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Nuclear Magnetic Resonance in Metals

Nuclear Relaxation in Magnetic Materials

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Studies of relaxation of nuclei in ferromagnetic and antiferromagnetic materials are reviewed. Two recent problems are discussed in more detail. One problem of interest in the interaction between nuclear spins is the diffusion of spin excitation through an inhomogeneously broadened line-spectral diffusion. The experimental observations in the case of the Co^{59} resonance in fcc cobalt metal are described. The general agreement of the experimental results and the phenomenological theory establishes that the spin-spin interaction is of unusually long range. A second problem associated with the relaxation of nuclear spins to the spin wave reservoir is provided in the antiferromagnetic resonance studies of $KMnF_3$. At high microwave power levels and at 4.2° a heating of the Mn^{55} nuclear spins may be observed. At 1.8 and 2.2° and at much lower power levels the experimental results suggest nuclear cooling. The related theoretical work of Oguchi and Keffer is noted.

1. Introduction

Nuclear resonance in ordered magnetic materials was first discovered by Poulis and Hardeman[1], who studied the resonance of protons in $CuCl_2 \cdot 2H_2O$. Hardeman *et al.*[2] have measured the proton spin-lattice relaxation time up to the Néel point in this material. Moriya[3] has examined the theory of relaxation in antiferromagnetic materials where the nuclear frequency lies below the bottom of the spin wave spectrum. He considers Raman scattering of spin waves by the protons with the coupling through the dipolar fields of the magnetic ions. At high temperatures, where the spin wave approximation is no longer valid, he treats the problem in terms of the fluctuations in the dipolar field. Good agreement with experiment can be obtained for $CuCl_2 \cdot 2H_2O$ by assuming an empirical density of states which also fits the T^4 drop in the magnetization and the heat capacity data. A similar analysis has been performed independently by van Kranendonk and Bloom[4].

With the observation of the F^{19} resonance in the iron group flourides[5] it has been possible to study nuclear relaxation in the spin wave region with greater precision[6]. Moriya's theory suggests that $1/T_1$ should increase as T^3 at temperatures high compared with the energy gap. At lower temperatures the relaxation should be an exponential function of temperature. However the observed relaxation shows a very much weaker temperature dependence than this theory suggests.

The direct observation of the Co^{59} resonance in CoF_2 has made possible the study of the relaxation of the nuclei on magnetic ions in this material[7]. The nuclear relaxation of the Mn^{55} nuclei in $KMnF_3$ has been studied indirectly by means of the shift in the antiferromagnetic resonance[8] and only a weak dependence of the relaxation rate on temperature has been observed. Moriya[9] has applied his earlier theory to the relaxation of nuclei on magnetic ions with corresponding results. He also points out that T_1 and T_2 need not be identical in an anisotropic medium and that if the fluctuations are restricted to the transverse fields we may expect the relation $T_2=2T_1$. Mitchell[10] has constructed a similar theory except that in-

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stead of using dipolar coupling he imagines that the nuclei and electrons are quantized along slightly different directions. Such a situation would permit the hyperfine coupling to be effective in Raman processes. This theory may give a relaxation rate in better agreement with experiment at low temperatures but the temperature dependence is still the same as that of Moriya.

Very recently Nakamura[11] and Pincus and Winter[12] have proposed a new low temperature relaxation mechanism, which should be effective in producing relaxation at frequencies below the gap. These authors point out that spin-wave phonon coupling will give a magnetic character to the acoustical phonon branch at frequencies below the bottom of the spin wave spectrum. Thus one may have direct relaxation processes down to the lowest temperatures. These theories are very sensitive to the coupling constant but still suggest a very promising solution to what has been a serious theoretical problem.

In ferromagnetic materials the lattice relaxation is also surprisingly rapid with only a very weak temperature dependence. The nuclear relaxation of Fe^{57} in yttrium iron garnet has been studied by Robert[13] and Weger[14]. A relation between T_1 and T_2 close to that proposed by Moriya[9] seems to be apparent. In the ferromagnetic metals, iron, cobalt, and nickel[15], the situation is complicated by domain wall effects but there is strong evidence that the relaxation rate for bulk nuclei is linear in the temperature. This relation over a wide temperature range seems to suggest conduction electron processes[16] but the observed relaxation is at least an order of magnitude too fast. Weger *et al.*[17] have proposed that the conduction electron-nuclear coupling may be considerably enhanced in a magnetic metal leading to more rapid relaxation. The still faster relaxation of nuclei in walls has been treated by Winter[18] in terms of damped wall motion.

In addition to the coupling between resonant nuclei and the lattice, these nuclei may interact with each other. Suhl[19] and Nakamura[20] have treated this interaction in terms of the virtual emission and reabsorption of spin waves. Such a mechanism gives nuclear linewidths in antiferromagnetic materials in good agreement with experiment. This coupling may also lead to the diffusion of spin excitation through space as is observed in ferromagnetic materials[14], where the excitation may be confined to the narrow walls between domains. There is also the possibility, where the over-all line width is determined by a field inhomogeneity, that the nuclear spin-spin coupling can transfer energy across the resonance line. Experiments by Weger[14] which demonstrate this transfer and the relevant theory are discussed in Section II.

One of the striking adjuncts of relaxation studies has been the polarization produced when an intermediate system in the relaxation process is disturbed in some way. This kind of process was first proposed by Overhauser[21]. Similar studies on ordered magnetic materials have been discussed by Oguchi and Keffer[22]. In Section III an experiment which Heeger[23] has performed on $KMnF_3$ is described. These experiments, which indicate that the Mn^{55} nuclear spins may be cooled by microwave excitation, are closely related to the proposal of Oguchi and Keffer.

2. Spectral Diffusion

In his classic paper on nuclear spin echoes, Hahn[24] showed that the spacial diffusion of nuclei through an inhomogeneous field could be studied from the intensity of the "stimulated" echo. In this measurement a pair of rf pulses are applied separated by a time τ. At a time 2τ the usual spin echo, which decays with a characteristic time T_2, may be observed. If a third pulse is applied at a time t following the second pulse, a second echo is developed. Hahn found that for various values of t, the decay of this echo was exponential with a characteristic relaxation time

$$1/T' = 1/T_1 + D\tau^2 , \qquad (1)$$

where T_1 is the lattice relaxation time and D is a constant which is related to the spacial diffusion of the spins.

Following a pair of 90° pulses a system of stationary spins will have a periodic variation in the component of spin density along the applied field:

$$I_z(\omega) = I_0(\omega)\{1-\exp(-t/T_1) \times [1+\exp(-\tau/T_2)\cos\omega\tau]\}) , \qquad (2)$$

With the application of a third 90° pulse a

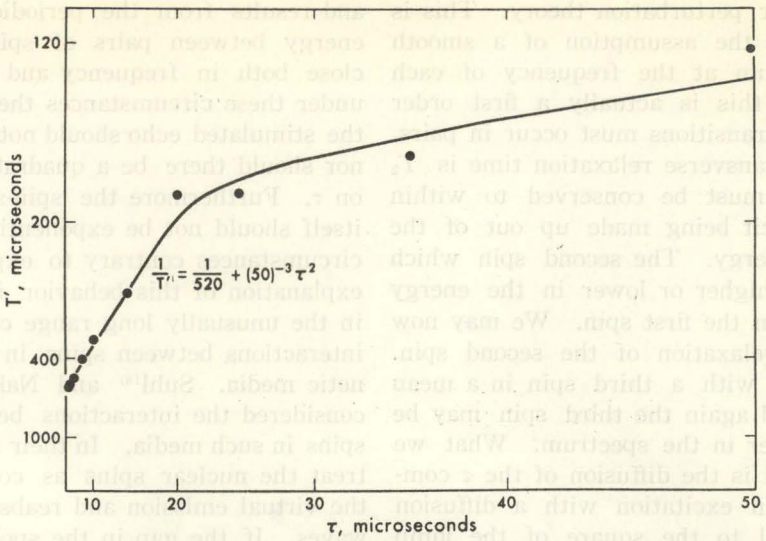

Fig. 1. Plot of the relaxation rate for the stimulated echo as a function of the square of the time between the initial pulses. The linear increase in rate is characteristic of a diffusion process.

stimulated echo of intensity

$$I_y = \frac{1}{2} I_0 \exp(-t/T_1) \exp(-2\tau/T_2) \qquad (3)$$

will be observed. But if there is the possibility of spacial diffusion of the nuclear spins through the field inhomogeneity, the oscillation of the z component will be partially washed out by this motion. We write for the equation of motion of the z component

$$\frac{\partial I_z(\omega)}{\partial t} = -\frac{I_z(\omega) - I_0(\omega)}{T_1} + D\frac{\partial^2 I_z(\omega)}{\partial \omega^2} \qquad (4)$$

where D is the constant for the diffusion of the z component of spin along the frequency spectrum. This diffusion constant is simply the spacial diffusion coefficient times the gradient of the resonance frequency squared. The solution of Eq. (4) is the same as without diffusion except that in place of the lattice relaxation rate $1/T_1$ we have an apparent longitudinal time of the form given in Eq. (1). Actually a simple result of this kind is expected only as long as the inverse time $1/\tau$ is larger than the change in frequency experienced by a spin in going one mean free path so that the process is in fact one of diffusion. At the other limit $1/\tau$ must be smaller than the line width. This is only because we have neglected the effects of the limited spectrum in the derivation of this expression. Experimental studies using this technique[25] generally confirm the theory.

In the experimental investigation of the Co^{59} nuclear relaxation in fcc cobalt metal, a study of the stimulated echo has been made[14) 26]. In Fig. 1 are shown the results of Weger[14] for the variation of $1/T'$ with τ^2 as observed at 77°K. At this temperature the spin-spin relaxation is observed to be about 30 μ sec. The lattice relaxation at high powers is exponential with a characteristic time of 1.2 msec. The experimental results of Fig. 1 are quite similar to those for a diffusion process. For very short values of the time between pulses τ the stimultated echo decays exponentially with the lattice time T_1. The rate of increase of $1/T'$ with τ^2 is closely linear. For values of τ approaching T_2 the relaxation rate increases less rapidly, suggesting that the value $1/T_2$ may provide a limiting rate for the longitudinal relaxation. It seems quite unusual that the results should so closely parallel the situation with liquids where the nuclear spins are carried bodily through the resonance spectrum by spacial diffusion. But we must clearly look to some other mechanism for an explanation.

Some time ago the author[27] was interested in the effects of weak coupling between paramagnetic impurity centers in a diamagnetic crystal where the over-all resonance width was inhomogeneous in character. In this theory the single spin relaxation was treated

by first order perturbation theory. This is equivalent to the assumption of a smooth power spectrum at the frequency of each spin. But if this is actually a first order process spin transitions must occur in pairs. Now if the transverse relaxation time is T_2 then energy must be conserved to within $1/T_2$, the deficit being made up out of the interaction energy. The second spin which flips may be higher or lower in the energy spectrum than the first spin. We may now consider the relaxation of the second spin. It will relax with a third spin in a mean time T_2. And again the third spin may be higher or lower in the spectrum. What we have described is the diffusion of the z component of spin excitation with a diffusion constant equal to the square of the jump distance divided by the jump time or

$$D \simeq (1/T_2)^3 . \qquad (5)$$

The experimental results of Fig. 1 suggest a spin-spin time $T_2 \simeq D^{-1/3} = 50\,\mu$ sec, which is to be compared with the observed time of about $30\,\mu$ sec. Considering that the theoretical arguments are qualitative this agreement may not be unreasonable.

Anderson[28] has examined this problem carefully because of the interesting related problem of charge transport between localized impurity centers. Anderson finds that if (1) the interactions between spins are small compared with the width of the resonance spectrum and (2) the interactions between spins fall off faster than $1/r^3$, then the energy will remain localized and there is no diffusion. For a pair of spins in strong interaction there may be exchange of energy back and forth, but there is very little liklihood that a pair of strongly interacting spins will also be sufficiently close in frequency to permit real energy transfer. And more distant sites, which may be close in energy, are not important because the interaction weakens faster than the number of such spins increases. For the interaction falling off exactly as $1/r^3$ as in the case of dipolar interaction there is real diffusion, but the diffusion coefficient is very much smaller than suggested by Eq. (5).

How then are we to understand the appearance of diffusion in the case of the Co^{59} resonance in ferromagnetic cobalt. One possibility is that the diffusion is only apparent and results from the periodic exchange of energy between pairs of spins, which are close both in frequency and position. But under these circumstances the relaxation of the stimulated echo should not be exponential nor should there be a quadratic dependence on τ. Furthermore the spin-spin relaxation itself should not be exponential under such circumstances contrary to experiment. The explanation of this behavior is to be found in the unusually long range character of the interactions between spins in ordered magnetic media. Suhl[19] and Nakamura[20] have considered the interactions between nuclear spins in such media. In their formalism they treat the nuclear spins as coupled through the virtual emission and reabsorption of spin waves. If the gap in the spectrum is small compared with the maximum spin wave energy then the interaction is of quite long range and takes the simple form for a ferromagnetic medium:

$$W_{ij} = \frac{\hbar\omega^2}{8\pi s\omega_{ex}} \frac{a}{r_{ij}} \cdot \exp\left[-\left(\frac{\omega_{loc}}{\omega_{ex}}\right)^{1/2} \frac{r_{ij}}{a}\right] [I_i^+ I_j^- + I_i^- I_j^+] , \qquad (6)$$

where ω_{loc} and ω_{ex} are defined by the dispersion relation $E(k) = \hbar(\omega_{loc} + \omega_{ex} a^2 k^2)$. Thus the interaction falls off only as $1/r$ at short distances and has an exponential cut-off at a distance which is a domain wall thickness and is of the order of 30 lattice constants in cubic cobalt. The rms interaction as given by Suhl[19] is

$$\langle \Delta\omega^2 \rangle^{1/2} = (\omega^2/s\omega_{ex})[I(I+1)/24\pi]^{1/2} (\omega_{ex}/\omega_{loc})^{1/4} \qquad (7)$$

If we take $\omega_{ex}/\gamma \sim 10^6$ oe we compute a relaxation time

$$\langle \Delta\omega^2 \rangle^{-1/2} = 7.1\,\mu \text{ sec}$$

which is an order of magnitude shorter than the observed time. But the perturbation theory indicates why the observed time will not be as short as the second moment suggests. Since the over-all line width is much larger than the computed spin-spin coupling, we can expect that the broadening will inhibit the relaxation. Most of the spin-spin coupling is associated with spins at large distances and we will expect for the relaxation rate[27]

$$1/T_2 \sim \langle \Delta\omega^2 \rangle / \delta\Omega \qquad (8)$$

where $\delta\Omega$ is the effective width inhibiting

relaxation. A value of $\delta\Omega/2\pi$ equal to 100 kc/sec is in agreement with the observed value of T_2 and is more consistent with the general relaxation behavior than is the observed half width of 800 kc/sec. This suggests that there is a local inhomogeneity in the resonance field of the order of 100 oe and that the over-all line width corresponds to inhomogeneities on a scale large compared with the screening distance. It appears then that the occurrence of spectral diffusion may be readily understood in terms of the quite long range interaction between nuclear spins in a magnetic medium.

Perhaps a final word should be said concerning the resonance excitation mechanism. As has been noted[29] the excited nuclei lie in and near domain walls. At low rf powers the observed signal is from those nuclei near the centers of walls and from thoes walls which are most free to move. As the rf field is increased other nuclear spins contribute to the signal. The observed lattice relaxation time depends on power level ranging from 150 μ sec at 77°K and at low power levels to the value of 1.2 msec at high powers quoted earlier. Thus although the numbers quoted here differ somewhat from those of Sugibuchi *et al.*[26], the same general relations as given by Eqs. (1) and (5) apply to both sets of data.

3. Nuclear Cooling Through Spin Wave Excitation

As a second problem, which suggests a method for studying nuclear-spin wave coupling, and possibly spin wave relaxation itself, we describe some recent microwave observations in antiferromagnetic $KMnF_3$.

At room temperature $KMnF_3$ is paramagnetic and has the perovskite structure[30]. At the Néel temperature of 88.3°K there are orthorhombic distortions, which lead to a canting of the magnetic sublattices very similar to that of NiF_2[31] but with a much smaller moment[32]. The structure is still very nearly cubic so that the antiferromagnetic resonance modes should be quite low in frequency even though the exchange field is of the order of 10^6 oe as indicated from the static susceptibility at the Néel point. For the external field along a ⟨100⟩ direction, which is the direction of the weak moment, resonance is expected at a field given by[23]

$$H_0=-\frac{5}{2}H_{A2}+\left[\frac{9}{4}H_{A2}^2+\left(\frac{\omega}{\gamma}\right)^2+5H_EH_{A4}-2H_EH_{A1}\right]^{1/2} \quad (9)$$

The field H_{A2} is associated with the canting and has been measured to be 1300 oe[32]. The field H_{A4} arises from the zero point cubic anisotropy and has been estimated by Pearson[33] to be 0.3 oe. The field H_{A1} is associated with the axial distortion in the crystal. Crystal field terms and dipolar terms are of the order of 80 oe each but opposite in sign. The observed resonance field at 4.2°K and 9.43 kMc/sec is 2740 oe, suggesting a value for H_{A1} of 4.5 oe. One would expect that these fields would all be reasonably independent of temperature below 4.2°K and that no temperature dependence of H_0 should be expected. But as shown in Fig. 2 there is a very strong temperature dependence with the field dropping by nearly 1000 oe on cooling to 1.8°K. The explanation of this behavior is found in the anisotropy field contributed by the Mn^{55} nuclei. These nuclei are magnetized by the hyperfine field and in

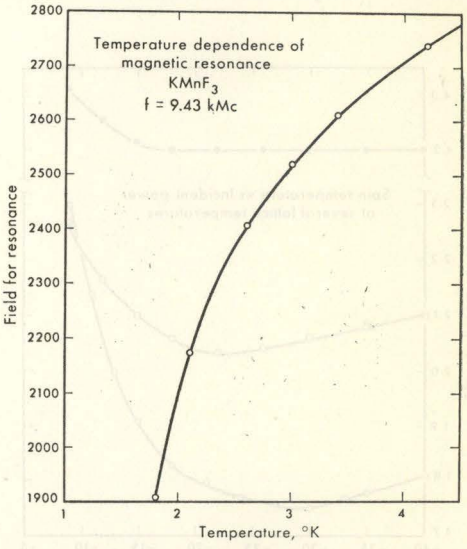

Fig. 2. Temperature dependence of the antiferromagnetic resonance in $KMnF_3$ with the static field along a <100> direction. The solid curve is theoretical and is based on the anisotropy arising from the hyperfine interaction.

turn contribute a field which may be computed from hyperfine data[34] to be

$$H_{A1}^{n} = 8.0/T \text{ oe.}$$

The theoretical curve shown in Fig. 2 is drawn taking H_{A_1} to have a temperature dependent component of this magnitude. The exchange field was adjusted to 1.6×10^6 oe in order to fit the experimental points. Thus the field for resonance provides a very sensitive indication of the Mn^{55} nuclear temperature. This interpretation of the field shift has been fully confirmed by the observation of the Mn^{55} nuclear resonance absorption around 628 Mc/sec by means of the induced shift in the resonance field as a result of the partial nuclear saturation[8].

At 4.2°K for microwave powers above 6 mw incident on the microwave cavity the resonance is observed to shift to higher fields. This is the power level at which breakdown occurs as suggested by other measurements[23] and it may be presumed that the field shift reflects an increase in the nuclear temperature through coupling to the spin waves. This observation already suggests that coupling between nuclei and the spin system may be strong since precautions are taken in these experiments to maintain the lattice temperature constant. Similar experiments have been performed at 1.8 and 2.1°K with the results shown in Fig. 3. It may be seen that at these lower temperatures there is a decided cooling of the nuclei at powers well below breakdown. It may be that at these power levels most of the spin wave excitation is confined to the low frequency part of the spectrum.

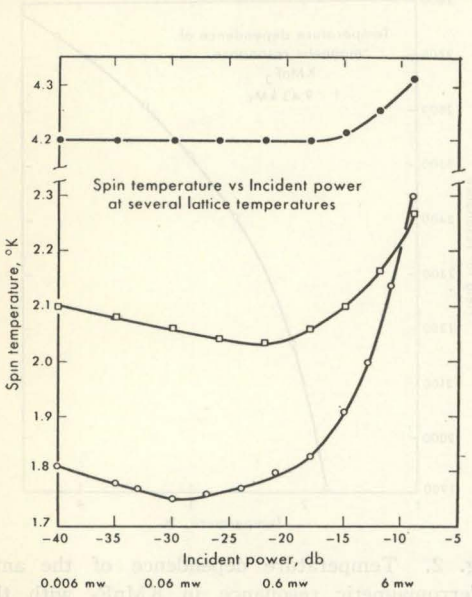

Fig. 3. Apparent spin temperature of the Mn^{55} nuclei as a function of incident microwave power. The spin temperature is determined from the field for antiferromagnetic resonance.

Oguchi and Keffer[22] have pointed out the possibility of Overhauser nuclear polarization in an axial antiferromagnet as long as the excitation is contained in the low frequency regions of the spin wave spectrum. But according to their arguments strong spin-spin coupling will inhibit this polarization. Although the situation which they have considered is not identical with the present problem their general considerations may be relevant.

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DISCUSSION

C. KITTEL: The contribution of the Mn nuclear interaction to the effective field might perhaps make a perceptible contribution to the EPR line shifts observed in dilute alloys of Mn in Cu.

A. M. PORTIS: Where the manganese spins have a low local anisotropy, the nuclear hyperfine interaction may be important at temperatures in the liquid helium range.

T. OGUCHI: Can you apply external magnetic field along the easy axis in $KMnF_3$?

A. M. PORTIS: The presence of canting in this material makes it preferable to apply the field in the transverse direction. One could perform experiments with the field along the *c* axis but unfortunately this still would not give the kind of mode structure which you and Keffer have considered.

H. SUHL: Several years ago, Dr. M. T. Weiss of Bell Telephone Laboratories observed what he interpreted as small power shifts in the *g*-factor of ferromagnetic resonance in manganese ferrite. Perhaps in this case, too, the change in temperature of the manganese nuclei is responsible for the effect observed by Dr. Weiss.

A. M. PORTIS: The additional anisotropy field amounts to 2 oe at 4.2°K. High precision *g*-factor measurements may well have revealed shifts of this magnitude in the observed field for resonance.