# Nuclear Magnetic Resonance Modes in Magnetic Material. I. Theory

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In a magnetic medium the nuclear spins are coupled by the Suhl-Nakamura indirect interaction. This interaction is weak but has a very long range $b$. It is known to contribute to the nuclear spin relaxation. It also gives rise to a displacement of the nuclear magnetic resonance frequency which is important at temperatures in the helium range for materials with a large concentration of nuclei and large $b$. More generally the indirect interaction gives rise to a spectrum of nuclear spin waves. This spectrum may be shown to be meaningful even when the nuclei are far from order because of the long range of the interaction. Different methods to observe this spectrum are discussed.

## I. INTRODUCTION

NUCLEAR magnetic resonance has been observed in a large number of ferromagnetic and antiferromagnetic compounds.[1] The resonance frequency $\omega_n$ is usually derived by the following arguments: If the hyperfine interaction between the nuclear spin $\mathbf{I}$ and the electron spin $\mathbf{S}$ is $A\,\mathbf{I}\cdot\mathbf{S}$, there is an average hyperfine field acting on the nucleus, of magnitude

$$H_n=-A\langle S\rangle/\hbar\gamma_n, \tag{1.1}$$

where $\gamma_n$ is the nuclear gyromagnetic ratio, and $\langle\ \rangle$ denotes a thermal average. Equation (1.1) for the resonance field is in fact correct only to first order in the coupling constant $A$. It neglects all correlations between the motions of $\mathbf{I}$ and $\mathbf{S}$. This is obviously a good approximation in many cases, since the hyperfine interaction is very small compared to the exchange coupling $J$ between electron spins. In fact, if one looks at the exact eigenmodes of a single nuclear spin in a ferromagnetic matrix,[2] one finds that the deviations from Eq. (1.1) are of relative order $A/J$ and thus completely negligible at all temperatures.

The situation is changed if we have a large density of nuclei; then if one of them, $\mathbf{I}_i$, is tilted by an angle $\theta$ with respect to the electron magnetization, it distorts the electron spin arrangement. The distortion is of order $(A/J)\langle I_z\rangle\theta$, and thus very small, but it has a long range in space and thus reacts on the motion of many other nuclear spins. The number of active neighbors is of order $J/\hbar\omega_e$ (where $\omega_e$ is the electron resonance frequency) and the relative correction to Eq. (1.1) is then of order $(A/J)\langle I_z\rangle(J/\hbar\omega_e)=A\langle I_z\rangle/\hbar\omega_e$. This "frequency pulling" will thus be important at low temperatures ($\langle I_z\rangle$ not too small) provided that (a) the concentration of nuclear spins is large (this will be realized with $Co^{59}$ and $Mn^{55}$) and (b) the electron spin resonance frequencies are low (small anisotropy fields). When these conditions are realized the nuclear resonance behavior may be drastically different from what it is in the usual case. This possibility was mentioned in a previous note.[3] The purpose of the present paper is to give a more thorough discussion of the effect and of its consequences on nuclear induction signals. In Sec. II we derive the macroscopic equations for the coupled nuclear-electron spin system for various cases of interest (ferromagnets, antiferromagnets, Bloch walls$\cdots$). In Sec. III we come back to the microscopic description, and derive the spectrum of the nuclear spin waves. The most remarkable result is that these spin waves correspond to well-defined excitations of the nuclear spin system even at comparatively high temperatures ($\sim$1°K), where the nuclear spins are strongly disordered. Section IV is concerned with a discussion of some effects of demagnetizing fields on the nuclear spin wave spectrum. In Sec. V we discuss the effects of the frequency pulling on nuclear resonance signals for both steady state and transient behavior.

## II. MACROSCOPIC EQUATIONS OF MOTION

### Ferromagnetic Case

Let us first consider a saturated ferromagnetic material, of electronic magnetization $\mathbf{M}$ and nuclear magnetization $\mathbf{m}$. The field acting on the nuclei is the sum of the external field $\mathbf{H}_0$ (along the $z$ direction) plus the

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[1] J. M. Winter, J. Phys. Radium (to be published).

[2] A discussion of a similar problem can be found in P. G. DeGennes and F. Hartmann-Boutron, Compt. Rend. **253**, 2922 (1961).

[3] P. G. DeGennes, F. Hartmann-Boutron, and P. A. Pincus, Compt. Rend. **254**, 1264 (1962).

hyperfine field $H_n(\mathbf{M}/M_0)=\alpha\mathbf{M}$. The equation of motion for the nuclear spins is thus

$$d\mathbf{m}/dt=\gamma_n\mathbf{m}\times(\mathbf{H}_0+\alpha\mathbf{M}). \tag{2.1}$$

Similarly, the field acting on the electron spin is $\mathbf{H}_0+\mathbf{H}_A+\alpha\mathbf{m}$ (where $\mathbf{H}_A$ is the anisotropy field); at the comparatively low nuclear frequencies in which we are interested the electrons follow this field adiabatically, i.e., $\mathbf{M}$ is parallel to $\mathbf{H}_0+\mathbf{H}_A+\alpha\mathbf{m}$. For small transverse motions of $\mathbf{M}$ we may write:

$$\begin{aligned} M_z&=M_0;\\ M^+=M_x+iM_y&=M_0\alpha m^+/(H_0+H_A). \end{aligned} \tag{2.2}$$

We shall now assume that Eq. (2.1) may be linearized in the usual way to describe small amplitude motions of $\mathbf{m}$ around its equilibrium value $\mathbf{m}_0$. This assumption is not entirely trivial since the nuclear spins are usually far from saturation. It will be justified by microscopic considerations in Sec. III. We then obtain from (2.1)

$$\begin{aligned} dm^+/dt&=-i\omega m^+\\ &=-i\gamma_n[(H_0+\alpha M_0)m^+-m_0\alpha M^+], \end{aligned} \tag{2.3}$$

and inserting (2.2) we arrive at the resonance condition:

$$\omega=\gamma_nH_n[1-\eta(m_0/M_0)]+\gamma_nH_0; \tag{2.4}$$

$\eta=\alpha M_0/(H_0+H_A)=H_n/(H_0+H_A)$ is the enhancement factor relating the effective rf field to the applied rf field in the nuclear resonance experiment.[4] Equation (2.4) predicts a frequency pulling in zero external field of relative value

$$\begin{aligned} -\delta\omega/\omega&=\eta m_0/M_0 \qquad (2.5)\\ &=(\omega_n/\omega_e)(\langle I_z\rangle/\langle S_z\rangle)\\ &\cong[I(I+1)/3S](\omega_n/\omega_e)(\hbar\omega_n/k_BT), \qquad (2.6) \end{aligned}$$

where $\omega_n=\gamma_nH_n$ and $\omega_e=\gamma_e(H_0+H_A)$. Equation (2.5) applies for 100% isotopic abundance. Taking $\omega_n=3\times10^9$; $H_A=10^3$ Oe, $I=S=5/2$ (these being plausible values for cubic compounds of $Mn^{2+}$) we would have $\omega_e\sim3\times10^{10}$ and $\delta\omega/\omega\sim3\times10^3/T$. The shift in frequency would be important for such a case at temperatures below 2°K. (A more complete comparison between the shift and the width of the resonance line will be given in Sec. III.)

Equation (2.5) shows that we may expect a large frequency pulling in all situations where the enhancement factor is large. This suggests that the effect might be important in Bloch walls where $\eta$ values of the order $10^3$ and more are met. In fact it may be shown that a formula very similar to (2.5) applies in a Bloch wall. This is discussed in detail in Appendix A.

Equation (2.4) also implies that the relation $\omega(H_0)$ between resonance frequency and external field is nonlinear since $\eta$ depends on $H_0$. The apparent gyromagnetic ratio defined as $\gamma_{\rm app}=\partial\omega/\partial H_0$ is given by

$$\gamma_{\rm app}=\gamma_n[1+\eta^2(m_0/M_0)]. \tag{2.7}$$

The effect on $\gamma_{\rm app}$ is more spectacular since an extra factor of $\eta$ ($\sim100$) comes into play. Of course this is somewhat fictitious since to measure $\gamma_{\rm app}$ one needs rather large magnetic fields for which $\eta$ is strongly reduced.

Finally, if the electron motion is damped, the nuclear frequency acquires a small imaginary part $(1/T_1)_n$. This relaxation effect however is very small: it vanishes in the adiabatic approximation of Eq. (2.2). If one replaces (2.2) by the complete equation of motion for the electron spins, including a relaxation of $\mathbf{M}$ towards the *instantaneous* value of the field $\mathbf{H}_0+\mathbf{H}_A+\alpha\mathbf{m}$, one obtains:

$$(T_{1n}\delta\omega_n)^{-1}=\eta(\gamma_n/\gamma_e)(T_{2e}\omega_e)^{-1}. \tag{2.8}$$

For $\omega\ll\omega_e$ and $\omega_eT_{2e}\gg1$ and taking $(T_{2e}\omega_e)^{-1}=10^{-1}$, $(\gamma_n/\gamma_e)=10^{-3}$, $\eta=100$ we obtain $(T_{1n}\delta\omega_n)^{-1}\sim10^{-2}$. Thus the relaxation rate $T_{1n}^{-1}$ given by Eq. (2.8) is very small; and there are other more important effects contributing to the linewidth (some of them will be discussed later).

## Antiferromagnetic Case

We shall now consider the frequency pulling in an antiferromagnet where we must distinguish two sublattices of electronic spins $\mathbf{M}_1$ and $\mathbf{M}_2$ and the corresponding two nuclear spin sublattices $\mathbf{m}_1$ and $\mathbf{m}_2$.

Neglecting damping, the equations of motion corresponding to (2.1) and (2.2) are

$$\begin{aligned} d\mathbf{M}_1/dt&=\gamma_e\mathbf{M}_1\times(\mathbf{H}_0+\mathbf{H}_A-\lambda\mathbf{M}_2+\alpha\mathbf{m}_1),\\ d\mathbf{M}_2/dt&=\gamma_e\mathbf{M}_2\times(\mathbf{H}_0-\mathbf{H}_A-\lambda\mathbf{M}_1+\alpha\mathbf{m}_2),\\ d\mathbf{m}_1/dt&=\gamma_n\mathbf{m}_1\times(\mathbf{H}_0+\alpha\mathbf{M}_1),\\ d\mathbf{m}_2/dt&=\gamma_n\mathbf{m}_2\times(\mathbf{H}_0+\alpha\mathbf{M}_2), \end{aligned} \tag{2.9}$$

where $\lambda$ is the molecular field constant and is related to the effective exchange field by $\lambda M_0=H_{\rm ex}$. In the small oscillation approximation (2.9) becomes

$$\begin{aligned} -\omega M_1^+&=\gamma_e[-H_{\rm ex}M_2^+ +\alpha M_0m_1^+\\ &\qquad -M_1^+(H_0+H_A+H_{\rm ex}+\alpha m_0)],\\ -\omega M_2^+&=\gamma_e[H_{\rm ex}M_1^+ -\alpha M_0m_2^+\\ &\qquad -M_2^+(H_0-H_A-H_{\rm ex}-\alpha m_0)],\\ -\omega m_1^+&=\gamma_n[\alpha m_0M_1^+ -m_1^+(H_0+\alpha M_0)],\\ -\omega m_2^+&=\gamma_n[-\alpha m_0M_2^+ -m_2^+(H_0-\alpha M_0)], \end{aligned} \tag{2.10}$$

where $M_0=M_{10}=-M_{20}$ and $m_0=m_{10}=-m_{20}$. On solving the secular equation (2.10), one finds the nuclear resonance frequencies are given by:

$$\begin{aligned} \omega/\gamma_n&\cong H_n[1-(2\omega_{\rm ex}\omega_n\gamma_em_0/\omega_1\omega_2\gamma_nM_0)]^{1/2}\\ &\quad\pm H_0[1+(\omega_n^2\gamma_e^2m_0/\omega_1\omega_2\gamma_n^2M_0)], \end{aligned} \tag{2.11}$$

where $\omega_{\rm ex}=\gamma_eH_{\rm ex}$ and $\omega_{1,2}$ are the two antiferromagnetic resonance frequencies, i.e., $\omega_{1,2}/\gamma_e=(2H_{\rm ex}H_A)^{1/2}\pm H_0$. For many antiferromagnetics where $(2H_{\rm ex}H_A)^{1/2}\gg H_0$, the fractional frequency pulling reduces to $\frac{1}{2}(m_0/M_0)$

[4] A. M. Portis and A. C. Gossard, J. Appl. Phys. **31**, 205S (1960). A. C. Gossard, thesis, University of California, Berkeley, 1960 (unpublished).

$\times(H_n/H_A)$, i.e., one half of the value (2.5) obtained for the ferromagnetic case in zero field. The nuclear $g$ shift given by the second term in (2.11) is of the order of $\gamma_e\omega_n/\gamma_n\omega_{ex}$ smaller than the frequency pulling and is thus negligible. Notice that there exist two degenerate nuclear resonance frequencies which are split by an external field. The two frequencies clearly correspond to the two nuclear sublattices one of which is magnetized parallel to $H_0$ and the other antiparallel.

We conclude that, here again, the effect will be important only if we have a very low anisotropy field $H_A$. This is actually the case in $KMnF_3$,[5] and might also happen in $MnCO_3$.[6] However, both these compounds are canted antiferromagnets for which Eqs. (2.9) and (2.10) must be modified. This is done in the second paper of this series[7] and the result is

$$\omega/\gamma_n=H_n[1-(2\omega_{ex}\omega_n\gamma_e m_0/\omega_{1,2}{}^2\gamma_n M_0)]^{1/2}. \quad (2.12)$$

Notice that the two nuclear resonance frequencies are split even in the absence of an external field. This arises because the electronic resonance modes are linearly polarized in a canted antiferromagnet, but circularly polarized in a usual Néel antiferromagnet. In a case such as $MnCO_3$,[6] this splitting may be considerable because one electronic resonance mode may be at an infrared frequency of the order of $10^{12}$ cps, while the other branch is at microwave frequencies ($\sim 10^9$ cps). Of course, the pulling caused by the infrared mode will always be negligible, but, using the previous estimates for $Mn^{55}$ nucleus, the pulling arising from the microwave electronic mode may be of the order of several percent. For example, at an electronic resonance frequency of 9 kMc/sec,

$$|\delta\omega_n/\omega_n|\sim|\gamma_e\omega_{ex}\omega_n m_0/\gamma_n\omega^2 M_0|\sim 0.4, \quad (2.13)$$

for $\omega_n\simeq 4\times 10^9$ cps and an exchange field of $10^6$ Oe.

Such a large effect may occur in both $KMnF_3$ and $MnCO_3$. Heeger *et al.*[5] have shown that the effective anisotropy field acting on the electronic spins and arising from the nuclear spins through the hyperfine interaction $A\langle I_z\rangle/\hbar\gamma_e$ gives a significant contribution to the microwave resonance frequency. In fact, the frequency pulling in a canted system is just the square of the fraction of the electronic resonance frequency arising from the hyperfine interaction. The reason for the large effect is just that the anisotropy field arising from the nuclei (of the order of a few oersteds at liquid helium temperature) is just of the same order of magnitude as the ordinary anisotropy field, which is enhanced by the exchange field, and is enhanced in the same manner. This frequency pulling seems to be the basis for the nonlinear effects observed by Heeger *et al.*[7,8] in $KMnF_3$.

[5] A. J. Heeger, A. M. Portis, D. T. Traney, and G. Witt, Phys. Rev. Letters **7**, 307 (1961).
[6] M. Date, J. Phys. Soc. Japan **15**, 2251 (1960).
[7] A. M. Portis, A. J. Heeger, and G. Witt (to be published).
[8] A. J. Heeger, A. M. Portis, and G. Witt, presented at the International Conference on Magnetic and Electric Resonance and Relaxation, Eindhoven, July, 1962 (unpublished).

## III. MICROSCOPIC INTERPRETATION

### Connection with the Suhl-Nakamura Interaction

We now proceed to show that the frequency shift $\delta\omega$ of Eq. (2.5) is due to the indirect interaction between nuclei, as derived by Suhl[9] and Nakamura.[10] Let us consider for instance a ferromagnetic Bravais lattice, each electron spin $\mathbf{S}_n$ being coupled only to one nuclear spin $\mathbf{I}_n$. The linearized equations of motion for both systems are

$$\omega S_n{}^+=\textstyle\sum_{n,m}\omega_{nm}(S_n{}^+-S_m{}^+)+\omega_e S_n{}^+ -(A/\hbar)[\langle I_z\rangle S_n{}^+-SI_n{}^+]; \quad (3.1)$$
$$\omega I_n{}^+=-(A/\hbar)(SI_n{}^+-\langle I_z\rangle S_n{}^+)+\gamma_n H_0 I_n{}^+,$$

where $S^{-1}\hbar\omega_{nm}$ is the exchange coupling between electron spins located at site $n$ and $m$ and we have assumed that the electron system is completely saturated ($\langle S_z\rangle=S$). The eigenmodes of Eq. (3.1) are the traveling waves

$$S_n{}^+=ue^{i\mathbf{q}\cdot\mathbf{R}_n}; \quad I_n{}^+=ve^{i\mathbf{q}\cdot\mathbf{R}_n}.$$

In terms of $u$ and $v$ Eq. (3.1) becomes

$$\begin{aligned}[\omega-\omega_{0q}+(A/\hbar)\langle I_z\rangle]u-(A/\hbar)Sv=0;\\ -(A/\hbar)\langle I_z\rangle u+[\omega+(A/\hbar)S-\gamma_n H_0]v=0,\end{aligned} \quad (3.2)$$

where $\omega_{0q}=\omega_e+\sum_m\omega_{nm}[1-e^{i\mathbf{q}\cdot(\mathbf{R}_m-\mathbf{R}_n)}]$ is the usual electronic spin wave frequency. From (3.2) we derive the secular equation

$$[\omega-\omega_{0q}+(A/\hbar)\langle I_z\rangle][\omega+(A/\hbar)S-\gamma_n H_0] -(A/\hbar)^2S\langle I_z\rangle=0. \quad (3.3)$$

When $\hbar\omega_e\gg AS$ this has a high frequency solution ($\omega\sim\omega_{0q}$) representing the electron spin waves and a low frequency solution

$$\omega_q\cong-(AS/\hbar)[1+(A\langle I_z\rangle/\hbar\omega_{0q})]+\gamma_n H_0, \quad (3.4)$$

representing nuclear spin waves. The constant term $(AS/\hbar)$ stems from the average hyperfine field and the $q$ dependent term comes from the indirect interaction between nuclei through the electron spins. Equation (3.4) can also be obtained by writing the linearized equations of motion for the nuclear spins alone when coupled by the Suhl-Nakamura interaction

$$\mathcal{H}_1=-\tfrac{1}{2}A^2S\sum_{m,n}I_m{}^+I_n{}^-N^{-1}\sum_{\mathbf{q}}\frac{e^{i\mathbf{q}\cdot(\mathbf{R}_m-\mathbf{R}_n)}}{\hbar\omega_{0q}} =\sum_{m,n}u_{mn}I_m{}^+I_n{}^-. \quad (3.5)$$

The dispersion relation (3.4) is represented in Fig. 1. For $q=0$, Eq. (3.4) leads again to the shifted frequency Eq. (2.6). For large $q$'s, $\omega_{0q}$ being of the order of the exchange frequencies, the interaction term becomes negligible, and $\omega$ is equal to the unshifted frequency

[9] H. Suhl, Phys. Rev. **109**, 606 (1958)
[10] T. Nakamura, Progr. Theoret. Phys. (Kyoto) **20**, 542 (1958).

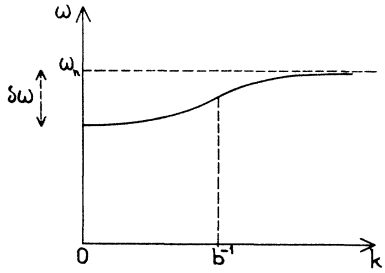


FIG. 1. The nuclear spin wave spectrum.

$\gamma_n(H_n+H_0)$. The transition between these two limiting behaviors takes place for $q$ values such that $\omega_{0q}\sim 2\omega_e$. Since $\omega_{0q}\cong\omega_e+\omega_{ex}a^2q^2$, where $a$ is an interatomic distance and $\omega_{ex}$ an exchange frequency, this occurs when $q^{-1}\sim a(\omega_{ex}/\omega_e)^{1/2}\gg a$. The physical meaning of this result is simply that the Suhl interaction has a range $b=a(\omega_{ex}/\omega_e)^{1/2}$ and thus gives a significant contribution to the nuclear precession frequency only at wavelength larger than $b$. Since $b\gg a$ in the cases of interest, it is only for a very small fraction of the modes that the frequency is shifted from the conventional value.

These remarks also give a clearer meaning to the change in gyromagnetic ratio Eq. (2.7). When we apply an external magnetic field $H_0$ we change the Zeeman energy of the nuclei, but we also change the range $b$ of the interaction between them; the whole nuclear spin wave spectrum is then modified.

It is also of interest to estimate the velocity $\partial\omega/\partial q$ of typical nuclear spin waves from Eq. (3.4). $\partial\omega/\partial q$ is maximum when $ab\sim 1$ and is then

$$(\partial\omega/\partial q)_{\max}\sim b\delta\omega\sim a\omega_n\eta(m_0/M_0)(\omega_{ex}/\omega_e)^{1/2}.$$

Using our previous values $\omega_n=3\times10^9$, $\eta(m_0/M_0)=3\times10^{-3}T^{-1}$, $(\omega_{ex}/\omega_e)^{1/2}=30$ and taking $a=3$ Å we get $(\partial\omega/\partial q)_{\max}=10^2T^{-1}$ cm/sec, a nonnegligible velocity. It must be realized however, that the mean free path $l$ is small. $l\sim b\delta\omega/\Delta\omega$ for the high velocity spin waves (where $\Delta\omega$ is the line width of the corresponding mode). As we shall see later, $(\delta\omega/\Delta\omega)$ is of the order 50 in favorable cases such as $KMnF_3$ at 4°K, and then $l\sim 15\ \mu$. Of course, the mean free path could be increased by working at lower temperatures.

### Validity of the Linearization Procedure

We now proceed to show that the linearization procedure used to derive Eq. (3.3) is indeed justified even at rather high temperatures. For this purpose we consider the power spectrum $P_q(\omega)$ of the quantity

$$A_q^+=\sum_i e^{i\mathbf{q}\cdot\mathbf{R}i}I_i^+; \tag{3.6}$$

$$P_q(\Omega)=\int dt\,\langle A_q^-(0)A_q^+(t)\rangle e^{i\Omega t}. \tag{3.7}$$

When the spin wave excitations are meaningful, $P_q(\omega)$ shows a sharp peak at the spin wave frequency $\omega_q$. At very low temperatures ($k_BT\sim A$), the nuclear spins being all lined up, this situation will clearly be realized. We are interested, however, in higher temperatures (in the helium range) for which the average polarization of the nuclei ($\langle I_z\rangle/I$) is small.

For such cases of strong disorder $P_q(\omega)$ is best studied by a method of moments. Let us consider the first moment

$$\bar{\Omega}_q=\left(\int P_q(\Omega)\Omega d\Omega\right)\Big/\left(\int P_q(\Omega)d\Omega\right) \tag{3.8}$$

$$=i\langle A_q^-dA_q^+/dt\rangle/\langle A_q^-A_q^+\rangle. \tag{3.9}$$

We compute $dA_q^+/dt=(i/\hbar)[\mathcal{H},A_q^+]$ with the Hamiltonian $\mathcal{H}=\mathcal{H}_0+\mathcal{H}_1$, where $\mathcal{H}_0$ is the first order Hamiltonian $\mathcal{H}_0=\sum_n ASI_n^z$ and $\mathcal{H}_1$ is the second-order Suhl interaction (3.5). The thermal averages are also to be taken with respect to this Hamiltonian:

$$\langle O\rangle=\mathrm{Tr}[Oe^{-\beta\mathcal{H}}]/\mathrm{Tr}[e^{-\beta\mathcal{H}}].$$

Then

$$\hbar\Omega_q=-AS+\frac{2\sum_{n,m,p}\langle I_n^-I_m^+I_p^z\rangle u_{mp}e^{i\mathbf{q}\cdot(\mathbf{R}_p-\mathbf{R}_m)}}{\sum_{n,m}\langle I_n^-I_m^+\rangle}. \tag{3.10}$$

At the temperatures of interest we may, to a very good approximation, make the substitution

$$\langle I_n^-I_m^+I_p^z\rangle\rightarrow\langle I_n^-I_m^+\rangle\langle I^z\rangle\rightarrow (\tfrac{2}{3})I(I+1)\langle I^z\rangle\delta_{nm} \tag{3.11}$$

for $p\neq m$, $n$. This neglects only some small correlations brought in by the Suhl interaction of order $A^2/Jk_BT$ while the term retained is of order $\langle I^z\rangle\sim A/k_BT$. For the same reason the terms $p=n\neq m$ and $p=m\neq n$ can be neglected. Finally the term $n=m=p$ which corresponds to the self energy of nucleus $I_n$ is always negligible as explained in the introduction (being only one particular term of a long range interaction), and we may as well make approximation (3.11) on this term too. The result is then simply

$$\hbar\bar{\Omega}_q=-AS+2\langle I^z\rangle\textstyle\sum_p u_{mp}e^{i\mathbf{q}\cdot(\mathbf{R}_m-\mathbf{R}_p)} \tag{3.12}$$

and thus the first moment $\bar{\Omega}_q$ coincides with the spin wave frequency (3.4).

Our next problem is then to determine the width of the power spectrum $P_q(\omega)$. If this width comes out to be small (when compared with $|\bar{\Omega}_q+(AS/\hbar)|$), then we may say that the frequency $\bar{\Omega}_q$ corresponds to a well defined elementary excitation of wave vector $\mathbf{q}$. We derive the width from the reduced second moment $\langle\Omega_q^2\rangle_{\mathrm{av}}-\bar{\Omega}_q^2=(\Delta\Omega_q^2)$ and also simplify the calculation by going to the limit of complete disorder in the nuclear spins ($AS\ll k_BT$). This clearly will give us an overestimate of the width. It is found that $(\Delta\Omega_q)^2$ is independent of $q$ in this limit and thus identical to the value $(\Delta\Omega_0)^2$ computed by Suhl[9] for the uniform mode:

$$\frac{(\Delta\Omega_q)^2}{4\pi^2}=\frac{(\Delta\Omega_0)^2}{4\pi^2}=\frac{I(I+1)}{24\pi S^2}\frac{\omega_n^4}{\omega_{ex}^{3/2}\omega_e^{1/2}}. \tag{3.13}$$

As pointed out above we are mainly interested in the ratio $[\bar{\Omega}_q+(AS/\hbar)]/\Delta\Omega_q \leq (\delta\omega_0/\Delta\Omega_0)$ between the total bandwidth of the spin wave spectrum and the width of one individual spin wave mode. This is given by

$$(\delta\omega_0/\Delta\Omega_0) = (2\pi)^{-1}[24\pi/I(I+1)]^{1/2}\langle I_z\rangle(\omega_{ex}/\omega_e)^{3/4}. \quad (3.14)$$

For nuclei such as $Mn^{55}$ and $Co^{59}$, assuming a low anisotropy ($\omega_e/\gamma_e \sim 10^3$ Oe) and a reasonable value of exchange ($\omega_{ex}/\gamma_e \sim 10^6$ Oe), we find that $(\delta\omega_0/\Delta\Omega_0)$ is larger than 1 when $T$ is below $\sim 3°$K. In such a case the nuclear spin waves are well defined at temperatures $\sim 1°$K where the nuclear polarization level is only of order 1%.

Apart from all theoretical consideration (3.14) is of course very important since it gives us the temperature region in which the frequency shift $\delta\omega_0$ of the uniform mode is large when compared to the Suhl width $\Delta\Omega_0$: all frequency pulling effects can be observed only when $|\delta\omega_0/\Delta\Omega_0| > 1$.

In fact, (3.14) can be obtained by the following simple argument. Let us consider the field $F_i$ acting on the $i$th nuclear spin arising from all the other nuclear spins. Because the nuclei are far from saturation $F_i$ is a random field with its associated distribution function $P(F_i)$. The average field $\bar{F}_i$ is proportional to the polarization:

$$\bar{F}_i = C\langle I_z\rangle/I.$$

One can estimate the width of the distribution by noticing that the number, $N$, of spins contributing to the local field is very large: $N \sim (b/a)^3 \sim [H_{ex}/(H_0+H_A)]^{3/2}$. In the temperature range of interest, the field $F_i$ is therefore the sum of a large number of random, nearly independent contributions. The width of the distribution is therefore of the order of $CN^{-1/2}$. There will exist well defined collective modes if this width is small relative to the mean displacement $\bar{F}_i$.

The condition is, therefore,

$$N^{1/2}\langle I_z\rangle/I > 1,$$

which is within a numerical factor of the order of unity identical to (3.14).

### Specific Heat of the Nuclear Spin System

The standard expression for the nuclear specific heat in the "high temperature" limit ($k_BT > \hbar\omega_n$) is[11]

$$C = Nk_B[I(I+1)/3](\hbar\omega_n/k_BT)^2. \quad (3.15)$$

At first sight one might wonder whether the frequency shift should not be added to $\omega_n$ in (3.15). Actually this is not so, and (3.15) is the correct formula, even in the presence of frequency pulling in the range $\hbar\omega_n \ll k_BT$. This may be seen in a formal way by a trace method carried to 4th order in $A$. More physically we may argue as follows: the frequency pulling affects only the frequency of the long wavelength nuclear spin waves ($kb < 1$). As pointed out before the relative number of shifted modes is very small of order $(a/b)^3 \cong (\omega_e/\omega_{ex})^{3/2} \sim 10^{-4}$. When $\hbar\omega_n < k_BT$ all modes are excited, and the contribution of the shifted ones to the specific heat is negligible. On the other hand when $\hbar\omega_n > k_BT$ (i.e., at temperatures below $10^{-2°}$K), only the bottom of the nuclear spin wave spectrum is excited: This is precisely the region of the shifted modes and their effect on the specific heat will then become important.

[11] W. Marshall, Phys. Rev. **110**, 1280 (1958), Appendix A.

### IV. DEMAGNETIZATION FIELD EFFECTS

Until now, we have neglected the demagnetizing fields. It is known that they modify the electronic spin wave spectrum for low value of the wave vector $\mathbf{q}$[12] in a ferromagnet. Here we calculate the modifications of the nuclear spin wave spectrum arising from these effects. It will be shown that the nuclear spin wave spectrum is also anisotropic and therefore, effects such as parallel pumping[13] and Suhl instability[14] should be investigated.

Consider the equations of motion for the $\mathbf{q}$ component of the nuclear magnetization:

$$\begin{aligned} dm_{qx}/dt &= \gamma_n m_{qy}\alpha M_z - \gamma_n m_z \alpha M_{yq} + \gamma_n(H_0 - N_zM)m_{qy}; \\ dm_{qy}/dt &= -\gamma_n m_{qx}\alpha M_z + \gamma_n m_z \alpha M_{qx} - \gamma_n(H_0 - N_zM)m_{qx}. \end{aligned} \quad (4.1)$$

The corresponding equations for $M_{qx}$ and $M_{qy}$ are[12]

$$\begin{aligned} \frac{dM_{qx}}{dt} &= M_{qy}\left[\gamma_e H_A + \gamma_e(H_0 - N_zM) + \frac{4\pi}{q^2}q_y^2\gamma_e M + \omega_{ex}(aq)^2\right] \\ &\quad + \left[\frac{4\pi\gamma_e M}{q^2}q_xq_y\right]M_{qx} - \alpha\gamma_e M m_{qy}; \\ \frac{dM_{qy}}{dt} &= -M_{qx}\left[\gamma_e H_A + \gamma_e(H_0 - N_zM) + \frac{4\pi}{q^2}q_x^2\gamma_e M + \omega_{ex}(aq)^2\right] \\ &\quad - \left[\frac{4\pi\gamma_e M}{q^2}q_xq_y\right]M_{qy} + \alpha\gamma_e M m_{qx}. \end{aligned} \quad (4.2)$$

Without any loss of generality $q_y$ may be assumed to be zero. The nuclear frequency being low the time derivatives of $M_{qx}$ and $M_{qy}$ are neglected.

[12] C. Herring and C. Kittel, Phys. Rev. **81**, 869 (1951).
[13] E. Schlomann, J. J. Green, and U. Milano, J. Appl. Phys. **31**, 386S (1960).
[14] H. Suhl, J. Phys. Chem. Solids **1**, 209 (1957).

$M_{qy}$ and $M_{qx}$ may then be expressed in terms of $m_{qy}$ and $m_{qx}$; the nuclear equations of motion then become:

$$\begin{aligned} dm_{qx}/dt&=\gamma_n m_{qy}[\alpha M+H_0-N_zM] \\ &\quad -\gamma_n\alpha m(\alpha M/C_q)m_{qy}; \\ dm_{qy}/dt&=-\gamma_n m_{qx}[\alpha M+H_0-N_zM] \\ &\quad +\gamma_n\alpha m(\alpha M/D_q)m_{qx}, \end{aligned} \tag{4.3}$$

with

$$\begin{aligned} C_q&=H_0-N_zM+H_A+(\omega_{ex}/\gamma_e)(aq)^2; \\ D_q&=H_0-N_zM+H_A+(\omega_{ex}/\gamma_e)(aq)^2+4\pi M\sin^2\theta_q, \end{aligned}$$

where $\theta_q$ is the angle between the wave vector $\mathbf{q}$ and the $z$ axis. The nuclear spin wave frequency is easily obtained as

$$\begin{aligned} \omega_{nq}^2&=\gamma_n^2[H_n+H_0-N_zM-\alpha m(\alpha M/C_q)] \\ &\quad\times[H_n+H_0-N_zM-\alpha m(\alpha M/D_q)]. \end{aligned} \tag{4.4}$$

The nuclear frequency depends on the angle $\theta_q$. The equations (4.3) show that a small ellipticity is induced in the nuclear motion. This ellipticity is usually very small because it affects only the second term in (4.3). As for a ferromagnet, Eq. (4.4) is not valid when the wave vector $q$ goes to zero. For $q=0$ we have to consider the coupled motion of the two uniform modes. The resonance frequency is

$$\begin{aligned} \omega_{n0}^2&=\gamma_n^2[H_n+H_0-N_zM-\alpha m(\alpha M/C_0)] \\ &\quad\times[H_n+H_0-N_zM-\alpha m(\alpha M/D_0)], \end{aligned}$$

where

$$\begin{aligned} C_0&=H_A+H_0+(N_x-N_z)M; \\ D_0&=H_A+H_0+(N_y-N_z)M. \end{aligned}$$

When $0<q<1/L$, $L$ being the dimension of the sample, the electronic eigenmodes are magnetostatic modes and the nuclear eigenmodes have the spatial behavior of these electronic modes.

We notice that the perturbation of the nuclear spin wave spectrum due to demagnetizing effects occurs for wave vectors less than $(1/c)=(1/a)(4\pi\gamma_e M/\omega_{ex})^{1/2}$, and $c$ is usually of the same order as $b$, the range of the Suhl-Nakamura interaction.

The occurrence of an ellipticity in the nuclear motion suggests that a parallel pumping experiment is possible within the nuclear system. We add an oscillating field $h\cos2\omega_0 t$ along the $z$ axis and also include a transverse damping term. Then the equations of motion become

$$\begin{aligned} dm_{qx}/dt&=\gamma_n m_{qy}(\alpha M+H_0-N_zM)-\gamma_n m\alpha M_{qy} \\ &\quad+\gamma_n m_{qy}h\cos2\omega_0 t-(m_{qx}/T_2); \\ dm_{qy}/dt&=-\gamma_n m_{qx}(\alpha M+H_0-N_zM)+\gamma_n m\alpha M_{qx} \\ &\quad-\gamma_n m_{qx}h\cos2\omega_0 t-(m_{qy}/T_2). \end{aligned} \tag{4.5}$$

By the same technique $M_{qy}$ and $M_{qx}$ are expressed in terms of $m_{qx}$ and $m_{qy}$, but now there is in $C_q$ and $D_q$ an oscillating term $h\cos2\omega_0 t$. This term may be neglected, its effect is to change $h$ into $h[1-\eta^2(m/M)]$.

Equations (4.5) are written now as

$$\begin{aligned} dm_{qx}/dt&=\gamma_n m_{qy}c_q-(m_{qx}/T_2); \\ dm_{qy}/dt&=-\gamma_n m_{qx}d_q-(m_{qy}/T_2), \end{aligned}$$

with

$$\begin{aligned} c_q&=H_n+H_0-N_zM-(\alpha^2 mM/C_q); \\ d_q&=H_n+H_0-N_zM-(\alpha^2 mM/D_q). \end{aligned}$$

The problem is now formally identical to the problem of parallel pumping in a ferromagnetic system. The critical field $h_c$ which produces instability is given by

$$(\gamma_n h_c/4)(c_q-d_q)(c_q d_q)^{-1/2}>1/T_2. \tag{4.6}$$

It is quite clear that this condition is very difficult to satisfy for three reasons:

(a) there is no enhancement factor for a longitudinal field $h$;
(b) the transverse damping is very large;
(c) the ellipticity of the nuclear motion, which is measured by $e=(c_q-d_q)(c_q d_q)^{-1/2}$ is very small. This term is approximately given by

$$\begin{aligned} e&=\alpha^2 mM/(C_q-D_q)/H_n C_q D_q \\ &\simeq\alpha^2 mM/H_n H_0\simeq H_n m/H_0 M. \end{aligned}$$

Thus, even at very low temperature, this term is very small.

## V. NUCLEAR RESONANCE IN THE PRESENCE OF PULLING

### Steady State Behavior

In this section we would like to show in what way an appreciable frequency pulling may change the nuclear resonance absorption. In particular we shall show that nonlinear absorption effects may arise from the nonlinear nature of the frequency pulling. The nonlinear effect of the frequency pulling arises because the resonance frequency shift is proportional to the nuclear polarization itself. Thus the nuclear absorption line at low power levels will be centered near the pulled frequency, but at high power levels when the nuclear polarization may be small, the absorption line may then be centered near the unshifted frequency $\omega_n$. In other words, if one were to apply a rf field at $\omega_n$, at low powers one would find very little absorption since the applied signal would be well off resonance. As one increases the power, at a certain power level the line would be able to snap over to $\omega_n$ and thus a nonlinear absorption versus power curve might be observed. Such is the observed type of behavior in $KMnF_3$.[7,8]

In order to determine the response of the nuclear system to an effective rf field $h^*$, where $h^*=\eta h$, we may consider a rate equation for the $z$ polarization of the nuclear spin system as is, for example, given in Abragam,[15] by

$$dm_z/dt=-2Wm_z+(m_0-m_z)/T_1, \tag{5.1}$$

[15] A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University Press, New York), Chaps. II and IV.

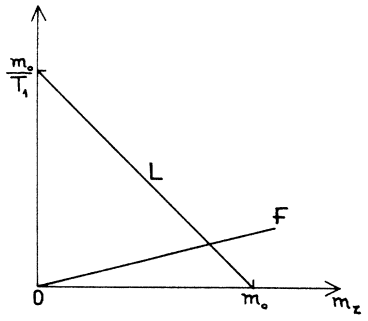


FIG. 2. A parametric plot of Eq. (4.5) in the absence of frequency pulling. The line $L$ represents the left-hand side of (4.5) and $F$ represents the right-hand side. The stable solution is given by the intersection of $F$ and $L$.

where $m_0$ is the thermal equilibrium value of the magnetization and where the transition probability per unit time, induced by the rf field is given by

$$W=(\gamma_n h^*)^2(\pi/2)f(\omega). \tag{5.2}$$

The function $f(\omega)$ is the normalized shape function of the resonance line. For example for a Gaussian line $f(\omega)$ is given by

$$f(\omega)=(2\pi)^{-1/2}\Delta^{-1}e^{-(\omega-\omega_0)^2/2\Delta^2}, \tag{5.3}$$

where $\Delta$ is the linewidth in frequency units and $\omega_0$ is the resonance frequency. Under steady state conditions, (5.1) and (5.2) give

$$(m_0-m_z)/T_1=\pi f(\omega)(\gamma_n h^*)^2 m_z. \tag{5.4}$$

The characteristic transverse time $T_2$ is defined as $\pi f(\omega_0)$ and is given by

$$T_2^{-1}=(\pi/2)^{1/2}\Delta \tag{5.5}$$

for a Gaussian line. The right-hand side (rhs) of (5.4) represents the rate at which energy is absorbed from the radio frequency field, and the left-hand side (lhs), the rate at which energy is transmitted to the lattice; of course, in equilibrium these two quantities must be equal. The solution of (5.4) gives the power and frequency dependence of the nuclear absorption signal. For the usual case, where there is negligible frequency pulling, $f(\omega)$ is independent of $m_z$ and (5.4) can easily be solved to give the standard results. However, in the presence of appreciable frequency pulling $\omega_0$ is a function of the nuclear magnetization $m_z$ and thus one must resort to graphical solutions of (5.4). In Fig. 2 we give the trivial graphical solution of (5.4) in the absence of frequency pulling. The ordinate of the line of negative slope, $L$, is proportional to the rate at which energy is delivered to the lattice [lhs of (5.4)], while the line of positive slope, $F$, is given by the rhs of (5.4). The slope of $F$ is proportional to the power and for slopes greater than unity the line is effectively saturated. On resonance ($\omega=\omega_0$) this just gives the usual saturation requirement that $(\gamma_n h^*)^2 T_1 T_2 \sim 1$. At a fixed power level, the frequency dependence of the ordinate of intersection will trace out the nuclear absorption line.

In the presence of appreciable frequency pulling the curve $F$ will be nonlinear and there exists the possibility of multiple intersections or multiple roots of (5.4). We shall graphically investigate several possibilities under the assumption of a Gaussian line (5.3). We shall take the frequency pulling shift in the form

$$\delta\omega=-\beta\omega_n m_z, \tag{5.6}$$

where $\beta$ is assumed to be independent of the nuclear magnetization. This assumption is not strictly valid since the electronic resonance frequency will depend appreciably on $m_z$ when the frequency pulling is large. However, this will usually be a correction to the large $m_z$ dependence given in (5.6). For a Gaussian line with frequency pulling, (5.4) becomes

$$f(\omega)=(2\pi)^{-1/2}\Delta^{-1}\exp[-(\Delta\omega+\beta\omega_n m_z)^2/2\Delta^2], \tag{5.7}$$

where $\Delta\omega=\omega-\omega_n$. Let us suppose that an rf field is applied between $\omega_n$ and $\omega_n-\delta\omega$. In Fig. 3 we show qualitatively the behavior of (5.4). At low power levels, $F_1$, there is only one solution corresponding to very little absorption. However at sufficiently high powers, $F_2$, new solutions appear corresponding to much smaller values of $m_z$ and correspondingly higher energy absorption. For the special case $\omega_n-\omega\gg\Delta$ the first point of a contact for the high absorption solution may easily be seen to occur at

$$(\pi/2)(\gamma_n h^*)^2 T_1 T_2 \approx [\omega-(\omega_n-\delta\omega)](\omega_n-\omega)^{-1}. \tag{5.8}$$

This is generally of the order of the usual saturation condition. The two extreme solutions for high and low absorption may be seen to be stable with respect to small fluctuations in $m_z$. The central solution is unstable. For example, for the central solution, if there is a small fluctuation with $\delta m_z>0$ the relaxation rate will exceed the absorption and thus the system will be driven to the low absorption solution. Similarly for $\delta m_z<0$ the system will be driven to the high absorption solution. In fact, the condition for stability is clearly that the slope of the rf field absorption curve, $F$, be greater than the slope of the relaxation time $L$. At frequencies $\omega<\omega_n$ such that $\Delta\omega<0$, the curves $F_1$ and $F_2$ will shift to the right, with decreasing absorption for a fixed power. For $\omega>\omega_n$, the curves $F_1$ and $F_2$ will shift to the left, making it rapidly very difficult to obtain a high absorption solution. For a given power level, the maximum absorption will occur at that frequency such that the high absorption root first appears. Consequently, the frequency for peak

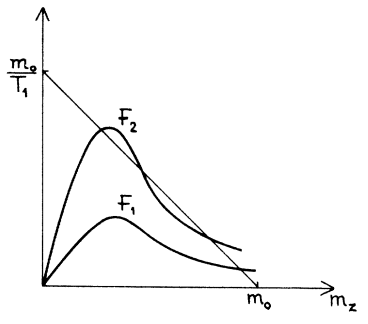


FIG. 3. A parametric plot of Eq. (4.5) in the presence of frequency pulling. $F_1$ and $F_2$ represent two different power levels. The two extreme solutions (for $F_2$) are stable. This sketch is not drawn to scale in order to give a better demonstration of the qualitative behavior.

absorption will be a function, both of power level and temperature, and will usually lie between the shifted and unshifted nuclear resonance frequencies. As the power increases, the peak frequency will approach $\omega_n$, and as the power decreases, the peak frequency will approach $\omega_n-\delta\omega$. As the temperature increases, the pulling effect will decrease and the peak frequency will tend toward $\omega_n$. The line shape in the presence of strong frequency pulling will probably be very asymmetric. The absorption on the high frequency side of the maximum should fall off much more steeply than on the low-frequency side and the width of the observed line will be of the order of a fraction of the frequency pulling, and may be much greater than the natural width. Of course, the precise critical power level will depend strongly on $T_1$ and $T_2$. This nuclear saturation at the critical power level is just the type of effect which has been observed in $KMnF_3$.

There remains the question of how the spin system can be pulled to small values of $m_z$ from the other stable solution $m_z\approx m_0$. There exists a critical rf field, $h_c$, above which the high absorption solution is the only equilibrium solution to (4.5). For a Gaussian line this critical field is given by

$$(\pi/2)(\gamma_n h_c^*)^2T_1T_2 \approx \Delta^2\exp\{[\omega-(\omega_n-\delta\omega)]^2/2\Delta^2\}/\delta\omega(\omega_n-\omega), \quad (5.9)$$

for $\omega_n-\omega\gg\Delta$. For sufficiently broad lines and/or frequencies sufficiently near the pulled frequency, $\omega_n-\delta\omega$, the high absorption solution will be reached in a time of the order of $T_1$. As the power is decreased from $h_c$, the low-absorption solution would not appear until the first contact point (given by 5.8) is reached. Thus, one could observe a region of hysteresis in the nuclear saturation for power levels between these two contact points. Of course, the precise value of $h_c$ depends very strongly on the exact nuclear resonance line shape. An experiment in which one sweeps from low to high frequency should also give rise to hysteresis in the same way. In fact, the condition for the second contact (5.9) is strictly not valid when $(\gamma_n h^*)^2T_1T_2>1$. Then it is known[16] that there exist large changes in the line shape especially in the wings which may change the condition for $h_c$ drastically. However, the excitation of the pulled solution will probably be nucleated by other phenomena[17] such as spin pinning.

At high power levels, one might wonder whether or not Suhl instabilities[14] might occur, as in ferromagnets, via the coupling, through the dipolar fields, of the $q=0$ nuclear spin wave mode with degenerate $q\neq0$ modes. In Appendix B, it is shown that such an effect would occur at much higher power levels than, for example, given by (5.8).

[16] A. Redfield, Phys. Rev. **98**, 1787 (1955).

[17] A. M. Portis, G. Witt, and A. J. Heeger, to be presented at the Eighth Annual Conference on Magnetism and Magnetic Materials, Pittsburgh, November, 1962 (unpublished).

## Spin Echoes

We now investigate the behavior of a coupled electron nuclear system when a strong rf field pulse $H_1$ is applied at a frequency $\omega$ in the vicinity of the nuclear resonance frequency.

At the beginning of the pulse, the magnetization **m** is tilted, $m_z$ is reduced, and the instantaneous precession frequency $\omega_n[1-\eta(m_z/M_0)]$ increases; the nuclear system is then submitted to a rf field which is not any more tuned to the correct frequency and the magnetization becomes insensitive to $H_1$. The main conclusion is that it is difficult to make 90 pulses when the frequency shift $\delta\omega$ is large. Numerically, for a ferromagnet the effect is computed as follows: in a frame rotating at frequency $\omega$, the equations of motion for the nuclear magnetization are:

$$dm_x/dt=(\Delta\omega+\mu\delta\omega)m_y; \quad (5.8)$$

$$dm_y/dt=-(\Delta\omega+\mu\delta\omega)m_x+\gamma_nH_1\eta m_0\mu; \quad (5.9)$$

$$d\mu/dt=-\gamma_nH_1\eta(m_y/m_0), \quad (5.10)$$

where $\Delta\omega=\omega-\omega_n$ and $\mu=(m_z/m_0)$. Combining (5.8) and (5.10) we obtain

$$(\Delta\omega+\mu\delta\omega)(d\mu/dt)=-\gamma_nH_1\eta m_0^{-1}(dm_x/dt). \quad (5.11)$$

This may be integrated (with the boundary condition $\mu=1$ for $m_x=0$) and gives $m_x$ explicitly as a function of $\mu$. Eliminating then $m_y$ between (5.9) and (5.10), one obtains a second-order equation for $\mu$, formally identical to the equation of motion of a classical point in a static one-dimensional field:

$$d^2\mu/dt^2=dF(\mu)/d\mu; \quad (5.12)$$

$$F(\mu)=8^{-1}(\delta\omega)^2(1-\mu)P(\mu); \quad (5.13)$$

$$P(\mu)=\mu^3+(1+4x)\mu^2+(4y^2+4x^2-1)\mu+4y^2-4x^2-4x-1; \quad (5.14)$$

$$x=\Delta\omega/\delta\omega; \quad y=\gamma_n\eta H_1/\delta\omega. \quad (5.15)$$

The "energy integral" for this problem yields

$$(d\mu/dt)^2=4^{-1}(\delta\omega)^2(1-\mu)P(\mu),$$

where the integration constant is chosen to ensure $d\mu/dt=0$ when $\mu=1$. This system starts from this value $\mu$, then decreases, and $d\mu/dt$ remains negative until $P(\mu)$ vanishes. At this point, $\mu$ starts to increase and goes back to 1. Thus, if we want to make a 90° pulse ($\mu$ going from 1 to 0) we need that $P(\mu)$ does not vanish in the interval $0<\mu\leq1$. A detailed study of $P(\mu)$ shows that the minimum value of $y$ (or $H_1$) for which this is realized is $y=4^{-1}(2^{1/2}-1)\sim0.1$. The pulse frequency for which this is obtained corresponds to $x=-\frac{1}{2}$.

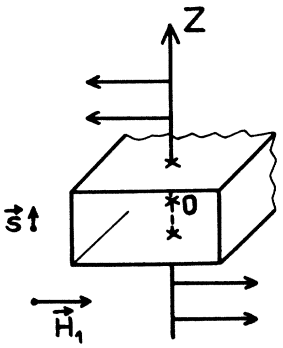


FIG. 4. Bloch wall. In the interior of the Bloch wall the magnetization rotates remaining parallel to the $xy$ plane perpendicular to $O_3$.

Thus, to make 90° pulses, in the most favorable case we need an rf field $H_1$ such that

$$(\delta\omega)^{-1}(\eta\gamma_n H_1)=0.1 \quad \text{or} \quad H_1=0.1\alpha m_0. \tag{5.16}$$

In the liquid helium range this leads to fields of order 0.1 to 1 G (for 100% isotopic abundance). At lower temperatures it would be considerably more difficult to apply echo techniques.

Up to now, we have discussed only the motion when the rf field was applied. The last question is: What happens after the rf pulse? The answer is given simply by Eqs. (5.8), (5.9), and (5.10) with $H_1=0$ (for times shorter than the spin lattice relaxation time $T_1$). Then $m_z$ retains the constant value which has been prescribed by the pulse conditions and the transverse components of the magnetization process at the frequency, $\omega_n[1-\eta(m_z/M_0)]$.

## ACKNOWLEDGMENTS

The authors are especially indebted to Professor A. Portis and Professor A. Heeger for their discussions and correspondence concerning the experimental situation in $KMnF_3$ and to Professor N. Bloembergen for his suggestion of the occurrence of a degeneracy in the nuclear spectrum. We have also benefited from discussions with C. Robert. One of us (P. P.) would like to express his thanks to Professor A. Abragam and the entire Magnetic Resonance Group at Saclay for their kind hospitality dubing the tenure of a National Science Foundation Postdoctoral fellowship.

## APPENDIX A. FREQUENCY SHIFT IN BLOCH WALLS

We derive the frequency shift for a 180° wall in a uniaxial crystal. The general notation and structure of the wall at rest is represented on Fig. 4. In a state of motion there are small, $z$ dependent deflections $M_z, M_\theta$, and $m_z$, $m_\theta$, of the electron and nuclear magnetization. The component $M_z$ (along the axis perpendicular to the wall) is always negligible. The equations of motion for the nuclear spins are

$$\begin{aligned} i\omega m_\theta &= dm_\theta/dt=\gamma_n\alpha M_0 m_z, \\ i\omega m_z &= dm_z/dt=\gamma_n\alpha(-M_0 m_\theta+m_0 M_\theta). \end{aligned} \tag{A1}$$

The variation $M_\theta(z)$ of the electronic magnetization is related to the overall displacement of the wall $S$ by

$$M_\theta=-M_0(\partial\theta/\partial z)S, \tag{A2}$$

where $\theta$ is the turn angle in the undisturbed Bloch wall. For the simple case at hand

$$\partial\theta/\partial z=e^{-1}\sin\theta, \tag{A3}$$

where $e$ is the wall thickness.

The displacement $S$ can be related to the fields acting on the wall; the external rf field $H_1$ and the fields from the nuclei $\alpha\mathbf{m}$:

$$m_w\frac{d^2S}{dt^2}+\beta\frac{dS}{dt}+CS=2M_0H_1-\alpha M\int m_\theta d\theta. \tag{A4}$$

In this equation, $m_w$ is the wall mass (per cm$^2$), $\beta$ a damping coefficient, and $C$ is related to the static permeability of the material. The right-hand side $dE/dS$ gives the change in magnetic and hyperfine energy per cm$^2$, $dE$, when the wall is displaced by an amount $dS$; it may correctly be called the pressure acting on the wall.

It is convenient to introduce at this stage the maximum enhancement factor $\eta_{\max}$ for the rf field acting on the nuclei. $\eta_{\max}$ is obtained for nuclei at the center of the wall; it may be calculated by neglecting the small hyperfine contribution to the pressure in (A4).

$$\begin{aligned} \eta_{\max} &= -(\alpha M_\theta/H_1)_{\theta=\pi/2} \\ &= 2\alpha M_0{}^2 e^{-1}(-m_w\omega^2+i\beta\omega+C)^{-1}. \end{aligned} \tag{A5}$$

$\eta_{\max}$ as defined here is generally complex. We know, however, from the results of Portis and Gossard,[5] that at room temperature in cobalt $\eta_{\max}$ is essentially real and of order 1500. Let us now come back to the calculation of the resonance frequency for which we can put $H_1=0$. We obtain from (A2), (A4), and (A5)

$$M_\theta=(\tfrac{1}{2})\eta_{\max}e(\partial\theta/\partial Z)\int m_\theta d\theta. \tag{A6}$$

Thus, the dependence of all amplitudes $M_\theta$, $m_\theta$, $m_z$ is given by $\partial\theta/\partial z$. Putting $m_\theta=R(\partial\theta/\partial z)=Re^{-1}\sin\theta$, we

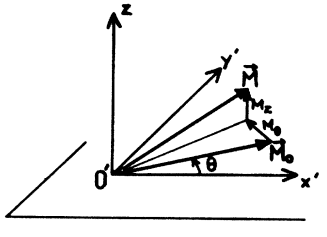


FIG. 5. Vectors relating to Bloch wall. $M_0$ is the equilibrium position of the magnetization in the $x'y'$ plane. $M$ is the deflected magnetization.

get $\int m_\theta d\theta = 2R/e$ and from (A6)

$$M_\theta = \eta_{\max} m_\theta. \tag{A7}$$

If we now insert (A7) in (A1) we obtain the secular equation:

$$\begin{aligned} &\omega^2 = \omega_n{}^2[1-\eta_{\max}(m_0/M_0)]; \\ &\omega \cong \omega_n[1-\tfrac{1}{2}\eta_{\max}(m_0/M_0).\ ] \end{aligned} \tag{A8}$$

Equation (A8) is very similar to Eq. (2.4) for the frequency shift in the bulk material. The factor $\frac{1}{2}$ obviously comes from the fact that, in the Bloch walls, the effective rf field acting on the nuclei is linearly polarized. Equation (A8) was derived for a simple case but remains qualitatively correct for all situations.

In fcc cobalt, with $\eta_{\max}=1500$, $M=1400$ emu, $m_0=3.3\times10^{-2}T$, we obtain from (A8), $(\omega-\omega_n)/\gamma_n\sim10^3$ Oe at $T=4°$K. This estimate, however, is correct only if $\eta_{\max}$ does not change significantly from room temperature to 4°K. In fact, in the case of a metal like cobalt, the damping coefficient $\beta$ is probably due to eddy current effects, and is proportional to the conductivity,[12] $\sigma$. From the data of Portis and Gossard[5] we estimate $\beta\omega/C\sim0.1$ at room temperature. At low temperatures, $\beta$ depends critically on the residual resistivity of the cobalt particles and we cannot make a very definite prediction. Assuming, for instance, $\sigma_{T=0}/\sigma_{T=300}=10$, we would have, at very low temperatures, $\beta\omega\sim C$. The real and imaginary parts of $\eta_{\max}$ are then equal, the shift and the intrinsic width of the resonance are then comparable and of order 500 Oe. It would thus be of interest to study simultaneously $\eta_{\max}$ and $\delta\omega$ on cobalt particles in the helium range. Of course, as in the case of the bulk material, the resonance frequency is power dependent through $m_0$ and the shift $\omega-\omega_n$ can be observed only at very low power levels.

## APPENDIX B. SUHL INSTABILITY WITHIN THE NUCLEAR SYSTEM

In this Appendix we calculate the critical field for the Suhl instability. We start from the equations of motion (4.1) for the nuclear magnetization

$$dm_{qx}/dt=\gamma_n[\alpha M_z+H_0-N_zM_z]m_{qy}-\gamma_n\alpha m_zM_{qy}.$$

The electronic term $M_{qy}$ is now expressed in terms of $m_{qy}$ and we obtain

$$dm_{qx}/dt=\gamma_n[\alpha M_z+H_0-N_zM_z-(\alpha^2m_zM_z/C_q)]m_{qy}, \tag{B1}$$

and a similar equation for $m_{qy}$.

If a strong rf field is applied at a frequency corresponding to the uniform nuclear mode, $m_z$ and $M_z$ are strongly affected. The effects related to the reduction of $m_z$ are discussed in Sec. V. If the electronic and nuclear motions are elliptical, terms oscillating at a frequency $2\omega_0$ will appear in $m_z$ and $M_z$. These terms produce an instability for the nuclear spin waves degenerate with the uniform mode.

Let us calculate now the amplitudes $\delta M_z$ and $\delta m_z$ of the oscillating parts of $M_z$ and $m_z$.

We write the equations for the motion of $M_z$ and $m_z$ disregarding damping terms and nonuniform components:

$$\begin{aligned} &dM_{0z}/dt=\gamma_e[M_{0y}(\alpha m_{0x}+h_{0x})-M_{0x}(\alpha m_{0y}+h_{0y})], \\ &dm_{0z}/dt=\gamma_n\alpha(m_{0y}M_{0x}-m_{0x}M_{0y}). \end{aligned} \tag{B2}$$

We neglect the direct coupling between the rf field and the nuclear magnetization.

$M_{0x}$ and $M_{0y}$ are expressed in terms of $h_x$, $h_y$, $m_{0x}$, and $m_{0y}$. We obtain

$$\begin{aligned} &M_{0x}=M_0(\alpha m_{0x}+h_x)/D_0, \\ &M_{0y}=M_0(\alpha m_{0y}+h_y)/C_0. \end{aligned} \tag{B3}$$

$C_0$ and $D_0$ are defined in Sec. IV.

It is interesting to compare the magnitude of the field due to the nuclear motion $\alpha m_{0x}$ to the magnitude of the external applied field $h_x$. $m_{0x}$ at resonance is given by

$$m_{0x}\sim\gamma_n\eta h_xT_2m_0.$$

The ratio $p$ of the two quantities is

$$p=\alpha m_{0x}/h_x=\alpha m_0\eta\gamma_nT_2=(\omega_0T_2)\eta(m_0/M_0). \tag{B4}$$

At low temperature, $p$ may be larger than unity. If $\eta=10^2$, $(m_0/M_0)=3\times10^{-4}$, $\omega_0T_2=10^3$, then $p=30$.

The calculations will be done assuming $p\gg1$ and, therefore, $h_x$ and $h_y$ will be neglected in the Eqs. (B3). If this condition is not valid, the critical fields will be larger than our estimation. Equations (B2) become

$$\begin{aligned} &dM_{0z}/dt=\gamma_eM_0p^2h_xh_y(D_0-C_0)/D_0C_0, \\ &dm_{0z}/dt=\gamma_nM_0p^2h_xh_y(D_0-C_0)/D_0C_0. \end{aligned} \tag{B5}$$

$(D_0-C_0)/(D_0C_0)^{1/2}$ is a measure of the ellipticity of the electronic uniform mode; for a thin plate perpendicular to the $z$ axis, we have

$$(D_0-C_0)/D_0C_0=4\pi M/(H_0+H_A)(H_0+H_A+4\pi M),$$

and if $4\pi M\gg H_0$, Eqs. (B5) become

$$\begin{aligned} &dM_{0z}/dt=\gamma_eM_0p^2h_xh_y/(H_0+H_A), \\ &dm_{0z}/dt=\gamma_nM_0p^2h_xh_y/(H_0+H_A). \end{aligned}$$

The amplitudes $\delta M_z$ and $\delta m_z$ are easily obtained:

$$\begin{aligned} &\delta M_z=p^2(\gamma_eM_0/\gamma_nH_n)h^2/4(H_0+H_A), \\ &\delta m_z=p^2(M_0/H_n)h^2/4(H_0/H_A), \end{aligned}$$

$h$ being the amplitude of the rotating applied field.

The $\alpha\delta M_z$ term behaves exactly as an external oscillating field applied along the $z$ axis, and the problem is identical to the parallel pumping problem. The critical field is given by

$$\gamma_n\alpha\delta M_z\eta(m/M)\geq1/T_2$$

which may be written as

$$(\gamma_n\eta hT_2)^2 \geq (\omega_n T_2)^{-1}[\eta(m/M)]^{-2}(M/m)(\gamma_n/\gamma_e).$$

With the usual assumptions, the equation is

$$(\gamma_n\eta hT_2)^2 \geq 3.$$

The critical field we obtain is much larger than the field given by the usual saturation condition. With such a field all the approximations made in this Appendix are not valid.

The effect of the $\delta m_z$ term is examined. The calculations are similar and lend to the condition

$$\alpha^2 M_z \delta m_z / C_q \geq 1/T_{2q}.$$

We obtain

$$(\gamma_n\eta hT_2)^2 \geq 8(\omega_n T_2)^{-1}(\eta m/M)^{-2}.$$

Or with the assumptions, $(\gamma_n\eta hT_2)^2 \geq 10$.

The conclusion is that it is impossible to reach a critical field giving rise to Suhl instability.

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# Specific Heats of Transition Metal Superconductors

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Specific heats have been measured on superconducting transition metal elements, alloys and compounds which cover a wide range in $T_c$ and a large portion of the $d$ band. A strong dependence of $T_c$ upon the density of states in the $d$ band indicates that the superconducting electrons are $d$ electrons. The electron interaction parameter, $V$, of the Bandeen-Cooper-Schrieffer theory is found to be approximately 0.4 eV for all the metals investigated. The phonon frequency involved in the electronic interaction is less than that predicted by theory and changes over a range of about a factor of 5 when the Fermi level is moved to different parts of the $d$ band. The product $N(O)V$ exceeds the weak coupling limit for many specimens, yet the results for these do not depart from the general behavior.

## INTRODUCTION

THE experimental investigation of transition metal elements, alloys, and compounds by Matthias and Hulm have emphasized certain regularities in the appearance of superconductivity throughout the periodic system. The connection between these regularities and the Bandeen-Cooper-Schrieffer theory of superconductivity[1] is given by the expression

$$kT_c = 1.14\langle\hbar\omega\rangle_{\rm av} \exp[-1/N(0)V], \quad (1)$$

where $T_c$ is the critical temperature, $\langle\hbar\omega\rangle_{\rm av}$ the average energy of the phonons which scatter electrons at the Fermi surface, $N(0)$ the density in energy of electronic states at the Fermi surface, and an adjustable parameter $V$, which measures the difference between the Coulomb repulsion and the phonon-induced interaction of electrons close to the Fermi surface. However, nearly all of the published data describe the behavior of $T_c$ as a function of the average number of valence electrons per atom and, therefore, do not constitute a test of Eq. (1). If Eq. (1) is approximated by

$$T_c \approx \theta_D \exp[-1/N(0)V], \quad (2)$$

where $\theta_D$ is the Debye temperature, one sees that a measurement of specific heat versus temperature, which yields $T_c$, $\theta_D$, and $N(0)$, will allow the behavior of $V$ to be determined. Some specific-heat data have been published for alloys of Ti-Mo,[2] Ti-V-Cr,[3] and[4] Ti-V but they range over only a factor of 4 in $T_c/\theta_D$, not enough for any general conclusions to be drawn concerning $V$. In this paper we report data on elements, alloys, and compounds of the transition metals in which $T_c/\theta_D$ is varied by a factor of 300. It is found that $V$ is a constant, as Pines[5] suggested it might be for $d$-band metals. However, an unexpected result indicates that the phonon frequency involved in the electronic interaction is less than that predicted by theory and changes over a range of about a factor of 5 when the Fermi level is moved to different parts at the $d$ band.

## EXPERIMENTAL

In order to test the theory, results of moderate accuracy on a large number of samples were required. For this purpose a calorimeter was developed in which heat capacity was measured by a pulse method designed for speed, small samples, and for use in an ordinary cryostat mounted between the poles of an

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