} sites are caused by point dipoles at the thulium sites. The electric-field-gradient (efg) tensors at the Al^{27} a and d sites were found, and compared with those for corresponding sites in other rare-earth aluminum and iron garnets.

This present study[3] of Al^{27} spin-lattice relaxation time T_1 in TmAlG was conducted in the hope that T_1 would be governed by magnetic field fluctuations caused by the Tm^{3+} ions. Such relaxation has been found, but in addition we have observed

faster relaxation (T_1 dips) near room temperature, where certain of the broad Tm^{169} resonances cross certain Al^{27} resonances. These results yield information on the dynamics of the thulium-ion transitions among its energy levels.

In this paper a brief experimental description is followed by a discussion in Sec. III of the relation to $\{\chi\}$ of the Tm^{169} resonance locations inferred from the Al^{27} T_1 dips. Section IV deals with the cross relaxation responsible for these dips. From the cross-relaxation rates we infer the Tm^{169} linewidths at 8 and 14 MHz. In Sec. V, direct Al^{27} relaxation by Tm^{3+}-ion fluctuations is discussed. Inferences about the Tm^{169}-ion behavior are drawn from the Tm^{169} linewidths and from the direct Al^{27} relaxation. A general discussion appears in Sec. VI. An appendix is devoted to the calculation of quadrupolar spin-lattice relaxation for Al^{27}, which appears to be unimportant.

II. EXPERIMENTAL

The single crystal of TmAlG, which had been used in the previous NMR study,[1] was grown from a lead fluoride flux and its rotation axis was adjusted to within $\frac{1}{2}°$ by the Laue back-reflection technique.

Measurements at 8 and 14 MHz of T_1 for the Al^{27} a and d sites were made with applied field H_0 along $\langle 100 \rangle$ and $\langle 111 \rangle$ directions, respectively, and

the a-site linewidth was measured also. A $90°$-τ-$90°$ pulse sequence and boxcar integrator were used to measure T_1. The $90°$ pulse length was 32 to 45 μsec, depending on which transition was irradiated, and the receiver dead time following the pulse was 50 μsec. Transmitter, receiver, and integrator were built after the design of Clark.[4] A crossed-coil pulse head was used. The linewidth measurements were made with a Robinson oscillator[5] and a Princeton Applied Research model HR-8 lock-in amplifier. The applied field H_0 was produced by a Varian 12-in. electromagnet with Fieldial regulation.

The desired temperature for all measurements was obtained by flowing nitrogen gas over the sample. To obtain low temperatures a heater immersed in liquid nitrogen was used to produce cold gas. For high temperatures, nitrogen gas from a cylinder was heated. Temperature was measured with a thermocouple, with an estimated accuracy of $1\,°K$.

III. Al^{27}-Tm^{169} CROSSOVER

The Al^{27} and Tm^{169} resonant applied magnetic fields for a given spectrometer frequency $\omega/2\pi$ cross over (become equal) at certain temperatures because of a large and strongly temperature-dependent enhancement of the field H_L at the Tm^{169} nucleus, caused by the surrounding Tm^{3+} ions. At high temperature Tm^{169} resonance occurs when the applied field H_0 approaches the value $H_L \equiv \omega/\gamma_n$ required for resonance, while at low temperature a much smaller H_0 can give this same H_L at the Tm^{169} nucleus. Specifically, for a spectrometer frequency of 25 MHz, Al^{27} resonates at an H_0 of 22.54 kOe, disregarding the paramagnetic shifts which never exceed 4% and ignoring quadrupolar splitting. At 25 MHz, Tm^{169} resonates in a field H_L of 72.2 kOe, but at $1.5\,°K$ this H_L can be achieved with an applied field H_0 of only 0.750 to 20.658 kOe, depending on the thulium-ion site orientation relative to H_0 (see Fig. 2 of SJ).

As explained in more detail in SJ, the field H_L at the nucleus is the vector sum of $\vec{H}_0$ and the time-averaged hyperfine field $\vec{H}_{hf} = A\vec{H}_0 \cdot \{\underline{\chi}\}$. Because H_{hf} is comparable to H_0 and $\{\underline{\chi}\}$ is quite anisotropic, the orientation of the Tm^{3+}-ion moment can differ substantially from that of H_0. Here the hyperfine interaction constant $A = 172.5 \pm 3.6$ emu/g ion was obtained from Tm^{169} NMR studies in TmGaG[2] and in TmP, TmAs, and TmSb.[6] There are six chemically equivalent thulium sites having six sets of susceptibility-tensor axes in the directions $r(\chi_1) = (1,0,0)$, $r(\chi_2) = (0,1,\pm 1)$, $r(\chi_3) = (0,1,\mp 1)$, and cyclic permutations thereof. The three axes are inequivalent, as illustrated in SJ and Ref. 2. The structure contains chains of alternate Tm^{3+} and d-site Al^{3+} ions. Each chain lies along one of the

$\langle 100 \rangle$ directions, which is the symmetry axis for the aluminum d sites in that chain (see Fig. 1). Each aluminum a site has six nearest Tm^{3+} neighbors arranged consistent with the particular [111] symmetry axis for that site.

Our T_1 measurements for the a and d sites were made with $\vec{H}_0$ along one of the $\langle 100 \rangle$ and $\langle 111 \rangle$ directions, respectively, corresponding to rotation angles $\phi = 0°$ and $54.7°$ about the $\langle 01\bar{1} \rangle$ crystal rotation axis. For a particular spectrometer frequency $f = \gamma_n H_L/2\pi$, Eqs. (2) and (3) of SJ indicate two applied fields H_0 giving Tm^{169} resonance (see Fig. 2 of SJ), corresponding to

$$H_0(\phi = 0°) = H_L/(1 + A\chi_1), \tag{1}$$

$$H_0(0°) = H_L/[\tfrac{1}{2}(1 + A\chi_2)^2 + \tfrac{1}{2}(1 + A\chi_3)^2]^{1/2}, \tag{2}$$

$$H_0(54.7°) = H_L/[\tfrac{1}{3}(1 + A\chi_1)^2 + \tfrac{2}{3}(1 + A\chi_2)^2]^{1/2}, \tag{3}$$

$$H_0(54.7°) = H_L/[\tfrac{1}{3}(1 + A\chi_1)^2 + \tfrac{2}{3}(1 + A\chi_3)^2]^{1/2}. \tag{4}$$

The Al^{27} T_1 measurements were made on lines for which the first-order quadrupolar splitting was zero in that particular orientation, so that at crossover H_0 in Eqs. (1)–(4) is within about 100 Oe of ω/γ, while $H_L = \omega/\gamma_n$, giving $H_L/H_0 = 3.20$. (In this paper, subscripts n and l indicate thulium nucleus and ion, respectively, while for Al^{27} no subscripts are used.) If the denominators in Eqs. (1)–(4) are written as $1 + A\chi_w$, where χ_w is the appropriately weighted average of one or two
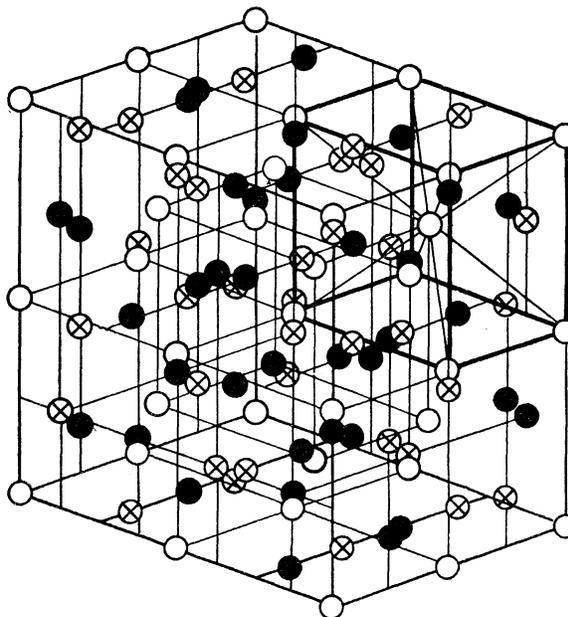

FIG. 1. Positions of the Al^{3+} and Tm^{3+} ions in the thulium aluminum garnet structure (after Ref. 14). The open, crossed, and filled circles represent site-a and -d aluminum ions and site-c thulium ions, respectively. The O^{2-} ions are not shown.
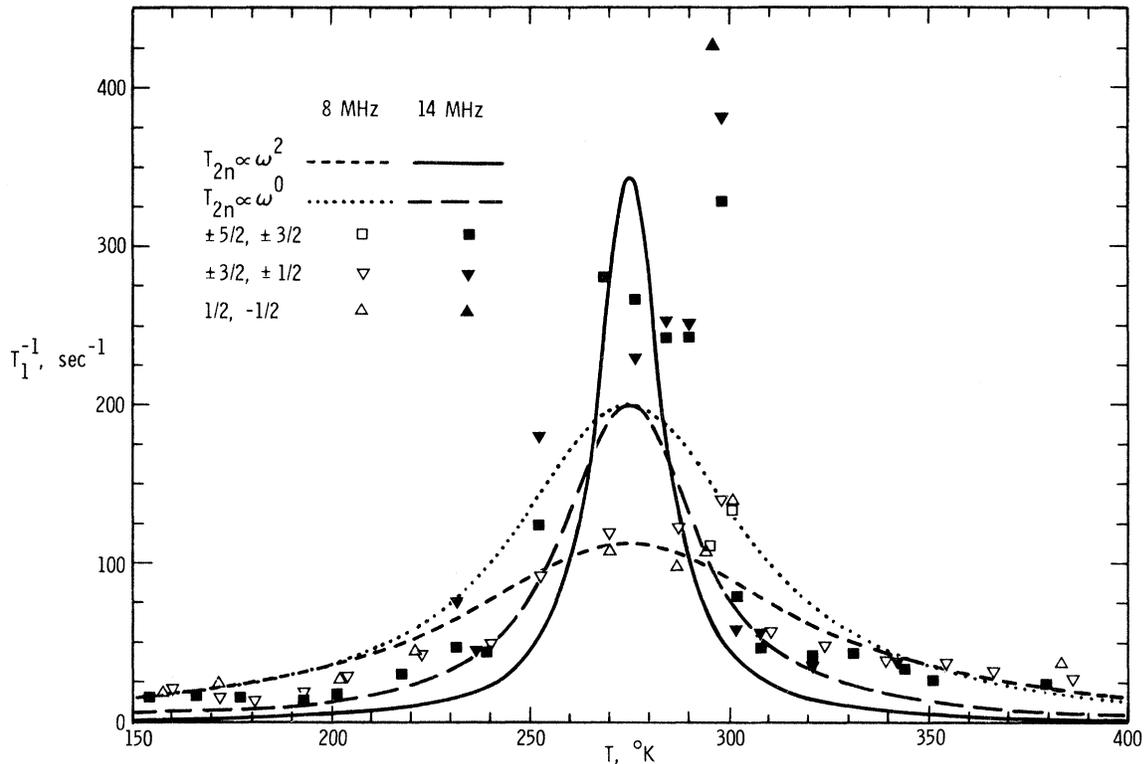
FIG. 2. Temperature dependence of T_1^{-1} for Al^{27} d sites. The symbols indicate experimental values for the d-site resonances which have second-order but no first-order splitting in the orientation used. The lines are calculated from Eqs. (16) and (19). The T_1^{-1}-measurement accuracy is $\pm 10\%$ except for the sharp peak at 14 MHz and 298 °K. For these three points the error is over $\pm 20\%$, so probably this peak is not real.

tensor components, then $\chi_w = 0.0128$ emu/g ion at crossover. The most pronounced T_1 dip occurs for the d sites with H_0 along a $\langle 111 \rangle$ direction, in the $(250-300)°$ K range as shown in Fig. 2. The free-thulium-ion susceptibility at 275 °K is $7.15/T = 0.026$ emu/g ion, or twice χ_w at crossover. Comparison with the inferred χ_i values in Table IV and Fig. 5 of SJ indicates that this crossover corresponds to the χ_1, χ_3 combination in Eq. (4), since χ_2 probably is so large that the crossover for the χ_1, χ_2 expression in Eq. (3) occurs above our maximum measurement temperature of 380 °K. Values calculated for χ_w at 275 °K from Table IV of SJ, using Eq. (4), are 0.021, 0.013, 0.035, and 0.024 emu/g ion from the χ_1, χ_3 combinations calculated omitting the $K_{\perp a}$, $K_{\parallel a}$, $K_{\perp d}$, and $K_{\parallel d}$ Al^{27} paramagnetic shifts, respectively. While omission of the $K_{\perp a}$ shift gives the best agreement with the measured $\{\chi\}$ at 1.5 °K, omission of the $K_{\parallel a}$ shift gives χ_w in (fortuitously) excellent accord with the value 0.0128 emu/g ion determined from the location of the crossover at 275 °K.

The T_1 dip for the a sites with H_0 along a $\langle 100 \rangle$ direction shown in Fig. 3 is weaker, and has

weaker frequency dependence. This dip also occurs near 275 °K. Because χ_2 is expected to be too large to give crossover corresponding to Eq.
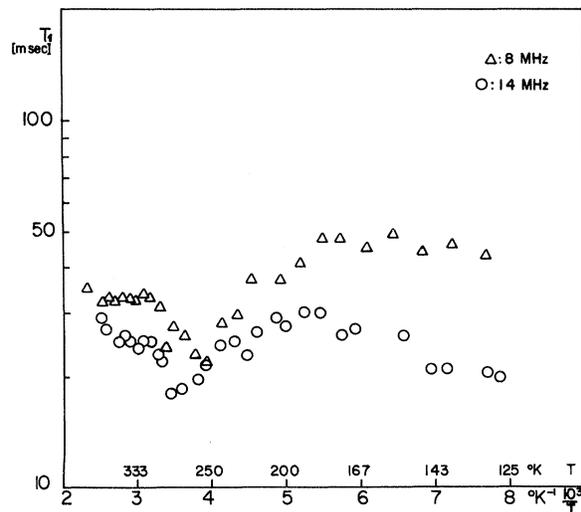

FIG. 3. Temperature dependence of T_1 for $Al^{27}a$ sites.

(2), we use Eq. (1) and obtain $\chi_w = \chi_1$. Comparison with Eq. (4) yields $\chi_1 = \chi_3 = 0.013$ emu/g ion at 275 °K, in accord with the rather broad range of predicted values from Table IV of SJ.

IV. CROSS RELAXATION

The energy flow in Al^{27} cross relaxation follows the steps $Al^{27} \rightarrow Tm^{169} \rightarrow Tm^{3+} \rightarrow$ lattice. Each reservoir is assumed to be unaffected by the previous one. For the Tm^{169} reservoir the justification is that T_{1n} and T_{2n} for Tm^{169} are short compared to T_1 for Al^{27}. Description of the relaxation accordingly will follow the sequence in reverse (cause $\rightarrow$ effect) order, beginning with the Tm^{3+} spin-lattice relaxation.

The Tm^{3+} spin-lattice relaxation time T_{1e} for 3-at.% Tm^{3+} in yttrium iron garnet (YIG) varies from 25×10^{-12} sec at 100 °K to 6×10^{-12} sec at 300 °K.[7] In this temperature range T_{1e} is short compared to the iron–rare-earth exchange time. Accordingly we expect that the same mechanisms control T_{1e} in both crystals. The thulium-ion environments are quite similar, but we expect only order-of-magnitude agreement between the T_{1e} values because the crystal-field energy-level schemes may differ significantly, as they apparently do for TmAlG and TmGaG, in view of the striking differences in the Tm^{3+} susceptibility tensors for these crystals.[1,2] We assume $T_{2e} \approx T_{1e}$ (lifetime broadening) because we expect thulium-thulium exchange and other broadening effects to be weak in comparison.

The model for the $Tm^{169} \rightarrow Tm^{3+}$ relaxation is based on limited knowledge of the Tm^{3+}-ion properties obtained from SJ and the present work. The thulium site has orthorhombic (D_2) symmetry, so the crystal field could completely lift the degeneracy associated with the thirteen m_J states for the free-Tm^{3+}-ion $^3H_6$ ground state. As discussed in Sec. V, the low-temperature susceptibility and relaxation appear to result from moments induced in the lowest crystal-field levels by the applied field H_0. In the (250–300) °K range in which both the a- and d-Al^{27}-site crossovers occur, Table IV and Fig. 5 of SJ show that the susceptibility is approaching free-ion behavior for the hyperfine-field fluctuations responsible for Tm^{169} relaxation. Thirteen nondegenerate levels each possessing only induced moments also give the free-ion susceptibility in the high-temperature limit. Our results indicate that the actual behavior of the Tm^{3+} ion near room temperature lies between these two extremes.

We describe the relaxation of both Tm^{169} and Al^{27} by the expressions[8]

$$T_1^{-1} = \tfrac{1}{2}\gamma^2 \int_{-\infty}^{\infty} \langle h_+(t)\, h_-(0) \rangle \, e^{-i\omega t}\, dt, \tag{5}$$

$$T_2^{-1} = \tfrac{1}{2}T_1^{-1} + \tfrac{1}{2}\gamma^2 \int_{-\infty}^{\infty} \langle h_z(t)\, h_z(0) \rangle \, dt, \tag{6}$$

where $h_\pm \equiv h_x \pm i h_y$ are used for the transverse fluctuating fields to facilitate handling of the rotating fields associated with crossover relaxation. These expressions are valid if the dipolar interactions are small compared to the Zeeman interactions, and the sources of the fluctuating fields are unaffected by the relaxing nuclei, as we have assumed.

To calculate the Tm^{169} relaxation times T_{1n} and T_{2n}, we make the approximation that the fluctuating field $\vec{h}_n(t)$ at the thulium nucleus is caused solely by the surrounding ion. By analogy with $\vec{H}_{hf} = A\vec{H}_0 \cdot \{\chi\} = AN_A \langle \vec{\mu}_e(t) \rangle$ we have

$$\vec{h}_n(t) = AN_A \vec{\mu}_e(t) = \vec{\mu}_e(t)/(0.213 \text{ Å})^3 , \tag{7}$$

and if the longitudinal and transverse fluctuations of an individual Tm^{3+}-ion magnetic moment are governed by single relaxation times T_{1e} and T_{2e}, respectively, we obtain

$$\langle h_{n+}(t)h_{n-}(0) \rangle = A^2 N_A^2 \langle \mu_{et}^2(0) \rangle \, e^{i\omega_e t - t/T_{2e}} , \tag{8}$$

$$\langle h_{nz}(t)h_{nz}(0) \rangle = A^2 N_A^2 \langle \mu_{ez}^2(0) \rangle \, e^{-t/T_{1e}} . \tag{9}$$

Substitution of Eqs. (8) and (9) into Eqs. (5) and (6) yields

$$T_{1n}^{-1} = A^2 N_A^2 \gamma_n^2 \langle \mu_{et}^2(0) \rangle \, T_{2e}/[1 + (\omega_e - \omega)^2 T_{2e}^2], \tag{10}$$

$$T_{2n}^{-1} = \tfrac{1}{2}T_{1n}^{-1} + A^2 N_A^2 \gamma_n^2 \langle \mu_{ez}^2(0) \rangle \, T_{1e}/(1 + \omega^2 T_{1e}^2), \tag{11}$$

in which terms containing ω can be neglected because T_{2e} and T_{1e} are very short. Here $\omega_e/2\pi H_0 = 1.633$ MHz/Oe if g_J has the value $\tfrac{7}{6}$ appropriate to the free Tm^{3+} ion.

Some comments on T_{1e} and T_{2e} are in order. We expect $T_{2e} \approx T_{1e}$ as explained earlier. The possibility that T_{1e} and T_{2e} depend on the magnitude of $\vec{H}_0$ is discussed in Sec. V. Because $\{\chi\}$ is approaching the free-ion value at the temperatures for which cross relaxation occurs, it appears that most or all of the crystal-field levels are populated. The Tm^{169} relaxation at these temperatures must be caused by one or more sets of effectively degenerate levels, to be consistent with the frequency dependence inferred for T_{2n} later in this section. Accordingly, the autocorrelation functions in Eqs. (8) and (9) are approximations to complicated unknown functions which may involve several frequencies ω_e and relaxation times T_{1e} and T_{2e}. We expect T_{1e} and T_{2e} to be dependent on the orientation of the thulium ion relative to $\vec{H}_0$, because the relative contributions of the different levels to the fluctuating moments causing nuclear relaxation depend on the direction of $\vec{H}_0$ as discussed in Sec. V, and different levels are likely to have different relaxation times.

In the Al^{27}-Tm^{169} or cross-relaxation part of

the relaxation process, the effective thulium nuclear moments $\vec{\mu}_{ni}$ are assumed to act as point dipoles in producing the local field $\vec{h}(t)$ at an Al^{27} site. Then for thulium sites having positions $-\vec{r}_i$ relative to an Al^{27} site,

$$\vec{h}(t) = \sum_i [3r_i^{-5} (\vec{r}_i \cdot \vec{\mu}_{ni})\vec{r} - r_i^{-3}\vec{\mu}_{ni}] , \quad (12)$$

and the autocorrelation functions are

$$\langle h_+(t)h_-(0)\rangle = \frac{9}{4}\sum_i r_i^{-6}\langle \mu_{nzi}^2(0)\rangle e^{-t/T_{1n}} \sin^2 2\theta_i$$
$$+\langle \mu_{nti}^2(0)\rangle e^{-t/T_{2n}}[(\cos^2\theta_i - \tfrac{1}{3})^2 e^{i\omega_n t}$$
$$+ \sin^4\theta_i\, e^{-i\omega_n t}] , \quad (13)$$

$$\langle h_z(t)h_z(0)\rangle = \frac{9}{4}\sum_i r_i^{-6}\langle \mu_{nzi}^2(0)\rangle e^{-t/T_{1n}}(3\cos2\theta_i+1)^2$$
$$+ \tfrac{1}{4}\langle \mu_{nti}^2(0)\rangle \sin^2 2\theta_i[e^{i\omega_n t} + e^{-i\omega_n t}] , \quad (14)$$

where θ_i is the angle between $\vec{r}_i$ and $\vec{H}_0$.

In calculating the cross relaxation we consider three effects of the anisotropy of $\{\chi\}$. First, it splits the Tm^{169} resonance so that for relaxation of d-site Al^{27} nuclei only the half of the thulium sites having H_0 given by Eq. (4) are responsible for the observed crossover. The third of the thulium sites corresponding to Eq. (1) are assumed responsible for a-site Al^{27} relaxation. Second, the field $\vec{H}_L$ at the thulium nucleus is not in general parallel to $\vec{H}_0$, but because the crossover occurs in the (250–300) °K range in which the Tm^{3+}-ion susceptibility tensor $\{\chi\}$ is believed to be reasonably isotropic (see Table IV and Fig. 5 of SJ), the simplifying assumption is now made that $\vec{H}_L$ is parallel to $\vec{H}_0$. Finally, the moment induced in the thulium ion by the thulium nuclear moment is anisotropic. This induced moment follows the precession of the nuclear moment, causing an enhanced Tm^{169} moment. The enhancement of the component μ_{nt} transverse to $\vec{H}_L$ is greater than for μ_{nz} because the largest susceptibility component χ_2 is perpendicular to $\vec{H}_0$ and nearly perpendicular to $\vec{H}_L$. We make the approximation that the enhancement of μ_{nt} is independent of orientation in the plane perpendicular to $\vec{H}_0$, and is a factor B_a greater than the enhancement for μ_{nz}.

For the mean-square fluctuating moments we use

$$\langle \mu_{nz}^2(0)\rangle = \tfrac{1}{3}(1+A\chi_z)^2\gamma_n^2\hbar^2 I_n(I_n+1) = \tfrac{1}{4}\gamma^2\hbar^2 , \quad (15)$$

$$\langle \mu_{nt}^2(0)\rangle = 2B_a^2\langle \mu_{nz}^2(0)\rangle ,$$

because the Tm^{169} moment is enhanced by the induced moment in the surrounding ion by the same factor $(1+A\chi_z)$ by which its resonant frequency is enhanced by the hyperfine field, and at crossover this enhancement factor is $\gamma/\gamma_n \equiv \gamma_{Al}/\gamma_{Tm} = H_L/H_0$.

Near crossover $\omega_n \approx -\omega$ (the gyromagnetic ratios of Tm^{169} and Al^{27} have opposite signs). Accordingly, only the terms containing $e^{-i\omega_n t}$ in Eqs. (13) and (14) are significant, and substitution into Eqs. (5) and (6) yields

$$T_1^{-1} = \tfrac{9}{8}\gamma^4\hbar^2 B_a^2 \sum_i r_i^{-6}\sin^4(\theta_i)\, T_{2n}/[1+(\omega_n+\omega)^2 T_{2n}^2] , \quad (16)$$

$$T_2^{-1} = \tfrac{1}{2}T_1^{-1} + \tfrac{9}{16}\gamma^4\hbar^2\sum_i r_i^{-6}(3\cos2\theta_i+1)^2 T_{1n} . \quad (17)$$

Comparable values for T_1 and T_2 are predicted by Eqs. (16) and (17). Experimentally, $T_2 \ll T_1$, so only Eq. (16) is applicable. In Eq. (16) the factor in brackets becomes unity at crossover and the lattice sum evaluated through fifth nearest neighbors yields $\tfrac{9}{4}\sum_i (r_i/r_0)^{-6}\sin^4\theta_i = 0.0244$, with $r_0 = 1.4946$ Å. The a-site lattice sum turns out to have exactly the same value.

From the measured d-site peak values of T_1^{-1}(14 MHz) = 300 sec^{-1} and T_1^{-1}(8 MHz) = 125 sec^{-1} shown in Fig. 2 we obtain T_{2n}(14 MHz) = 105B_a^{-2} μsec and T_{2n}(8 MHz) = 44B_a^{-2} μsec. The corresponding Tm^{169} linewidth $(\pi T_{2n})^{-1}$ is in the $3B_a^2$–$7B_a^2$-Oe range. The failure of SJ to observe the Tm^{169} resonance near room temperature, together with evidence presented below, indicated that B_a is larger than the value ≈ 2 estimated from Table IV and Fig. 5 of SJ. The failure to see the Tm^{169} signal near room temperature is not attributable to inhomogeneous broadening. Even at 1.5 °K, Tm^{169} lines only 100 G apart were resolved (Fig. 2 of SJ). At room temperature the susceptibility and the resulting inhomogeneous broadening are much smaller.

We analyze the d-site experimental results by using the approximation

$$\omega_n \simeq -\omega[1 + A(d\chi_w/dT)_{T_0}(T-T_0)] \quad (18)$$

for ω_n in Eq. (16) and obtain the Lorentzian curves shown in Fig. 2 for T_1^{-1} as a function of T. Here χ_w is the effective χ in Eq. (4) and $T_0 = 275$ °K is the T_1-dip temperature. The half-width at half-height occurs where

$$T_{2n}^{-1} = A(d\chi_w/dT)_{T_0}(T-T_0) . \quad (19)$$

From Fig. 5 of SJ we estimate $(d\chi_w/dT)_{T_0}$ to be 10^{-5} within an order of magnitude.

The curves in Fig. 2 are drawn to give best fit to the 8- and 14-MHz data for two choices of frequency dependence for T_{2n}. The ω^0 choice gives better agreement at the wings, while the ω^2 choice fits the peaks better. In the wings other relaxation mechanisms probably contribute significantly and the linear approximation for $\omega_n(T-T_0)$ given in Eq. (18) almost certainly breaks down. Accordingly, an ω to ω^2 dependence for T_{2n} which fits the peak best is considered to agree best with experiment.

The a-site results shown in Fig. 3 also exhibit H_0 dependence for the T_1 magnitude at the dip. Because of the uncertainty in the strength of other relaxation mechanisms at the dip, we can only estimate that T_{2n} has $\omega^{1/2}$ to ω^1 dependence for the a sites.

We now discuss what can be inferred about the thulium ion from the magnitude and frequency dependence of T_{2n}, which itself is inferred from the d-site Al^{27} cross-relaxation results. The relations between the thulium-ion behavior and the Tm^{169} relaxation times are given in Eqs. (10) and (11). One expects the transverse and longitudinal fluctuating moments of the ions to be roughly equal, in which case T_{2n} will depend on ω_e only if $\omega_e T_{2e}$ is near unity. If $\langle \mu_{et}^2 \rangle = 2 \langle \mu_{ez}^2 \rangle$ as required for isotropic fluctuations and if $T_{2e} = T_{1e} = T_e$, then $T_{2n} \propto \omega_e^x$, where $0 \leq x \leq \frac{1}{3}$. The "observed" values of x lie between $\frac{1}{2}$ and 2. To obtain such frequency dependence of T_{2n} we first must rule out induced moments as the source of the fluctuating field, because they would give $T_{2n} \propto H_0^{-2}$. Then we must also assume that the transverse fluctuating moments are several times larger than the longitudinal ones. This assumption is consistent with the larger mean transverse susceptibility for those thulium ions responsible for cross relaxation, although we expect no simple relation between components of the susceptibility tensor and corresponding fluctuating moment magnitudes.

In this region of strong frequency dependence of T_{2n},

$$T_{2n}^{-1} \simeq \tfrac{1}{2} A^2 N_A^2 \gamma_n^2 \langle \mu_{et}^2(0) \rangle / \omega_e^2 T_{2e} \qquad (20)$$

from Eqs. (10) and (11). In the relation $T_{2n}(14 \text{ MHz}) = 105 B_a^{-2}$ μsec obtained from Eq. (16), $B_a = 6$ yields 3 μsec for T_{2n}. In the derivation of Eq. (20), ω_e is the transverse precession frequency of a magnetic moment and it must be proportional to H_0 to give the right frequency dependence for T_{2n}. Precession and H_0 dependence are inconsistent with interpretation of ω_e as a crystal-field splitting but are exhibited by free ions, so for ω_e we use the free-ion value of 1.6×10^{11}/sec at the H_0 value giving Al^{27} resonance at 14 MHz. The T_{1e} for 3% Tm^{3+} in YIG is 6×10^{-12} sec at the crossover temperature of 275 °K. Use of these values gives $\tfrac{1}{2}\langle \mu_{et}^2(0) \rangle = 0.013 \mu_B^2$. This is about $1/1500$ of the free-ion value given in Eq. (24), giving an rms fluctuating moment about 40 times smaller than the free-ion value. The actual values of ω_e and T_{2e} may be different by perhaps an order of magnitude, but to obtain strong frequency dependence for T_{2n} they must obey $\omega_e T_{2e} \approx 1$, as does the above choice. These inferences of the thulium-ion properties agree quite well with those obtained in Sec. V from the direct relaxation results.

V. DIRECT RELAXATION

In this section we consider "direct" ($Al^{27} \to Tm^{3+} \to$ lattice) relaxation in which the $Al^{27} \to Tm^{3+}$ step involves magnetic dipolar interactions. For higher temperatures we use the same picture for the thulium ion as was used in Sec. IV to describe the $Tm^{169} \to Tm^{3+}$ part of the cross-relaxation process, as cross relaxation occurs in the middle of the high-temperature range. To interpret our low-temperature results we use a two-level model described in what follows.

As explained in Sec. IV, the orthorhombic (D_2) symmetry of the thulium site is low enough to allow the 13 m_J levels of the free Tm^{3+} ion to go to 13 nondegenerate crystal-field levels, but some of the higher levels appear to be effectively degenerate. The susceptibility results of SJ yield some clues about the spacing of the lowest levels. The temperature dependence of $\{\underline{\chi}\}$ suggests Van Vleck paramagnetism, which if two levels are of importance obeys

$$\chi = 2 N_A |\langle s | \mu_z | 0 \rangle|^2 \tanh(\delta/2kT)/\delta .$$

Figure 5 of SJ shows that $\chi_2(T)$ is consistent with an excited state having energy $\delta/k = 46$ °K relative to a nondegenerate ground state. The matrix element connecting these states apparently vanishes for H_0 in the directions corresponding to χ_1 and χ_3, because χ_1 and χ_3 have different temperature dependences than χ_2, suggesting that the states responsible for χ_1 and χ_3 have considerably larger energies, with δ/k near room temperature. At low temperature the largest magnetic moments by far are those induced by $\vec{H}_0$ components along the χ_2 axis at thulium sites, and the most frequent transitions are between the ground state and the lowest excited state. Mixing of these two states by $\vec{H}_0$ is the origin of the large magnetic moment in the ground state. An equal moment of opposite sign is induced in the lowest excited state, because the other states are much higher and have little effect on the induced moments. Accordingly, at low temperature the largest and most frequent field fluctuations originate in these two states, and a model based on these two states is the logical choice to explain the Al^{27} relaxation. The upper temperature limit for this model must be determined by comparison of its predictions with experiment, because the energies of the second and higher excited states are not known with much precision. We assume that the Tm^{3+} ion at the ith site has a magnetic moment

$$\vec{\mu}_i = \vec{H}_0 \cdot \{\underline{\chi}_{2i}\}/N_A \qquad (21)$$

in the ground state and the negative of this moment in the first excited state. For χ_2 we use the value

measured[1] at 1.5 °K of $\chi_2 = 0.551$ emu/g ion, which is temperature independent at low temperature. Since χ_1 and χ_3 are only 0.014 and 0.030 emu/g ion, respectively, at 1.5 °K, their contributions to the moment are ignored.

In Eq. (5) for T_1^{-1}, if w is the probability per unit time for a Tm^{3+} ion in the first excited state to return to the ground state, then the opposite probability is $we^{-\delta/kT}$ and the autocorrelation function is

$$\langle h_+(t)h_-(0)\rangle = \langle h_x^2(0) + h_y^2(0)\rangle \{\tanh(\delta/2kT)$$
$$+ [1 - \tanh(\delta/2kT)]\exp[-w(1 + e^{-\delta/kT})t]\} ,$$
(22)

where $\vec{h}(0)$ is found from Eq. (12), in which $\vec{\mu}_i$ from Eq. (21) is used. The constant term results because the field from a given ion is in the direction resulting from the ground state over one-half of the time. Relaxation caused by such biased field fluctuations has been treated previously for quadrupolar relaxation of deuterons in the ferroelectric phase of KD$_2$PO$_4$.[9]

The Fourier transform of Eq. (22) yields

$$T_1^{-1} = (2w)^{-1}\gamma^2\langle h_x^2(0) + h_y^2(0)\rangle \operatorname{sech}^2(\delta/2kT), \quad (23)$$

using the approximation $\omega/w(1 + e^{-\delta/kT}) \ll 1$. Our measurements did not extend down to the temperatures at which $\operatorname{sech}^2(\delta/2kT)$ has strong temperature dependence. From Eq. (23), T_1^{-1} is proportional to the square of the induced fluctuating moment, and thus is proportional to H_0^2. The a-site results shown in Fig. 3 approach this predicted H_0^2 dependence as temperature decreases in the (190–127)°K range. The d-site results which only extend down to 154 °K do not show appreciable field dependence at this temperature. This result indicates that for the crystal orientation used for the d-site measurements, induced moments do not make the major contribution to relaxation in the temperature range studied.

For a numerical comparison of predictions of this two-level model with experiment we choose the 14-MHz a-site T_1 of 20 msec at 127 °K, because it is shorter than the 8-MHz T_1 and less likely to be influenced by other relaxation processes. From this T_1 value and Eqs. (12), (21), (22), and (23) we obtain for the only adjustable parameter w the value 1.4×10^{11} sec^{-1}. This corresponds to a correlation time, or effective T_{1e} for this pair of levels, of $w^{-1}(1 + e^{-\delta/kT})^{-1} = 4.2 \times 10^{-12}$ sec, which is not too different from the T_{1e} of 20×10^{-12} sec at 127 °K inferred for 3-at.% Tm^{3+} ions in YIG.[7] Also the temperature dependences inferred for T_{1e} are quite similar, with T_{1e} decreasing with increasing temperature.

For the d-site results, and for the a-site results above 190 °K, away from the cross-relaxation dips

T_1 shows little field dependence and a model of relaxation caused by fluctuations of induced Tm^{3+}-ion moments is not valid. In the absence of detailed knowledge of the nature of the thulium ion in this higher-temperature region, we use the simplest model for permanent moments, which is the free-ion model.

For this model the Tm^{3+}-ion magnetic moment is decomposed into a component μ_{iz} parallel to $\vec{H}_0$ having relaxation time T_{1e} and a transverse component μ_{it} rotating with frequency ω_e and having relaxation time T_{2e}. The autocorrelation fluctuations for the field of an Al^{27} site then are given by Eqs. (13) and (14), with $\omega_n \rightarrow \omega_e$, $T_{1n} \rightarrow T_{1e}$, and $T_{2n} \rightarrow T_{2e}$.

For the free Tm^{3+} ion, which has a $^3H_6$ ground state for which $J = 6$ and $g_J = \frac{7}{6}$,

$$\tfrac{1}{2}\langle\mu_t^2(0)\rangle = \langle\mu_z^2(0)\rangle = \tfrac{1}{3}g_J^2\mu_B^2 J(J+1) = \tfrac{343}{18}\mu_B^2 . \quad (24)$$

The relaxation rates obtained by substitution from Eqs. (13), (14), and (15) into Eqs. (5) and (6) are

$$T_1^{-1} = \tfrac{343}{72}\gamma^2\mu_B^2\sum_i r_i^{-6}\{9\sin^2(2\theta_i)T_{1e}$$
$$+ [(3\cos2\theta_i - 1)^2 + 4]T_{2e}/(1 + \omega_e^2 T_{2e}^2)\} , \quad (25)$$

$$T_2^{-1} = \tfrac{1}{2}T_1^{-1} + \tfrac{343}{8}\gamma^2\mu_B^2\sum_i r_i^{-6}\{(3\cos2\theta_i + 1)^2 T_{1e}$$
$$+ \sin^2(2\theta_i)T_{2e}/(1 + \omega_e^2 T_{2e}^2)\} , \quad (26)$$

where terms $2\omega_e\omega T_{2e}^2$, $\omega^2 T_{2e}^2$, and $\omega^2 T_{1e}^2$ in the denominators are small and have been neglected. The lattice sums in Eq. (25) yield

$$T_1^{-1} = (1.79 \times 10^{15}\text{ sec}^{-2})[C_z T_{1e} + C_2 T_{2e}/(1 + \omega_e^2 T_{2e}^2)] , \quad (27)$$

where for the Al^{27} a and d sites $C_{za} = 0.211$, $C_{2a} = 0.638$, $C_{zd} = 0.345$, and $C_{2d} = 0.521$. The measured values of T_1 away from crossover dips range from 20 to 70 msec. For an estimate of the necessary electronic relaxation time, we let $T_1^{-1} = 20$ sec^{-1} and ignore the second term in Eq. (13) because $C_2 \approx C_z$; we expect $T_{2e} \approx T_{1e}$; and from the cross-relaxation results there is evidence that $\omega_e T_{2e} > 1$. We obtain $T_{1e} \approx 4 \times 10^{-14}$ sec, which is inconsistent with $\omega_e T_{1e} \approx \omega_e T_{2e} > 1$. Also it is much shorter than T_{1e} for 3-at.% Tm^{3+} ions in YIG, which is given as 6×10^{-12} sec at 300 °K.[7] If a more reasonable value 100 times larger (4×10^{-12} sec) is used for T_{1e}, then the magnetic moment fluctuations must be 10 times smaller than predicted by the free-ion model.

A dependence of T_{1e} and T_{2e} on the magnitude of H_0 may exist, particularly if certain levels are so close together that they are strongly mixed by H_0. The lowest two levels are not mixed strongly enough to cause saturation of the susceptibility,[1] but the apparent degeneracy of some higher levels could result from such mixing. Existence of such H_0 dependence for T_{1e} and T_{2e} could invalidate con-

clusions based on the H_0 dependence of T_1 and T_{1n}.

For both the two-level and free-ion-model calculations we carry out the lattice sums over thulium sites within $8.1A$, which includes 42 and 22 thulium sites surrounding aluminum a and d sites, respectively. An estimated correction of less than 1% was added for more distant thulium sites.

For both of these models, as well as for cross relaxation, the Al^{27} T_1 and T_2 predicted by Eqs. (5) and (6) are equal except for geometrical factors which tend to become equal upon taking lattice sums. Because T_2 as determined from the linewidth is of order 0.1 msec while T_1 always exceeds 2 msec, the linewidth is determined by causes other than the magnetic moment fluctuations. The a-site linewidth is shown in Fig. 4. Its behavior as a function of temperature is not understood, as it seems inconsistent with inhomogeneous broadening or quadrupolar broadening.

VI. DISCUSSION

We believe that we have observed both direct Al^{27} relaxation by thulium-ion magnetic moment fluctuations, and Al^{27} cross relaxation to the enhanced Tm^{169} moments, which in turn relax to their surrounding thulium ions. The Al^{27} T_1 results can be explained fairly well by assuming that the thulium-ion magnetic moment fluctuates with a correlation time of 10^{-12} to 10^{-11} sec. It appears that at low temperatures these fluctuating moments are induced mainly by the applied field H_0, while at higher temperatures they are field independent. Certain conclusions reached by SJ concerning the lowest crystal-field levels are consistent with our low-temperature results. The higher-temperature results indicate degeneracy among some of the higher crystal-field levels, giving a moment $\frac{1}{10}$ to $\frac{1}{100}$ as large as the free-ion moment, precessing at a frequency proportional to H_0. These

conclusions about the thulium ion are tentative because they are based on indirect reasoning from our Al^{27} T_1 results.

There are difficulties in inferring the Tm^{169} T_1 and T_2 from the cross-relaxation results, but they appear to be in the $(10^{-6}-10^{-5})$-sec range. This corresponds to a linewidth of order 100 Oe, so the Tm^{169} resonance which was studied by SJ at liquid-helium temperature could possibly be observed also at higher temperatures.

It may be possible to determine the Tm^{169} resonant frequencies indirectly over a wide temperature range by observing Al^{27} T_1 dips as a function of temperature. The Tm^{169} and Al^{27} frequencies could be matched at arbitrary temperatures by adjusting H_0, because the Al^{27} quadrupolar splitting in first order gives fractional shifts proportional to H_0^{-1}. From these Tm^{169} resonant frequencies the thulium-ion susceptibility tensor could be obtained over a wide temperature range. The temperature dependence of the susceptibility would be useful in determining the thulium-ion crystal-field levels. Similar techniques could be applied for indirect observation of magnetically broadened resonances in other crystals.

Cross relaxation has previously been used to observe rare spin systems[10] and nuclei whose resonance lines have excessive quadrupolar broadening.[11,12] This is believed to be the first observation of a magnetically broadened line by means of cross relaxation.

APPENDIX: QUADRUPOLAR RELAXATION

We assume that the anharmonic Raman (AR) process described by Van Kranendonk and Walker[13] is the strongest quadrupolar relaxation process. Then

$$T_1^{-1}(AR) = 34\pi\omega_D\gamma_G^2(c_1^2 + 4c_2^2)\frac{2I+3}{I^2(2I-1)}$$

$$\times(eQ/Mv^2)^2 T^{*2}E^*(T^*), \quad (28)$$

where $\omega_D = k\Theta/\hbar$ is the Debye frequency, γ_G is the Grüneisen constant, c_1 and c_2 are constants which we obtain from a point-charge model,[13] I and Q are nuclear spin and quadrupole moment, e is
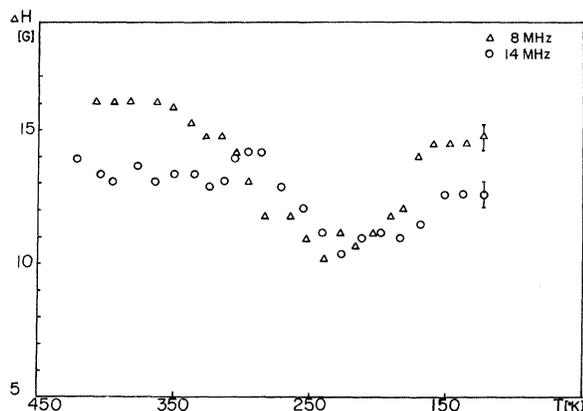

FIG. 4. Temperature dependence of linewidth between absorption derivative peaks for Al^{27} a sites.

elementary charge, M is aluminum atomic mass, v is sound velocity, and $T^* = T/\Theta$, where Θ is the Debye temperature. The function $E^*(T^*)$ has for NaCl-type crystals the form[13]

$$E^*(T^*) = 1.4 \times 10^4 T^{*5}(1 - 340\, T^{*2} + \cdots)$$

$$\text{for } T^* < 0.02 ,$$

$$= 1 - 0.056 T^{*-2} + \cdots \quad \text{for } T^* > 0.5. \quad (29)$$

The nearest (oxygen) neighbors around a-site Al²⁷ nuclei in TmAlG form a nearly perfect octahedron. Thus for the a site we can apply in first approximation the same formula as for NaCl-type crystals, in which nearest neighbors are octahedrally arranged.

Taking into account only the nearest neighbors around a-site Al²⁷ nuclei, we have, for c_1 and c_2,[13]

$$c_1 = 1.63\gamma_S e a^{-3}, \quad c_2 = 2.08\gamma_S e a^{-3}, \quad (30)$$

where e is the charge on each neighbor, a is the nearest-neighbor distance, and γ_S is the Sternheimer antishielding factor.

The sound velocity was calculated to be 4.2×10^5

cm/sec from known elastic constants for some natural garnets. The Debye temperature of 500 °K was calculated from the accurately known Θ for LuIG (lutetium iron garnet) using $\Theta \propto M_m^{-1/2}$, where M_m is the molecular mass.[14] For γ_G we take the value 1.2 found[15] for the natural garnet almandite-pyrope.

If we now evaluate the relaxation rate for the Al²⁷ a site in TmAlG at 300 °K from Eq. (28), using in Eq. (30) the values $\gamma_S = -2.59$ and $e = 1.2$ proton charges employed in the point-charge model of SJ, we get $T_1^{-1}(\text{AR}) = 0.07 \text{ sec}^{-1}$. This value is close to the measured[13] T_1 for Na²³ in NaCl (Na²³ and Al²⁷ have similar quadrupole moments and Sternheimer antishielding factors), but is more than two orders of magnitude smaller than any measured T_1^{-1} in TmAlG. One could argue that covalent effects[16] make the c_i much greater than given by Eq. (30). However, the predicted temperature dependence from Eqs. (28) and (29) ($T_1^{-1} \propto T^7$ at low temperature and T^2 at high temperature) does not appear. Accordingly we have no evidence for quadrupolar relaxation of Al²⁷ in TmAlG.

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Ferromagnetism in Degenerate Bands

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A criterion for ferromagnetism is developed for the case of a twofold degenerate band having a rapid variation of the density of states at the Fermi surface. An exchange splitting of spin-up and spin-down bands, which is different for the two different subbands, and an over-all splitting of the two subbands is obtained, even if the Stoner criterion is not fulfilled, i. e., for $1 > N(0)U$.

I. INTRODUCTION

Our understanding of ferromagnetism in the transition metals is still rather limited. The band

theory for itinerant-electron ferromagnetism, [1–3] mainly due to Slater, Stoner, and Wohlfarth, is able to explain some important aspects of the situation; in particular, the nonintegral saturation