Slow and Fast Relaxation in Magnetic Resonance in Ferrimagnetic $MnFe_2O_4$

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The Mn^{55} nuclear spin-lattice relaxation time, and the ferromagnetic-resonance linewidth in $MnFe_2O_4$ have been measured as a function of the temperature. The important features of the data are a peak in $1/T_1$ at 3°K; and two peaks in the ferromagnetic-resonance linewidth at 20° and 210°K, respectively. The low-temperature phenomena are described in terms of a slow relaxation theory based on the low-lying orbital levels of the Fe^{2+} impurities present; the peak in $1/T_1$ occurring when $\omega_N\tau\sim1$ and the peak in ΔH occurring when $\omega_0\tau\sim1$ where ω_N and ω_0 are the nuclear and ferromagnetic resonance frequencies, and τ is the relaxation time of the Fe^{2+} impurities. The high-temperature linewidth is the result of a direct transition (via the spin-orbit interaction) between these levels with annihilation of a $k=0$ magnon, and becomes appreciable when $\omega_1\tau\sim1$ where $\hbar\omega_1$ is the separation between the low-lying orbital levels. Analysis of the low- and high-temperature data yield consistent values for the level separation, $\hbar\omega_1\sim10°K$, and for the temperature dependence of τ. At low temperatures $1/\tau$ increases linearly with temperature suggesting a direct phonon or magnon relaxation process. Above 150°K, τ is limited by the lifetime of the quasifree electron on a given Fe ion.

I. INTRODUCTION

DURING the past few years a great deal of experimental and theoretical work has been done on the origin of ferromagnetic-resonance linewidths. The systems most studied are the rare-earth iron garnets[1]; both pure YIG [2] and YIG with small amounts of magnetic rare-earth impurities substituted for yttrium.[3] However, some of the results of these studies are considerably more general. In particular, one can often discuss the ferromagnetic system as a whole in terms of an essentially lossless ferromagnetic system (e.g., composed entirely of Fe^{3+} or Mn^{2+} ions) coupled to a lossy subsidiary system (e.g., Fe^{2+} or magnetic rare-earth impurities). In the case of the rare-earth iron garnets this division is experimentally evident from the fact that ultrapure YIG [2] has a linewidth of a few millioersteds at low temperatures while YIG with 1% rare-earth impurities may have a linewidth of a few hundred oersteds. This kind of a separation should be generally valid in view of the fact that Mn^{2+} and Fe^{3+} have a $3d^5$ atomic configuration. They are thus in an S state with orbital angular momentum equal to zero and are expected to have long relaxation times. On the other hand, Fe^{2+} and the magnetic rare-earth impurities (other than Gd^{3+} and Eu^{2+}) are not S-state ions. The nonzero orbital angular momentum couples these ions strongly to the phonon bath and gives relatively short relaxation times. Having made the above division one can trace the relaxation process in the following steps:

(1) A transfer of $k=0$ spin-wave energy to the lossy subsidiary system,

(2) Subsequent relaxation of the energy from the subsidiary system to the lattice.

The subsidiary system may therefore be thought of as kind of a "leak" for energy out of the essentially lossless ferromagnetic-spin system.

Two different, but *not necessarily* contradictory, theories have been proposed to describe the details of the above two-step relaxation process. The first,[4] originally proposed by Clogston, and recently clarified and applied to rare-earth substituted YIG by Van Vleck and Orbach[5] is known as the "slow relaxation" theory. The slow relaxation theory requires that the subsidiary system have low-lying energy levels which are significantly populated at the temperature in question; and that the splitting between the ground state and first excited state be anisotropic and depend on the orientation of the magnetization vector with respect to the crystal axes. Under these conditions, as the magnetization vector precesses in a resonance experiment a redistribution of the populations in the energy levels of the subsidiary system takes place. If the relaxation time τ for this redistribution is such that $1/\tau\sim\omega$, where ω is the precession frequency, an irreversible loss of energy from the ferromagnetic system will take place; thereby giving linewidth. The second or "fast" relaxation theory was originally proposed by de Gennes, Kittel, and Portis[6] with reference to the rare-earth garnets. They assume the lifetime of the subsidiary system in the states corresponding to the low-lying energy levels described above is so short that $\omega_1\tau\sim1$, where $\hbar\omega_1$ is the energy splitting between the ground state and first excited state. Under these conditions, the levels are sufficiently broad to al-

[1] G. P. Roderique, H. Meyer, and R. V. Jones, J. Appl. Phys. **31**, 3765 (1960).

[2] R. C. LeCraw and E. G. Spencer, Proc. Tokyo Phys. Soc. Japan **1**, 401, (1962).

[3] J. F. Dillon, Jr., Phys. Rev. **127**, 1495 (1962). P. E. Seiden, in *Magnetic and Electric Resonance and Relaxation*, edited by J. Smit (John Wiley & Sons, Inc., New York, 1963). J. F. Dillon, Tokyo Phys. Soc. Japan **1**, 376 (1962).

[4] A. M. Clogston, Bell System Tech. J. **34**, 739 (1955).

[5] J. H. Van Vleck and R. Orbach, Phys. Rev. Letters **11**, 65 (1963).

[6] P. G. deGennes, C. Kittel, and A. M. Portis, Phys. Rev. **116**, 323 (1959). R. L. White, Phys. Rev. Letters **2**, 465 (1958).

low a *direct* transition in which a $k=0$ spin wave is annihilated and one of the ions of the subsidiary system is left in its excited state with subsequent relaxation to the lattice. This kind of a theory can clearly be applied to other systems; the essential requirements being the above condition on τ, and an interaction between the ferromagnetic and subsidiary systems. It is to be noted that the conditions under which the above two mechanisms are important are quite different since usually $\omega \ll \omega_1$. Thus, in a given ferromagnetic system one might expect the slow relaxation theory to be important at low temperatures and the fast theory to be important at higher temperatures since $1/\tau$ is certainly a monotone increasing function of the temperature. Recent work[3,7] in the rare-earth iron garnets suggests that the linewidth peaks seen there are caused by slow relaxation, and that the system never reaches the condition appropriate to fast relaxation before it reaches its Curie point.

In this paper we present evidence for the observation of both slow and fast relaxation effects in the same ferromagnetic system $MnFe_2O_4$ (manganese ferrite). The lossy subsidiary system is the concentration of Fe^{2+} impurities always present on B sites of the spinel lattice. There is experimental evidence of low-lying energy levels in $MnFe_2O_4$.[8] The levels in question are orbital levels, and their separation is determined by a combination of the trigonal crystal field splitting and spin-orbit splitting of the Fe^{2+} orbital levels in the spinel lattice. The important features of the experimental data are a peak in $1/T_1$ at 3°K, where T_1 is the Mn^{55} nuclear spin-lattice relaxation time, and two peaks in the ferromagnetic-resonance linewidth; one at 14°K and one at 210°K. The low temperature phenomena are accurately described in terms of an application of the slow relaxation theory; and the higher temperature linewidth peak is consistently accounted for in terms of a fast relaxation theory appropriate to this system and developed in this paper. The results indicate that the separation between the low-lying Fe^{2+} levels in question is

$$\hbar\omega_1/k \simeq 8°K,$$

in rough agreement with the specific heat data.[8] The τ for these levels appears to be limited by direct phonon or magnon relaxation at low temperatures, and by the hopping of the sixth $3d$ electron from one Fe ion to the next at higher temperatures.

2. ENERGY LEVELS FOR Fe^{2+} IN $MnFe_2O_4$

The energy levels of Fe^{2+} in the spinel lattice have been discussed by Slonczewski.[9] We summarize his results here. The important feature of the spinel lattice is the existence of two kinds of sites with different point symmetry. The tetrahedral or A site is surrounded by a
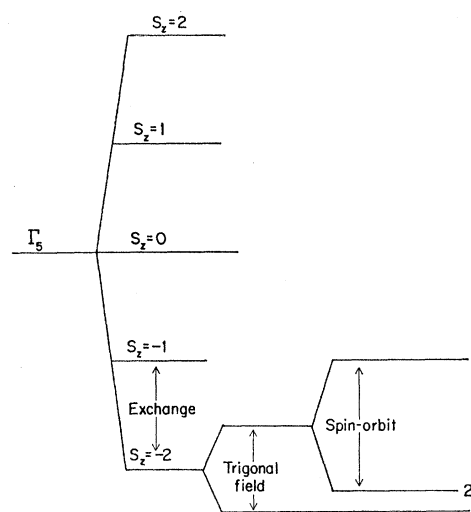
[7] R. W. Teale and K. Tweedale, Phys. Letters **1**, 298 (1962).
[8] B. Low, J. Appl. Phys. **33**, 1250 (1963).
[9] J. C. Slonczewski, Phys. Rev. **110**, 1341 (1958). J. C. Slonczewski, J. Appl. Phys. **325**, 253S (1961).

FIG. 1. Schematic energy level diagram for Fe^{2+} on B sites in the spinel lattice.

regular tetrahedron of oxygen ions, and the octahedral or B site is surrounded by an octahedron of oxygen ions. However the local symmetry about an octahedral site is not cubic but trigonal. In a *normal* spinel ferrite, the cation distribution is $(M^{2+})[Fe^{3+}]O_4$ where ( ) indicates A sites and [ ] indicates B sites. An inverse spinel has the distribution $(Fe^{3+})[M^{2+}Fe^{3+}]O_4$. Manganese ferrite is neither completely normal nor inverse. Neutron diffraction studies[10] indicate that $MnFe_2O_4$ is about 80% normal.

For an Fe^{2+} ion on a B site, the total Hamiltonian may be written

$$\mathcal{H}=\mathcal{H}_F+\mathcal{H}_C+\mathcal{H}_{ex}+\mathcal{H}_T+\mathcal{H}_{so},$$

where $\mathcal{H}_F$ is the Hamiltonian of the free ion (without spin-orbit energy), $\mathcal{H}_C$ gives the cubic-crystal field splitting ($\sim 10^4$ cm^{-1}), $\mathcal{H}_{ex}$ is the interatomic exchange energy ($\sim 10^3$ cm^{-1}), $\mathcal{H}_T$ is the trigonal crystal field, and $\mathcal{H}_{so}$ is the spin-orbit interaction ($\sim 10^2$ cm^{-1}). The free-ion terms $\mathcal{H}_F$ include intra-atomic exchange so that the ground state is described as $^5D_4$. This state is split by the cubic (octahedral) crystal field such that the lowest orbital state is a triply degenerate Γ_5 level. Each of the three levels within Γ_5 is fivefold spin degenerate as well. The interatomic exchange interaction, $\mathcal{H}_{ex}$, then removes the spin degeneracy leaving as the ground state an orbital triplet (Γ_5) with $S_z=-2$ as shown schematically in Fig. 1. This orbital triplet is then split by the trigonal field into a doublet and a singlet, and the doublet is finally split in first-order perturbation theory by the longitudinal part of the spin-orbit interaction. The sign of the trigonal field determines which is higher in energy, the doublet or the singlet. There is evidence, both experimental and theoretical,[11] that the sign of the

[10] J. M. Hastings and L. M. Corliss, Phys. Rev. **104**, 328 (1956).
[11] J. Smit, F. K. Lotgering, and R. P. vonStapele, J. Phys. Soc. Japan, **17**, Suppl. B-1, 268 (1962).

trigonal field is different for the normal and inverse spinel structures. This trigonal field arises from three separate contributions: (1) the neighboring metallic ions (2) the positions of the oxygen ions. (3) the electric dipoles of the oxygen ions. The latter two effects have a sign opposite to the first; and the sign of the total can change depending on which effects are predominant. Since manganese ferrite is only 80% normal, there will be many B sites which have surroundings partly characteristic of the normal structure and partly characteristic of the inverse structure. Thus, although the trigonal field splitting is typically of the order of $10^3 cm^{-1}$ in the fully inverse structure, it may be considerably smaller for many Fe^{2+} sites in manganese ferrite. If, in fact, the trigonal field splitting is comparable with the spin-orbit splitting ($\sim 80 cm^{-1}$), the interesting possibility arises of a pair of low-lying orbital levels split only by a few wave numbers, with the next excited state much higher in energy. This low-lying pair of energy levels is believed to be responsible for the relaxation phenomena described in this paper. At a given temperature the relative populations of the two levels is simply the Boltzmann factor. The energy splitting in question is clearly anisotropic for the spin-orbit splitting will depend on the orientation of the magnetization with respect to the crystal axes. Thus, when $\omega\tau \sim 1$ a slow relaxation theory is possible. One might also expect that the fast relaxation condition $\omega_1\tau \sim 1$ could be reached at temperatures lower than the Curie point for these are *orbital* levels and should have relatively shorter relaxation times than the exchange split *spin* levels of rare-earth ions in the garnets.

3. SLOW RELAXATION THEORY FOR $MnFe_2O_4$

The original slow relaxation theory as derived by Clogston[4] is directly applicable here for the subsidiary system is completely specified by a pair of energy levels. The two sublattice complications present in the rare-earth garnets does not enter into the present problem.[5] From Eq. (3–12) of Clogston's paper we may write

$$\Delta H = -\frac{n}{MkT}\sum_i \left[\left(\frac{\partial E_i}{\partial \theta}\right)\left(\frac{JN_{i\infty}}{\partial \theta}\right)\right.$$
$$\left. +\left(\frac{\partial E_i}{\partial \varphi}\right)\left(\frac{\partial N_{i\infty}}{\partial \varphi}\right)\right]\frac{\omega\tau}{1+(\omega\tau)^2},$$

where E_i is the energy of the ith level, n is the number of contributing Fe^{2+} impurities, and $N_{i\infty}$ is the equilibrium population in the ith level. For the two-level system of the present problem this simplifies to

$$\Delta\omega = \gamma\Delta H = \frac{C}{25\hbar}\left[\left(\frac{\partial \Delta E}{\partial \theta}\right)^2 + \left(\frac{\partial \Delta E}{\partial \varphi}\right)^2\right]$$
$$\times \frac{1}{kT}sech^2\left(\frac{\Delta E}{2kT}\right)\frac{\omega\tau}{1+(\omega\tau)^2}, \quad (1)$$

where C is the concentration of contribution Fe^{2+} impurities and $\Delta E = \hbar\omega_1$ is the energy splitting between the ground state and first excited state.

4. FAST RELAXATION THEORY FOR $MnFe_2O_4$

We wish to calculate the rate of energy loss from the process in which a $k=0$ magnon is annihilated, and an ion of the Fe^{2+} subsidiary system undergoes a transition from its lowest orbital state with one $k=0$ magnon in the total ferromagnetic system (which includes the Fe^{2+} spins) to its first excited orbital state with no magnons present. As described above, the Fe^{2+} energy levels are determined by the influence of the cubic crystal field, the interatomic exchange, the trigonal crystal field and the longitudinal part of the spin-orbit interaction. Denoting these terms as $\mathcal{H}_0$. we write the total Hamiltonian as

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{lifetime} + \frac{\lambda}{2}\sum_{Fe^{2+}}(L_i^+S_i^- + L_i^-S_i^+).$$

The term $\mathcal{H}_{lifetime}$ is that part of the Hamiltonian which determines the lifetime of the states corresponding to levels 1 and 2 of Fig. 1. This may be an interaction between the orbital angular momentum and the phonon bath or, may be the result of the finite lifetime of the sixth electron of Fe^{2+} on a given Fe site. In any case it must be sufficiently strong to significantly broaden the levels in question and hence is included in the unperturbed Hamiltonian. L and S are the orbital angular momentum and spin of the Fe^{2+} ion. This off-diagonal part of the spin-orbit coupling is the perturbation which causes the transitions in question. We assume for simplicity that the exchange coupling to the Fe^{2+} ions is identical to that with the Fe^{3+}. This is equivalent to neglecting the effect of the sixth $3d$ electron on the exchange interaction and should be a reasonable good approximation especially at high temperatures where this electron is relatively free to hop from one Fe site to the next. Introducing spin wave variables for S_i^+ and S_i^-:

$$S_i^+ = \left(\frac{S}{N}\right)^{1/2}\sum_k e^{-i\mathbf{k}\cdot\mathbf{r}_i}a_k,$$

$$S_i^- = \left(\frac{S}{N}\right)^{1/1}\sum_k e^{i\mathbf{k}\cdot\mathbf{r}_i}a_k^\dagger,$$

the above perturbation takes the form

$$\mathcal{H}' = \frac{\lambda}{2}\left(\frac{S}{N}\right)^{1/2}\sum_{Fe^{2+}}\sum_k(L_i^+e^{i\mathbf{k}\cdot\mathbf{r}_i}a_k^\dagger + L_i^-e^{-i\mathbf{k}\cdot\mathbf{r}_i}a_k).$$

The transition probability is calculated by using the golden rule

$$W = (2\pi/\hbar)\rho_F|\mathcal{H}_{12}'|^2,$$

where ρ_F is the density of final states and $\mathcal{H}_{12}'$ is the matrix element of the perturbing Hamiltonian from the

state with n_0 $k=0$ spin waves and orbital state 1; to a state with n_0-1 $k=0$ spin waves and orbital state 2 leaving all other magnon-occupation numbers constant. This matrix element is

$$\mathfrak{IC}_{12}' = (\lambda/2)(S/N)^{1/2}Ln_0^{1/2},$$

where L is the matrix element of L^- between orbital states 1 and 2. L may differ from its free-ion value due to partial quenching of the orbital angular momentum in the excited states so we shall leave it as a parameter. The density of final states at an energy ω above the ground state depends on the broadening of the levels by the lifetime τ. For $\omega \ll \omega_1$,

$$\rho_F = \frac{1}{\pi\hbar}\frac{\tau}{1+(\omega_1\tau)^2},$$

where as before ω_1 is the splitting frequency. Substituting in these expressions for ρ and $\mathfrak{IC}_{12}'$ one obtains after summing over the impurities

$$W = \frac{CS}{4\hbar}\frac{\lambda^2}{\hbar\omega_1}L^2\frac{\omega_1\tau}{1+(\omega_1\tau)^2},$$

where $C=n/N$ is the concentration of contributing Fe^{2+} impurities. Since the subsidiary system involved here is a simple two-level system, the only way it can proceed after excitation into its excited state is back toward equilibrium via interaction with the phonon bath or the hopping quasifree sixth electron. Thus, the diffusion arguments of deGennes, Kittel, and Portis[6] are not appropriate to the present case and the above transition probability is indeed the rate of loss of $k=0$ magnons. Thus, the present "fast" relaxation theory yields

$$\Delta\omega = \gamma\Delta H = \frac{CS}{4\hbar}\frac{\lambda^2}{\hbar\omega_1}L^2\frac{\omega_1\tau}{1+(\omega_1\tau)^2} \quad (2)$$

for the ferromagnetic resonance linewidth.

5. NUCLEAR RELAXATION OF Mn⁵⁵ IN MnFe₂O₄

The main difficulty in determining in a given case whether an observed linewidth peak is due to slow or fast relaxation effects is that each predicts a peak in linewidth as a function of temperature and of comparable magnitude. Thus, without extra information to determine the order of magnitude of τ a conclusive argument one way or the other is difficult. For this reason we consider the spin-lattice relaxation of the Mn^{55} nuclei in the same ferromagnetic medium. The dominant nuclear relaxation mechanism for Mn^{55} in low-anisotropy manganese ferrite arises from the *complex* frequency pulling brought about by relaxation in the ferromagnetic spin system.[12] This mechanism yields the following value

for T_1.

$$\frac{1}{T_1} = 2\frac{\delta\omega_N}{\omega_0}\eta\frac{\gamma_N}{\gamma_e}\frac{1}{T_{2e}}, \quad (3)$$

where $\delta\omega_N$ is the real part of the nuclear frequency pulling, ω_0 is the ferromagnetic resonance frequency, η is the single domain enhancement factor for nuclear excitation, γ_N and γ_e are the nuclear- and electronic-gyronmagnetic ratios, and $1/T_{2e}$ is the ferromagnetic relaxation time which limits the response of the ferromagnetic system to the applied rf field at the NMR frequency. This expression is the result of a solution of the coupled equations of motion of the ferromagnetic and nuclear spin systems being careful to relax the ferromagnetic magnetization vector always toward the instantaneous total effective field. In anticipation of the experimental results we assume that at 3°K where the peak in $1/T_1$ is observed, the time τ is sufficiently long that a slow relaxation theory is appropriate. Then

$$\frac{1}{\gamma_e T_{2e}} = \frac{A}{T}\text{sech}^2\left(\frac{\Delta E}{2kT}\right)\frac{\omega_N\tau}{1+(\omega_N\tau)^2}, \quad (4)$$

where A is a constant [see Eq. (1) above], and ω_N is the NMR frequency. This mechanism may be viewed as a coherent relaxation of the nuclear magnetization as a whole brought about by admixture of ferromagnetic character into the nuclear system. It is of particular interest in that it is the result of extra correlation induced in the nuclear spin system due to the long-range Suhl-Nakamura interaction between nuclei in a ferromagnetic medium. Even though the above mechanism is actually effective in relaxing only low-k nuclear excitations as a result of the k dependence of $\delta\omega_N$, in the present case the magnitude of $\delta\omega_N$ is comparable with the linewidth so that all nuclei remain on "speaking terms" with one another. The large linewidth therefore keeps the entire nuclear-excitation spectrum at a common spin temperature, and the nuclear system relaxes as a unit.

A comparison of nuclear and ferromagnetic relaxation effects similar to that proposed here has been made for rare-earth-doped YIG by Robert and Winter.[13] As a result of this work, an alternative mechanism for nuclear relaxation in a slow relaxing ferromagnetic medium has recently been proposed by Mme. Hartmann-Boutron[14] based on an indirect coupling of the nuclear spins to the relaxing impurities. This mechanism dominates in the case of Fe^{57} nuclei because of the low moment and small abundance of the isotope. However, for Mn^{55} the ratio of the frequency-pulling mechanism (A) to the Hartmann-Boutron mechanism (B) may be

[12] P. G. deGennes, P. A. Pincus, F. Hartmann-Boutron, and J. M. Winter, Phys. Rev. **129**, 1105 (1963).

[13] C. Robert and J. M. Winter, Comptes Rend. **253**, 2925 (1961).
[14] F. Hartmann-Boutron, J. Appl. Phys. Suppl. **35**, 153 (1964); also see Comptes Rend. **256**, 4412 (1962).

put in the form

$$\frac{(1/T_1)_A}{(1/T_1)_B} = 16\pi S\left(\frac{\hbar\delta\omega_N}{kT}\right)\left(\frac{\omega_{ex}}{\omega_0}\right)^{3/2} \simeq \frac{10^2}{T},$$

where ω_{ex} is the A-B exchange frequency for manganese ferrite ($\hbar\omega_{ex}/k \simeq 350°$K), and all other parameters are as defined above. Thus, at low temperatures, and in concentrated nuclear systems, the frequency-pulling mechanism appears to dominate by more than an order of magnitude.

6. EXPERIMENTAL RESULTS

The important features of the experimental data are shown in Fig. 2 and 3. As mentioned above a peak in $1/T_1$ is observed at about 3°K, and is shown by the experimental points of Fig. 2. In Fig. 3 we show the temperature dependence of the linewidth of the ferromagnetic resonance with the external field applied along a $\langle 111 \rangle$ direction. The linewidth data were taken in the usual way by measuring the power reflected from a shorted waveguide with a polished sphere (47 mils in diameter, with a 1-μ polish) of MnFe$_2$O$_4$ at the shorted end. The sample was kindly supplied by Dr. P. Seiden of IBM Research Laboratory and is believed to be high purity stoichiometric MnFe$_2$O$_4$. Data were taken from 1.6°K to room temperature. A scatter about the smooth curve drawn of approximately ± 3 Oe in ΔH near the high-temperature peak and somewhat less for smaller values of ΔH was observed. Two peaks in ΔH are evident, one at approximately 15°K and a second at 210°K.

The Mn^{55} T_1 data were obtained by a double resonance technique described earlier.[15] The same single-crystal sphere was used in the T_1 and the linewidth measurements. The double resonance technique makes use of the fact that in a ferromagnetic material, the field for electronic ferromagnetic resonance is shifted by
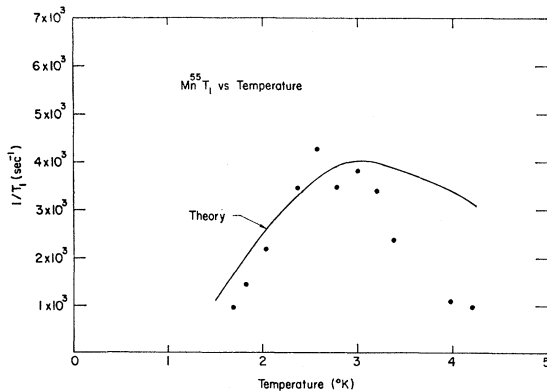
FIG. 2. $1/T_1$ versus temperature for Mn^{55} nuclei in MnFe$_2$O$_4$. The data were obtained by a double-resonance technique. The solid curve results from a slow relaxation theory.

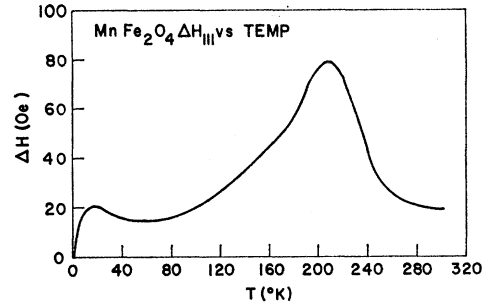[15] A. J. Heeger, S. K. Ghosh, and T. G. Blocker, III, J. Appl. Phys. **34**, 1034 (1963).

FIG. 3. Temperature dependence of the linewidth of the ferromagnetic resonance in MnFe$_2$O$_4$. The external field is along a $\langle 111 \rangle$ direction. The low-temperature peak arises from slow relaxation effects and the high-temperature peak from fast relaxation effects.

the amount

$$\delta H = (A/g\mu_B)\langle I_z \rangle$$

due to the hyperfine interaction with the polarized nuclear spins, where A is the hyperfine coupling constant, $g\mu_B$ is the electronic g value times the Bohr magneton and $\langle I_z \rangle$ is the expectation value of the nuclear spin. Using the value for A obtained from paramagnetic resonance, one finds $\delta H \sim 7/T$ Oe so that the shift is appreciable in the liquid-helium temperature range. If rf power is applied at the nuclear-resonance frequency $\langle I_z \rangle$ can be made arbitrarily small and the shift reduced to zero. Thus the position of the ferromagnetic resonance is a detector of nuclear absorption. For the measurements of spin-lattice relaxation time, a modulation technique was employed. If amplitude modulated rf power is applied at the NMR frequency, a periodic change in $\langle I_z \rangle$ at the modulation frequency will result. This effectively internally field modulates the electronic spin system and gives a ferromagnetic resonance signal, using narrow band detection, which is proportional to the change in nuclear magnetization (Δm_Z) at the modulation frequency. At a low modulation frequency the nuclei will follow the modulation and give maximum signal. As the modulation frequency increases beyond $1/T_1$ the nuclei will no longer be able to follow, and the resulting double-resonance signal will decrease. Thus the dependence of the signal on modulation frequency allows a direct measurement of T_1. Assuming the equation of motion for the Z component of the nuclear magnetization as given by Abragam[16]

$$dm_Z/dt = -2wm_Z - [m_Z - m_0/T_1],$$

where m_0 is the equilibrium value, and W is the transition probability, one finds that in response to low level amplitude modulated rf power, the magnitude of Δm_Z is given by

$$|\Delta m_Z| = |\Delta m_Z|_0/[1 + \omega^2 T_1^2]^{1/2},$$

where ω is the modulation frequency. Figure 4 shows the

[16] A. Abragam, *The Principles of Nuclear Magnetism* (Clarendon Press, Oxford, England, 1961), Chaps. II and IV.
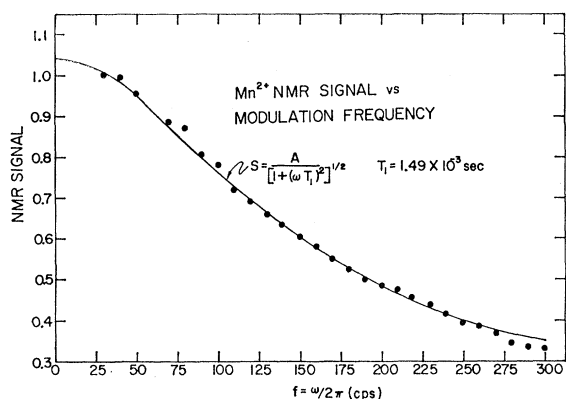
FIG. 4. Dependence of NMR signal on modulation frequency in the double resonance experiment. The solid curve is the expected theoretical curve for $T_1 = 1.49$ msec.

results of such a set of measurements at 1.65°K. The measured time is about 1.5×10^{-3} sec at 1.65°K. This kind of measurement was repeated at several temperatures in the helium range to obtain the data of Fig. 2.

7. COMPARISON OF EXPERIMENTAL RESULTS WITH THE SLOW AND FAST RELAXATION THEORIES

One is tempted to interpret the above data in the following manner:

(1) At low temperatures slow relaxation will yield a peak in $1/T_1$ when $\omega_N\tau \sim 1$ (see Eqs. (3) and (4)).

(2) At somewhat higher temperatures when $\omega_0\tau \sim 1$, a peak in the linewidth, again from slow relaxation, will result [see Eq. (1)].

(3) At still higher temperatures, when $\omega_1\tau \sim 1$ and a fast relaxation theory is appropriate, the second peak in ΔH will occur [see Eq. (2)].

In Fig. 5 we show, in more detail, the low-temperature peak in the ferromagnetic-resonance linewidth. The points are not raw data, but are obtained from the original data of Fig. 3 by subtracting off the extrapolated contribution from the high-temperature peak at the temperatures indicated in Fig. 5. Analysis of the data indicates that if a linear dependence of $1/\tau$ on the temperature is assumed, a self-consistent extrapolation is possible. At the temperatures in question, $T < 40°K$, we assume that $\omega_1\tau \gg 1$, so that the fast relaxation contribution is given by

$$\Delta H_{\text{fast}} \propto \frac{1}{\tau} \propto T .$$

The net contribution from the low-temperature peak is readily obtained, and is shown as the experimental points of Fig. 5. The solid curve is a plot of the expression

$$\Delta H = \frac{A}{T} \text{sech}^2\left(\frac{\Delta E}{2kT}\right)\frac{\omega\tau}{1+(\omega\tau)^2},$$

using the values $\Delta E/k \simeq 8°K$, $1/\tau = 1.45 \times 10^9 T$, and $A = 8.5 \times 10^2$. The resultant splitting ΔE is in qualitative agreement with the polycrystalline specific-heat measurements.[8] The linear dependence of $1/\tau$ on temperature confirms the extrapolation procedure described above for separating the fast and slow contributions at low temperatures.

As discussed in Sec. 5, the slow relaxation theory predicts at peak in $1/T_1$ at a lower temperature with a magnitude given by Eqs. (3) and (4). All quantities in Eqs. (3) and (4) are known or calculable. The frequency pulling is given by

$$\delta\omega_N/\omega_N = \eta m_0/M_0$$

where m_0 and M_0 are the nuclear and electronic magnetizations, respectively; and the constant A is determined by the fit to the slow relaxation theory described in the above paragraph. The solid curve of Fig. 2 is a plot of Eqs. (3) and (4) with no adjustable parameters using the same value of ΔE and $1/\tau$ as given above. The single domain enhancement factor

$$\eta = H_N/(H_0 + H_A)$$

is taken as 1.8×10^2. The magnitude of T_1 is correct, and the temperature dependence shows the qualitative features of the experiments. The more rapid falloff of the experimental points above 3°K is not presently understood. The agreement between theory and experiment is quite good for both the temperature dependence of the linewidth and $1/T_1$, and confirms the slow relaxation mechanism in $MnFe_2O_4$ at low temperatures. Furthermore, the quantitative agreement of the magnitude of $1/T_1$ with theory establishes the frequency pulling mechanism for the Mn^{55} nuclear relaxation.

The slow relaxation results described above yield a value for $\Delta E/k \sim 8°K$ and a temperature dependence for $1/\tau$; $1/\tau = 1.45 \times 10^9 T$ for $T < 40°K$. We next assume that the high temperature linewidth peak is the result of fast relaxation effects; and use the experimental data to determine the temperature dependence of τ and the
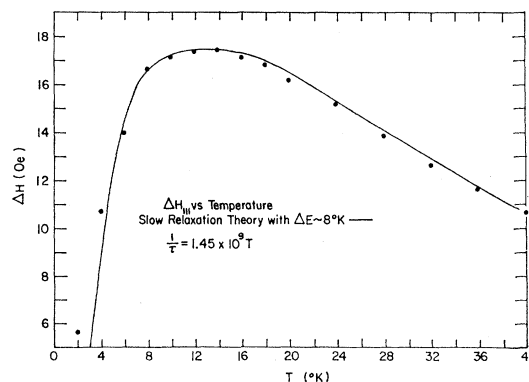

FIG. 5. Comparison of slow relaxation theory for ferromagnetic-resonance linewidth with experiment at low temperatures. The solid curve is a plot of Eq. (1) for $\Delta E/k = 8°K$ and $1/\tau = 1.45 \times 10^9 T$.
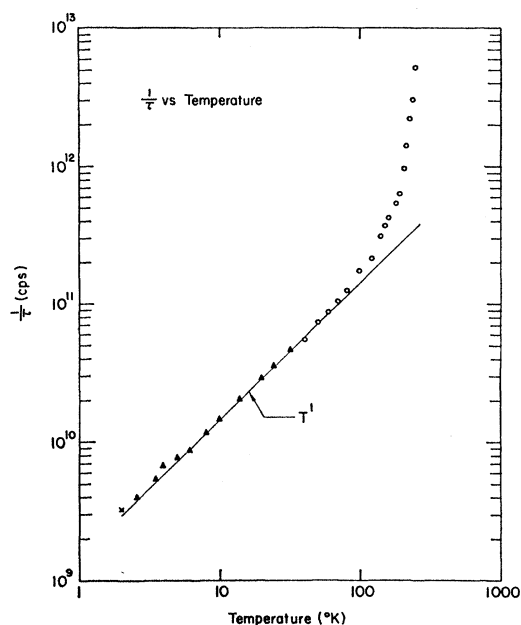
FIG. 6. Log-log plot of $1/\tau$ versus temperature as determined from the relaxation data. The point marked ✗ comes from nuclear-resonance measurements, the solid triangles from the slow relaxation theory, and the open circles from the fast relaxation theory.

magnitude of ω_1 from Eq. (3). If this assumption is correct, the resulting τ and ω_1 must be consistent with the low-temperature values.

Figure 6 shows the results of such an analysis. $1/\tau$ is plotted as a function of temperature on a log-log graph. The results cover two orders of magnitude in temperature and three orders of magnitude in $1/\tau$. The point marked with X is obtained from the nuclear resonance results ($\omega_N\tau=1$), the solid circles demonstrate the accurate fit of the slow relaxation theory at low temperatures; and the open circles are obtained from the fast relaxation theory with $\omega_1=1.4\times10^{12}$, or

$$\hbar\omega_1/k=10°K .$$

The value for ΔE from the slow theory at low temperatures ($\Delta E\sim8°K$) and the fast theory at higher temperatures ($\Delta E\sim10°K$) are in excellent agreement. Furthermore, the values of $1/\tau$ from essentially *three separate theories* join continuously. The remarkable self-consistency of all these results appears to confirm the interpretation of slow relaxation at low temperatures and fast relaxation at higher temperatures in MnFe₂O₄.

Finally, we note that both the slow and fast theories predict linewidth peaks proportional to the number of contributing Fe²⁺ impurities. From Eq. (2), one finds that a concentration C such that

$$CL^2\sim5\times10^{-4}$$

is needed in order to account for the magnitude of the 210°K. Similarly, using Eq. (1), and assuming that the

anisotropy in ΔE is comparable with ΔE itself, (the specific-heat data on polycrystalline material suggests a continuous distribution of ΔE's up to about 20°K) one finds

$$C\sim5\times10^{-3}$$

To be consistent, one needs a value of $L^2=.1$ in the crystal. Although this is quite small, it does not appear impossible.

The above concentration is roughly an order of magnitude less than that obtained from the specific-heat data. The origin of this discrepancy is not presently understood, but may simply reflect the fact that the single-crystal sphere used in the relaxation measurements is more nearly stoichiometric. This is perhaps consistent with the fact that the ferromagnetic-resonance widths reported here are the narrowest to be found in the literature for nominal MnFe₂O₄.

8. ORIGIN OF THE RELAXATION TIME OR LIFETIME τ

The linear dependence of $1/\tau$ on the temperature for $T<100°K$ suggests that a direct relaxation process to the phonon or magnon bath is dominant. As indicated in Sec. 2, the splitting between the doublet and singlet is sensitive to the magnitude of the trigonal crystal field; and the magnitude of this crystal field is clearly proportional to the trigonal distortion of the lattice. Consequently, the orbital angular momentum is strongly coupled to lattice strains or phonons. This kind of process was first calculated by Van Vleck[17] in connection with paramagnetic spin-lattice relaxation times. The result is proportional to the number of thermal phonons within a narrow frequency band, and hence is proportional to the temperature.[18] Similar arguments can be made using the magnon bath for there is a high density of magnon states 8°K above the ground state.

Figure 6 shows a strong deviation from linearity for temperatures greater than 100°K. It appears that another, faster mechanism determines the width of the Fe²⁺ levels at these higher temperatures. A possible mechanism for limiting the lifetime of these Fe²⁺-orbital states is the well known mobility of the sixth $3d$ electron of Fe²⁺ among B sites of the spinel lattice. As far as this extra electron is concerned, any Fe site is equivalent. However, to get from one site to the next the electron must go over a relatively large energy barrier, for while hopping, it is not bound to either ion. This is clearly an example of a thermally activated process; the probability of hopping being proportional to $\exp(-\epsilon/$

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

[18] For $\Delta E/2kT>1$, the direct process τ becomes independent of temperature [R. Orbach, J. Appl. Phys. **33**, 2144, (1962)]. This temperature independence does not seem to show up below 4°K; however, the NMR experiments in this range are not particularly sensitive to τ. Most of the temperature dependence shown in Fig. 2 arises from the explicit temperature dependence of Eq. (4). A temperature-independent τ for $T<4°K$ would improve the agreement between theory and experiment in Fig. 5 in this temperature range. Thus, even for $T<\Delta E/2k$ the direct process is not inconsistent with the data.
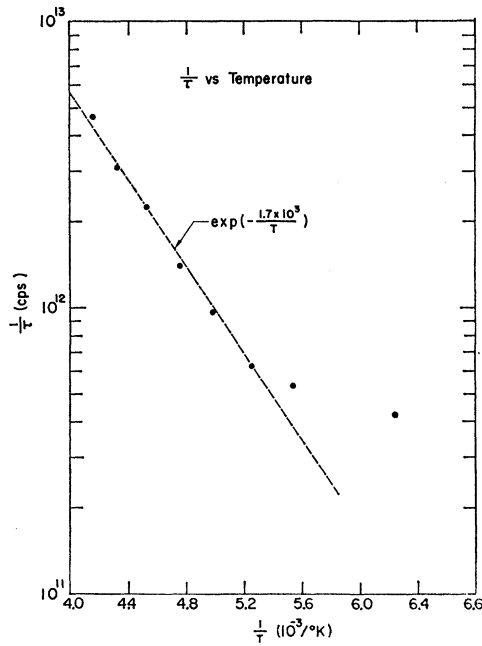
FIG. 7. Semilog plot of $1/\tau$ versus $1/T$ at higher temperatures. The exponential variation indicates that the width of the orbital levels is determined by the lifetime of the 6th $3d$ electron on a given Fe ion as a result of the hopping mechanism.

kT), where ϵ is the activation energy. The validity of this model in the manganese-ferrite system has been adequately demonstrated by resistivity measurements.[19] These measurements give the result,

$$\rho = \rho_0 e^{-\epsilon/kT}$$

as expected from the above model; and furthermore give a value for the activation energy of approximately 0.1eV. In Fig. 7 we show the high-temperature values of $1/\tau$ on a semilogarithmic plot as a function of $1/T$, where T is the temperature in °K. The straight line nature of the curve indicates a temperature dependence of the form

$$\frac{1}{\tau} = \frac{1}{\tau_0} e^{-(1.7 \times 10^3/T)}$$

The activation energy of 1.7×10^3°K ~ 0.2 eV agrees favorably with the resistivity results. Thus, although direct phonon or magnon relaxation determines the width of the Fe^{2+} orbital states at lower temperatures, at the temperature of the maximum in ΔH this width,

[19] K. Zaveta, Czech. J. Phys. 9, 748 (1959).

is determined by the lifetime of the quasifree electron on a given Fe site.

9. CONCLUSION

In this paper we have presented experimental and theoretical evidence indicating the importance of "fast" and "slow" relaxation effects in $MnFe_2O_4$. The details of the theories are different from the rare-earth substituted garnets, e.g., the origins of the energy levels and relaxation times or lifetimes, but the essential ideas are in many ways quite similar.

It is interesting to note that the concentration of Fe^{2+} ions contributing to the relaxation phenomena ($\sim 10^{-3}$) is quite small compared to concentrations usually believed present in "stoichiometric" $MnFe_2O_4$. The same kind of conclusion is reached by Smit et al.[11] in connection with the effect of Fe^{2+} on the magnetocrystalline anisotropy of the Mn-Fe spinels. These results emphasize the importance of the details of the Fe^{2+} trigonal field splitting in determining the magnetic properties of these materials. More detailed calculations of these trigonal field splittings in a partially normal and partially inverse environment would be of interest.

Note added in proof. We have calculated the magnitude of the direct relaxation process to the magnon bath as suggested by the linear temperature dependence discussed in Sec. 8 above. Again using the nondiagonal part of the spin-orbit Hamiltonian as the perturbation, one calculates

$$\frac{1}{\tau} = \frac{\lambda^2 S}{8\pi\hbar^2} L^2 \frac{(\Delta E/\hbar)^{1/2}}{(\gamma H_E)^{3/2}} \frac{kT}{\Delta E}.$$

Substituting in all the previously determined parameters, one obtains

$$\frac{1}{\tau} \cong 2 \times 10^9,$$

in excellent agreement with experiment. Details will be published elsewhere.