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# Acoustic Nuclear Magnetic Resonance in Antiferromagnetic Insulators[*]

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A proposal of phonon-induced nuclear magnetic resonance in antiferromagnetic insulators has been considered theoretically. We have found that such an experiment can serve as an extremely useful tool to measure properties such as the phenomenological coupling constant associated with the one phonon–one magnon magnetoelastic coupling. The mechanism with which the coherent lattice energy is absorbed by the nuclear spin system is a two-step process in which a phonon first excites a virtual spin wave via the magnetoelastic coupling and then a nuclear spin is flipped through the decay of the virtual spin wave via the off-diagonal matrix elements of electron-nuclear hyperfine interaction. The resulting attenuation coefficient is proportional to the square of the phenomenological coupling constant. This then remains the only unknown parameter, presuming that the hyperfine coupling constant has been predetermined by conventional microwave nuclear magnetic resonance. The order-of-magnitude estimates indicate that the effect should be well within the experimentally observable region.

## I. INTRODUCTION

THE prospect of acoustic nuclear magnetic resonance in antiferromagnetic insulators is interesting in itself,[1] but in addition we find that it can serve as an extremely useful tool to measure properties such as the phenomenological coupling constant associated with the one phonon–one magnon magnetoelastic coupling. At low temperatures, this coupling has its origin in both crystalline field effects and the spatial modulation of the ordered electron-spin dipole interaction. The phenomenological interaction is of the form

$$G\sum_j \left[S_j^z S_j^x e_{xz}(j)+S_j^z S_j^y e_{yz}(j)\right]. \tag{1.1}$$

Here $G$ is the phenomenological coupling constant, the $S_j$'s are the electron-spin operators at the $j$th site, and the $e$'s are the strain components. Before one can objectively assess the effects of this interaction on the magnetothermal porperties, one must have an accurate experimental determination of the coupling constant $G$.

An obvious way of measuring $G$ would be the direct acoustic excitation of antiferromagnetic spin waves. However, one would then need energies comparable to the antiferromagnetic spin-wave energy gap, $E_g=\hbar(2\omega_e\omega_A)^{1/2}$, where $\hbar\omega_e$ and $\hbar\omega_A$ correspond to the exchange and anisotropy energies, respectively. These energies would often necessitate phonon production in submillimeter range, a region at present not experimentally feasible.

Pincus and Winter[2] attempted to estimate $G$ in $MnF_2$ by making use of the longitudinal nuclear-spin relaxation data obtained by Jaccarino and Walker.[3] Their conjecture was that the low-temperature relaxation was primarily due to the relaxation mechanism, nucleus-virtual spin-wave thermal phonon. However, their attempt at correlating the theoretical expressions with the experimental relaxation times resulted in an unrealistically large value of the coupling constant. The explanation for this failure presumably lies in the neglect of strongly competing relaxation mechanisms; therefore, one must find a process that will select a single excitation or relaxation channel. This can be accomplished by turning the thermal phonon-relaxation process around and investigating directly the coherent energy flow from the lattice into the nuclear-spin system. That is, one simply looks at the ultrasonic attenuation due to the acoustic resonance of the nuclear spins that are coupled to the electron magnets via the hyperfine interaction. Here we have explicitly selected the mechanism, and do not have to worry about competing processes.[4,5] The antiferromagnetic magnons that enter are in virtual states, thus the phonon frequencies for resonance correspond to the nuclear Larmour frequencies in the hyperfine field, characteristically in the $10^2$ to $10^3$ Mc/sec range.

In this paper, we first derive an indirect nuclear-phonon Hamiltonian via the method of canonical transformation in order to eliminate the electron variables. Then, we calculate the attenuation from the effective interaction. In the formulation, we consider the addition of an external magnetic field parallel and perpendicular to the easy axis (we assume a uniaxial anisotropy). These additions not only allow us to predict the field dependence of the attenuation, but moreover provide the standard experimental procedure of sweeping the resonance while keeping the driving frequency constant. We have also shown in Appendix B that in the absence of an external field, the effective nuclear spin-phonon Hamiltonian can be derived quickly on the basis of a simple semiclassical vector model.

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[*] Supported by the National Science Foundation.

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[1] Acoustic magnetic resonance experiments have been a useful tool for many years. For a complete bibliography, see D. I. Bolef, Science **136**, 359 (1962).

[2] P. Pincus and J. Winter, Phys. Rev. Letters **7**, 269 (1961).

[3] V. Jaccarino and L. R. Walker, J. Phys. Radium **20**, 341 (1959).

[4] There will be an effect also due to the spatial modulation of the direct electron-nuclear dipole interaction. However, the effect of this mechanism on the absorption will be down by a factor of at least $(A\gamma_e/\gamma_n\hbar\omega_A)^2$, where $A$ is the hyperfine coupling constant. This will in general be a small effect ($\sim$20 for $MnF_2$).

[5] The spatial modulation of the exchange interaction will be biquadratic in the phonon and spin-wave fields.

## II. EFFECTIVE NUCLEAR SPIN-PHONON HAMILTONIAN

The total Hamiltonian of the system composed of nuclear spins, electron spins, and the lattice can be represented in the form

$$\mathcal{H}=\mathcal{H}_n+\mathcal{H}_e+\mathcal{H}_p+\lambda_1 V_{ne}+\lambda_2 V_{ep}. \qquad (2.1)$$

The terms in the Hamiltonian are defined in the following manner: (1) $\mathcal{H}_n$ is the nuclear Hamiltonian which has Zeeman terms arising from both the applied fields and the stationary hyperfine field. In addition, it has the terms that contribute to the nuclear-resonance linewidth, such as the nuclear dipole interaction. The pseudodipolar terms arising from the indirect exchange of antiferromagnetic spin waves are not present, but appear later on, after the canonical transformation is performed. (2) $\mathcal{H}_e$ is the Hamiltonian of the antiferromagnetic-ordered system. We represent this by the standard Heisenberg exchange model with the addition of a uniaxial anisotropy field $\mathbf{H}_A$ and an external field $\mathbf{H}_0$:

$$\mathcal{H}_e=2J\sum_{\langle ij\rangle}\mathbf{S}_i\cdot\mathbf{S}_j-2\gamma_e\hbar H_A\sum_j(S_{ja}{}^z-S_{jb}{}^z)$$
$$+2\gamma_e\hbar\mathbf{H}_0\cdot\sum_j(\mathbf{S}_{ja}+\mathbf{S}_{jb}). \qquad (2.2)$$

Here we have divided our system into the conventional two-interpenetrating-sublattice model of antiferromagnets. These sublattices have been represented by $a$ and $b$, with the property that the nearest neighbor of an ion on $a$ lies on $b$ and vice versa. (3) $\mathcal{H}_p$ represents the free-phonon Hamiltonian which, in second quantized form, is represented by

$$\mathcal{H}_p=\sum_{k\lambda}\hbar\omega_{k\lambda}(a_k{}^{\lambda\dagger}a_k{}^{\lambda}+\tfrac{1}{2}). \qquad (2.3)$$

Here $\lambda$ is the polarization index. (4) The interaction term $\lambda V_{ne}$ is characterized by the off-diagonal components of the hyperfine coupling of the electron and nuclear spins. The total hyperfine coupling can be represented in general by a tensor form;

$$\sum_{lj}\mathbf{I}_l\cdot\mathbf{A}_{lj}\cdot\mathbf{S}_j.$$

The hyperfine field arises from the combined effects of the orbital, contact, and dipolar fields at the nuclear site. For many antiferromagnets, in particular for the $Mn^{++}$ ion in $MnF_2$, the orbital moment is quenched, and the electron distribution around a given ion is almost spherical, a fact reflected in a $g$ factor $\sim 2$. The anisotropic contributions of the coupling will arise from the dipole interaction. This effect, although not negligible, will be small. Thus, for our purposes, we can treat the hyperfine interaction as an isotropic form[6]

$$\sum_{lj}A_{lj}\mathbf{I}_l\cdot\mathbf{S}_j$$
$$=\sum_{lj}A_{lj}[I_l{}^zS_j{}^z+\tfrac{1}{2}(I_l{}^+S_j{}^-+I_l{}^-S_j{}^+)]. \qquad (2.4)$$

The latter two terms on the right-hand side are the off-diagonal terms representing the interaction. (5) The last term in our Hamiltonian is the one phonon–one magnon coupling which we have indicated previously by Eq. (1.1). For convenience in our subsequent calculation, we re-express this in terms of the transverse spin and strain components. These are defined by

$$S_j{}^{\pm}=S_j{}^x\pm iS_j{}^y,$$

and

$$e_{\pm z}=e_{xz}\pm ie_{yz}.$$

The magnetostrictive coupling will then assume the form

$$(G/2)\sum_j[S_{j\alpha}{}^zS_{j\alpha}{}^+e_{-z}(j)+S_{j\alpha}{}^zS_{j\alpha}{}^-e_{+z}(j)]. \qquad (2.5)$$

Here $\alpha$ is a sublattice index. Now we wish to obtain an effective Hamiltonian that incorporates only the nuclear spin-phonon dynamic variables. Effective or indirect Hamiltonians are derived most conveniently by the perturbation method of canonical transformation with a subsequent averaging over the intermediary system. In our case, the intermediary system corresponds to the electrons. The method used, which is described in more detail in Appendix A, is a slight generalization of the formulation in terms of matrix elements[7] in that the solution is expressed in terms of a general correlation function. The form, as indicated in Appendix A, is

$$\mathcal{H}_{\text{eff}}=\mathcal{H}_n{}'+\mathcal{H}_p{}'-\frac{i}{2}\lambda_1\lambda_2 P\int_{-\infty}^{0}dt$$
$$\times e^{\delta t}\langle[V_{ne}(t),V_{ep}(0)]+[V_{ep}(t),V_{ne}(0)]\rangle_{\text{elect}}. \qquad (2.6)$$

In (2.6), we have put a prime on the nuclear-spin contribution to the effective Hamiltonian to indicate that it incorporates now the pseudodipolar line-broadening terms due to the indirect exchange of spin waves between the nuclei. As discussed in the introduction, we will wish to include the effects of external magnetic fields applied perpendicular and parallel to the easy axis. Of course, the field effects enter in the evaluation of the correlation function in (2.6). The parallel-field case is a simple extension of the zero-field calculation, and can simply be shown to have a negligible effect as long as one does not approach the rather high critical-field region that induces the phenomenon of flipping the electron spins. However, the perpendicular field serves to cant the electron spins, and forces one to quantize the system of each of the sublattices along a differently rotated axis. The spin-wave analysis used in this case is similar to that used by Kanamori and Yosida.[8] The algebra, but not the physics, associated with the derivation of the perpendicular-field case is a good deal more complicated. Therefore, we will indicate only the results of the field dependence and merely go through the simpler zero-field derivation.

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[6] For a complete discussion of the hyperfine anisotropy, see R. G. Shulman and V. Jaccarino, Phys. Rev. **108**, 1219 (1957).

[7] See, for example, J. Bardeen and D. Pines, Phys. Rev. **99**, 1140 (1955).

[8] J. Kanamori and K. Yosida, Progr. Theoret. Phys. (Kyoto) **14**, 423 (1955).

We will restrict our consideration to temperatures considerably lower than the Néel temperature. In this region we can replace the sublattice electron-spin operators by the leading terms in the spin-wave expansion:

$$\begin{aligned} S_{ja}^{+} &\cong (4S/N)^{1/2} \textstyle\sum_{\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{j}} c_{\mathbf{k}}; \\ S_{j'b}^{+} &\cong (4S/N)^{1/2} \textstyle\sum_{\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{j}'} d_{\mathbf{k}}^{\dagger}; \\ S_{ja}^{z} &\cong S; \quad S_{jb}^{z} = -S. \end{aligned} \tag{2.7}$$

Here $N$ is the total number of magnetic ions. The field operators are Bose field operators with the commutation relations

$$[c_{\mathbf{k}}, c_{\mathbf{k}'}^{\dagger}] = [d_{\mathbf{k}}, d_{\mathbf{k}'}^{\dagger}] = \delta_{\mathbf{k},\mathbf{k}'}. \tag{2.8}$$

The Heisenberg Hamiltonian is not diagonal in the $c_{\mathbf{k}}$, $d_{\mathbf{k}}$ representation,[9,10] but is diagonalized via the canonical transformation

$$\begin{aligned} c_{\mathbf{k}} &= u_k \alpha_{\mathbf{k}} + v_k \beta_{\mathbf{k}}^{\dagger}; \\ d_{\mathbf{k}} &= v_k \alpha_{\mathbf{k}}^{\dagger} + u_k \beta_{\mathbf{k}}; \\ u_k^2 - v_k^2 &= 1. \end{aligned} \tag{2.9}$$

Here the $\alpha_k$'s and the $\beta_k$'s obey the same Bose-field commutation relations. The appropriate choice of the $u_k$'s and $v_k$'s which diagonalizes the Hamiltonian is given by

$$\begin{aligned} 2u_k v_k/(u_k^2 + v_k^2) &= -\gamma_k \omega_e/(\omega_e + \omega_A); \\ \gamma_k &= (1/z) \textstyle\sum_{\delta} \exp i\mathbf{k}\cdot\boldsymbol{\delta}. \end{aligned} \tag{2.10}$$

Here $\boldsymbol{\delta}$ represents the vector from a magnetic ion to the nearest neighbor, $\omega_e = 2zSJ$, and $z$ represents the number of nearest neighbors. The elementary excitations (antiferromagnetic magnons) satisfy the dispersion relation

$$\omega_k = [(\omega_e + \omega_A)^2 - (\gamma_k \omega_e)^2]^{1/2}. \tag{2.11}$$

In the nuclear-resonance mechanism we are considering, the magnons appear in virtual states only. Although we are off the energy shell in such virtual processes, of course, we must conserve the wave vector at each vertex. The phonon wavelengths corresponding to the nuclear Larmour frequency will be the order of $10^4$ interatomic distances. Of course, this is the extreme long-wavelength limit of the dispersion relation, and, for our purposes, we need only consider the uniform mode, $\omega_0 = (2\omega_e \omega_A)^{1/2}$.

We now want to calculate the effective Hamiltonian which is formally represented by Eq. (2.6). To do so, we first expand the interaction terms in terms of the magnon and phonon variables. The magnetostrictive coupling so expanded assumes the form

$$\lambda_2 V_{ep} = GS(S/2) \textstyle\sum_{\mathbf{k}} [e_{-z}(\mathbf{k})(u_k - v_k)(\alpha_{\mathbf{k}} - \beta_{\mathbf{k}}^{\dagger}) + \text{c.c.}]. \tag{2.12}$$

Here the Fourier components of the shearing strain are defined by

$$e_{\mp}(j) = (2/N)^{1/2} \textstyle\sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{j}} e_{\mp}(\mathbf{k}); \quad e_{\mp}^{*}(\mathbf{k}) = e_{\pm}(-\mathbf{k}). \tag{2.13}$$

These are expressed in terms of the phonon operators by

$$e_{\mp}(\mathbf{k}) = i \textstyle\sum_{\lambda} (\hbar/M\Omega_k^{\lambda})^{1/2} \times [(k_{\mp}\hat{\epsilon}_z + k_z \hat{\epsilon}_{\mp}) \cdot \hat{\epsilon}_{\lambda} (a_{\mathbf{k}}^{\lambda} + a_{-\mathbf{k}}^{\lambda\dagger})]. \tag{2.14}$$

Here $\Omega_k^{\lambda}$ is the phonon-dispersion relation, $M$ is the molecular mass, and $\hat{\epsilon}_{\lambda}$ is the unit polarization vector. We have used a circularly polarized representation, where

$$k_{\pm} = (1/\sqrt{2})(k_x \pm ik_y); \quad \hat{\epsilon}_{\pm} = (1/\sqrt{2})(\hat{\epsilon}_z \pm i\hat{\epsilon}_y). \tag{2.15}$$

The expansion of the hyperfine coupling in terms of the spin-wave operators is

$$\begin{aligned} \textstyle\sum_{lj} A_{lj} \mathbf{I}_l \cdot \mathbf{S}_j = SA \textstyle\sum_l (I_{la}^{z} - I_{lb}^{z}) &+ A(S/2)^{1/2} \textstyle\sum_{\mathbf{k}} [I_{\mathbf{k},a}^{-}(u_k \alpha_{\mathbf{k}} + v_k \beta_{\mathbf{k}}^{\dagger}) \\ &+ I_{\mathbf{k},b}^{-}(v_k \alpha_{\mathbf{k}} + u_k \beta_{\mathbf{k}}^{\dagger}) + \text{c.c.}]. \end{aligned} \tag{2.16}$$

The first term on the right-hand side corresponds to the stationary hyperfine-field term, and is incorporated into the unperturbed nuclear Hamiltonian. The $I_{\mathbf{k},a,b}^{\pm}$ are the Fourier components of the nuclear spin associated with the $\alpha$ sublattice. These are defined as follows:

$$\mathbf{I}_{\mathbf{j},\alpha}^{\pm} = (2/N)^{1/2} \textstyle\sum_{\mathbf{k}} I_{\mathbf{k},\alpha}^{\pm} e^{i\mathbf{k}\cdot\mathbf{j}}; \quad (I_{\mathbf{k},\alpha}^{\pm})^{*} = I_{-\mathbf{k},\alpha}^{\mp}. \tag{2.17}$$

The frequencies associated with the driven phonons and the nuclear Zeeman energy will be small compared to that of the uniform magnon mode. Thus, we can neglect the temporal development of these former operators compared to that of the rapidly oscillating magnon system. For example,

$$\lambda_2 V_{ep}(t) = GS(S/2)^{1/2} \textstyle\sum_{\mathbf{k}} [e_{-z}(\mathbf{k})(u_k - v_k) \times (\alpha_{\mathbf{k}} e^{-i\omega_k t} - \beta_{\mathbf{k}}^{\dagger} e^{+i\omega_k t}) + \text{c.c.}]. \tag{2.18}$$

Equations (2.16) and (2.18) are now inserted into the commutator of the effective interaction given by (2.6). Taking the averages and performing the time integration, we obtain

$$V_{np} = (GS^2 A/2\hbar) \textstyle\sum_{\mathbf{k}} [(I_{-\mathbf{k},a}^{-} - I_{-\mathbf{k},b}^{-})] \times e_{+z}(\mathbf{k})(u_k - v_k)^2/\omega_k + \text{c.c.}]. \tag{2.19}$$

The factor containing the $u_k$ and $v_k$ coefficients for the Bogoliubov canonical transformation can be shown simply by using (2.10) and (2.11) to satisfy

$$(u_k - v_k)^2/\omega_k = 1/(\omega_e + \omega_A - \omega_e \gamma_k) \cong 1/\omega_A. \tag{2.20}$$

Taking the inverse Fourier transforms, we find that the effective interaction assumes the simple form

$$V_{np} = [AS^2 G\xi(H_0)/2\omega_A \hbar][\textstyle\sum_j I_{j,a}^{+} e_{-z}(j) - \textstyle\sum_{j'} I_{j',b}^{+} e_{-z}(j') + \text{c.c.}]. \tag{2.21}$$

Here we have added an additional factor $\xi(H_0)$ which expresses the external field dependence of the effective interaction. As mentioned before, there is no effect within the order considered for the parallel-field case. However, for the perpendicular-field case, there is indeed

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[9] T. Nakamura, Progr. Theoret. Phys. (Kyoto) **7**, 539 (1952).

[10] J. M. Ziman, Proc. Phys. Soc. (London) **65**, 540, 548 (1952).

a variation. We find

$$\xi(H_\perp)=\tfrac{1}{2}\{1+[1+(\gamma_e H_\perp)^2/\omega_e\omega_A]^{1/2}\}. \tag{2.22}$$

For the case of materials with high anisotropy fields, one would need rather large fields to get an appreciable effect. That is, the ratio of the attenuation coefficient in the presence of a field to the zero-field case is given just by

$$\alpha(H_\perp)/\alpha(0)=\xi^2(H_\perp). \tag{2.23}$$

However, attenuation experiments prove rather sensitive to changes in magnitude, and an observation of the field dependence could be expected, even with the moderate fields obtained with conventional magnets. With the effective nuclear spin-phonon Hamiltonian, one is now in a position to calculate the various effects of the lattice on the nuclear spin system and vice versa. In the next section, we will explicitly calculate the ultrasonic attenuation coefficient.

## III. ULTRASONIC ATTENUATION COEFFICIENT

We now perform a simple second-order perturbation calculation of the attenuation coefficient under the assumption of negligible saturation. The maximum power level for the validity of the neglect of saturation will be given shortly, when we discuss the particular case of MnF$_2$. The attenuation coefficient $\alpha_k{}^\lambda$ is the reciprocal of the phonon mean free path $\Lambda_k{}^\lambda$, and is given by

$$\alpha_k{}^\lambda=1/\Lambda_k{}^\lambda=(1/c_s n_k{}^\lambda)(dn_k{}^\lambda/dt). \tag{3.1}$$

Here $c_s$ is the speed of sound. The depletion of the $k$th mode is given by the rate equation

$$dn_k{}^\lambda/dt=W(-)_{n_k{}^\lambda\to n_k{}^\lambda-1}-W(+)_{n_k{}^\lambda\to n_k{}^\lambda+1}. \tag{3.2}$$

The probability of a simultaneous phonon absorption and a nuclear spin flip on the $\alpha$ sublattice is given by

$$\begin{aligned}P(-)_{m_\alpha,n_k{}^\lambda\to(m_\alpha-1),n_k{}^\lambda-1}=(2\pi/\hbar)\delta(E_{m_\alpha-1}-E_{m_\alpha}-\hbar\Omega_k{}^\lambda)\\ \times|\langle m_a-1,\,n_k{}^\lambda-1|V_{np}|m_\alpha,n_k{}^\lambda\rangle|^2.\end{aligned} \tag{3.3}$$

The same relations will apply to both sublattices and thus we can perform the calculation on one of them, and need only introduce a factor of 2 at the completion of the calculation to take both into account.

The square of the matrix element of the effective interaction is given by

$$\begin{aligned}|\langle m_\alpha-1,\,n_k{}^\lambda-1|V_{np}|m_\alpha,n_k{}^\lambda\rangle|^2=n_k{}^\lambda C_k{}^\lambda\Gamma_\lambda(\theta)\\ \times\langle m_\alpha|I_{\mathrm{k}\alpha}{}^+|m_\alpha-1\rangle\langle m_\alpha-1|I_{-\mathrm{k}\alpha}{}^-|m_\alpha\rangle.\end{aligned} \tag{3.4}$$

Here we have abbreviated the constants and the angular-dependent terms by

$$C_k{}^\lambda=[AS^2G\xi(H_\perp)/2\omega_A]^2(k^2/\hbar M\Omega_k{}^\lambda) \tag{3.5}$$

and

$$\Gamma_\lambda(\theta)=(1/k^2)|k_+(\hat{\epsilon}_z\cdot\hat{\epsilon}_\lambda)+k_z(\hat{\epsilon}_+\cdot\hat{\epsilon}_\lambda)|^2. \tag{3.6}$$

Here $\theta$ is the polar angle with respect to the $z$ axis. The absorption rate, and likewise the induced emission rates, are obtained from the $P$'s by taking the thermodynamic average over the initial nuclear spin configuration and summing over the final. For example,

$$W_{\alpha,n_k{}^\lambda\to n_k{}^\lambda-1}=\frac{\sum_{m_\alpha}e^{-E_{m_\alpha}/KT}P(-)_{m_\alpha\to m_\alpha-1,n_k{}^\lambda\to n_k{}^\lambda-1}}{\sum_{m_\alpha}e^{-E_{m_\alpha}/KT}}, \tag{3.7}$$

By an inspection of the matrix elements, we see that the absorption and emission probabilities are related by

$$\begin{aligned}&P(-)_{m_\alpha\to m_\alpha-1,n_k{}^\lambda\to n_k{}^\lambda-1}\\ &\qquad=P(+)_{m_\alpha-1\to m_\alpha,n_k{}^\lambda\to n_k{}^\lambda+1}\left(\frac{n_k{}^\lambda}{n_k{}^\lambda+1}\right).\end{aligned} \tag{3.8}$$

We are applying a narrow phonon beam; therefore, $n_k\gg1$, and the two probabilities are effectively equivalent. Hence we obtain the net absorption rate

$$\begin{aligned}\frac{1}{n_k{}^\lambda}\frac{dn_k{}^\lambda}{dt}=\frac{2\pi}{\hbar}C_k{}^\lambda\Gamma_k(\theta)\frac{\sum_{m_\alpha}[e^{-E_{m_\alpha}/KT}-e^{-E_{m_\alpha-1}/KT}]}{\sum_{m_\alpha}e^{-E_{m_\alpha}/KT}}\\ \times\delta(E_{m_\alpha-1}-E_{m_\alpha}-\hbar\Omega_k{}^\lambda)\\ \times\langle m_\alpha-1|I_{k\alpha}{}^+|m_\alpha-1\rangle\langle m_\alpha-1|I_{-k,\alpha}{}^-|m_\alpha\rangle.\end{aligned} \tag{3.9}$$

Even in the presence of large hyperfine fields of the order of 50 kOe, the nuclear Zeeman energy is small compared to the laboratory $KT$, and we can effectively use the high-temperature expansion. Hence

$$\frac{1}{n_k{}^\lambda}\frac{dn_k{}^\lambda}{dt}=\frac{(2\pi/\hbar)C_k{}^\lambda\Gamma_k(\theta)}{(KT)\mathrm{Tr}(\mathcal{E})}\Omega_k{}^\lambda g(\Omega_k{}^\lambda). \tag{3.10}$$

Here the unit trace, Tr$\mathcal{E}$, is equal to the total sublattice nuclear spin degeneracy, $(2I+1)^{N/2}$. We have defined the shape function of the nuclear resonance in the conventional manner;

$$g(\Omega_k{}^\lambda)=\hbar\sum_{m_\alpha}\frac{\delta(E_{m_\alpha}-E_{m_\alpha-1}-\hbar\Omega_k{}^\lambda)\langle m_\alpha|I_{k\alpha}{}^+|m_\alpha-1\rangle\langle m_\alpha-1|I_{-k\alpha}{}^-|m_\alpha\rangle}{\mathrm{Tr}[I_{k\alpha}{}^+I_{-k\alpha}{}^-]}, \tag{3.11}$$

where

$$\mathrm{Tr}[I_{k\alpha}{}^+I_{-k\alpha}{}^-]=\tfrac{2}{3}I(I+1)(2I+1)^{N/2}. \tag{3.12}$$

Adding a factor of 2 for the absorption due to the second sublattice, we obtain the attenuation coefficient in the form

$$\alpha_k{}^\lambda=(8b\pi/3KT\hbar c_s)C_k{}^\lambda\Omega_k{}^\lambda I(I+1)g(\Omega_k{}^\lambda)\Gamma_\lambda(\theta). \tag{3.13}$$

In the above we have added an additional factor $b$ which denotes the number of resonant nuclei per molecule. For example, in the material $MnF_2$ there are two equivalent fluorine sites per magnetic ion and $b$ would be two for the consideration of this particular resonance. However, $b$ is equal to unity if the Mn nuclear resonance is considered. The angular factor $\Gamma_\lambda(\theta)$ depends on the choice of phonon polarization. For the longitudinal case,

$$\Gamma_{\text{long}}(\theta)=\tfrac{1}{2}\sin^2 2\theta\,, \tag{3.14}$$

whereas for transverse polarization with the polarization in the plane of the propagation vector $\mathbf{k}$ and the $z$ axis, we have

$$\Gamma_{\text{trans}}(\theta)=\tfrac{1}{2}\cos^2 2\theta\,. \tag{3.15}$$

Using the Debye model for the lattice, and substituting the values for the various constants, we can re-express the attenuation coefficient in the form

$$\alpha_k{}^\lambda=\left[\frac{2GAS^2\xi(H_\perp)}{\omega_A}\right]^2\frac{b\pi^3\hbar I(I+1)(\Omega_k{}^\lambda)^2}{\boldsymbol{\Omega}M(K\Theta)^3KT}g(\Omega_k{}^\lambda)\Gamma_\lambda(\theta)\,. \tag{3.16}$$

Here $\boldsymbol{\Omega}$ corresponds to the volume of the primitive cell, and $\Theta$ is the Debye temperature.

A typical material for which the acoustic resonance would be appropriate is the $F^{19}$ nuclear resonance in rutile $MnF_2$. There $SA\cong 10^{-18}$ erg, $\Theta=450°\text{K}$, $H_A=10^4$ Oe, $\boldsymbol{\Omega}=3.9\times10^{-23}$ cm$^3$, $T_2\sim10^{-5}$ sec, $M=1.7\times10^{-22}$ g, and $\omega_e\omega_A=3\times10^{24}$ sec$^{-2}$. The at-resonance attenuation coefficient for optimum orientation will then be of the order of

$$\alpha_{\max}\cong(G^2/T)\times10^{30}\ \text{cm}^{-1}\,. \tag{3.17}$$

For this material, the presence of the large anisotropy field causes the attenuation to be dependent weakly on an external field, e.g., the ratio at 50 kG to the zero-field value is $\alpha(50)/\alpha(0)=0.87$. The order-of-magnitude estimate of the attenuation coefficient (3.17) implies that the attenuation should be readily observable at low temperatures. The magnetoelastic coupling constants have been measured for $Mn^{++}$ ions in MgO by Watkins and Feher[11] by the use of electron spin resonance measurements with the crystals subjected to a static strain, and by Shiren[12] using ultrasonic paramagnetic resonance techniques. Their results yield a value of $G\sim10^{-16}$ erg. The origin of the magnetostrictive coupling in the MgO crystals is primarily due to the crystalline fields, whereas in highly ordered materials such as $MnF_2$ one would anticipate large effects coming from the spatial modulation of the electron-electron dipole interaction. Indeed, Nakamura[13] has estimated $G\sim10^{-16}$ erg on the basis of the dipole interaction.

Of course, we must specify a maximum phonon power level below which the conditions of negligible saturation will be satisfied. Saturation effects become important when the driving field $H_1\approx(\gamma_n{}^2T_1T_2)^{-1/2}$. This corresponds to a strain $e\approx[\omega_A{}^2\hbar^4/T_1T_2(AGS^2)^2]^{1/2}$. Using the parameters indicated previously for $MnF_2$ along with the experimental longitudinal relaxation data obtained by Jaccarino and Walker,[3] we find that the saturation condition corresponds to a phonon flux of $\sim10^{-31}T/G^2$ $\mu$W/cm$^2$. Here $T$ is the absolute temperature. Taking an estimate of $G^2\sim10^{-32}$ ergs$^2$, we obtain a saturation flux of 10 $\mu$W/cm$^2$ at 1°K. In actual experiments this will be reduced by the $Q$ of the cavity.

In our order-of-magnitude estimates, we have specifically considered the case of $MnF_2$. The treatment is, however, quite general and should prove applicable to any antiferromagnetic insulating crystals satisfying the conditions of a strong, nearly isotropic hyperfine coupling. There is an enhancement over ordinary microwave resonance, because the nuclei on both sublattices are simultaneously driven. There remains a possibility, although no mechanism for such a process seems apparent at the moment, that similar to the acoustic paramagnetic resonance the acoustic nuclear resonance line may likewise narrow. Such an effect, coupled with the enhancement factor, may enable heretofore unobservable resonances such as the Mn nuclear resonance in $MnF_2$ to be observed via the acoustic nuclear magnetic resonance.

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## APPENDIX A

In this Appendix we give a generalization of the method of canonical transformations used to obtain indirect interactions. Those acquainted with the technique of adiabatic perturbation theory will note the similarity between the canonical transformation method and the unitary transformation which adiabatically switches on an interaction in the interaction representation.

Let us consider a system which is composed of three subsystems which we denote by $A$, $B$, and $C$. In drawing the analogy to the problem considered in the text, $A$ represents the nuclear spin system in the presence of the stationary hyperfine field, $B$ the antiferromagnetic spin waves, and $C$ the lattice. Furthermore, we suppose that the subsystems are coupled weakly, $A$ and $B$ by $\lambda_1V_{AB}$ and $B$ and $C$ by $\lambda_2V_{BC}$, these being analogous to the off-diagonal hyperfine and the magnetostrictive couplings.

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[11] G. D. Watkins and E. Feher, Bull. Am. Phys. Soc. **7**, 29 (1962).

[12] N. S. Shiren in *Magnetic and Electric Resonance and Relaxation, Proceedings of Colloque Ampère, Eindhoven July 1962*, edited by J. Smidt (Interscience Publishers, Inc., New York, 1963), p. 114.

[13] T. Nakamura (unpublished).

Let us define a new Hamiltonian $\mathcal{H}'$ via a canonical transformation.

$$\mathcal{H}'=e^{iQ}\mathcal{H}e^{-iQ}=\mathcal{H}_0+\lambda_1V_{AB}+\lambda_2V_{BC}+i[Q,\mathcal{H}]+(i^2/2!)[Q,[Q,\mathcal{H}]]+\cdots. \quad \text{(A1)}$$

Here $\mathcal{H}_0$ is the sum of the uncoupled Hamiltonians,

$$\mathcal{H}_0=\mathcal{H}_A+\mathcal{H}_B+\mathcal{H}_C. \quad \text{(A2)}$$

We want to determine $\mathcal{H}'$ up to terms bilinear order in $\lambda_1\lambda_2$; the neglected terms which would further serve to couple $A$ with $C$ will be the order of $(\lambda_1\lambda_2)^2$. Let us now explicitly choose the generating function $Q$ such that we force a cancellation in (A1);

$$i[\mathcal{H},Q]=\lambda_1V_{AB}+\lambda_2V_{BC}. \quad \text{(A3)}$$

This equation is just the Heisenberg equation of motion of the generating function. Hence

$$\partial Q/\partial t=e^{i\mathcal{H}t}(\lambda_1V_{AB}+\lambda_2V_{BC})e^{-i\mathcal{H}t}, \quad \text{(A4)}$$

which becomes, upon an expansion in powers of the coupling constant,

$$\partial Q/\partial t=e^{i\mathcal{H}_0t}(\lambda_1V_{AB}+\lambda_2V_{BC})e^{-i\mathcal{H}_0t}+O(\lambda_1\lambda_2). \quad \text{(A5)}$$

We now integrate this equation with the insertion of an adiabatic convergence factor and the retention of only the principal part.

$$Q=P\int_{-\infty}^{0}dt\, e^{\delta t}[\lambda_1V_{AB}(t)+\lambda_2V_{BC}(t)];$$
$$V(t)=e^{i\mathcal{H}_0t}Ve^{-i\mathcal{H}_0t}. \quad \text{(A6)}$$

The reason for the principal part is to make $Q$ conform to the conventional form in terms of exact matrix elements of the eigenstates of $\mathcal{H}$. These are simply obtained by taking the matrix elements of $Q$, (A4), and performing the time integration,

$$(E_m-E_n)Q_{mn}=-V_{mn}. \quad \text{(A7)}$$

The effective Hamiltonian for the combined systems of $A$ and $C$ is then obtained by averaging over the intermediary system $B$. That is,

$$\mathcal{H}_{\text{eff}}=\langle\mathcal{H}'-\mathcal{H}_B\rangle_B=\mathcal{H}_A'+\mathcal{H}_C'-(i/2)\lambda_1\lambda_2P\int_{-\infty}^{0}dt$$
$$\times e^{\delta t}\langle[V_{AB}(t),V_{BC}(0)]+[V_{BC}(t),V_{AB}(0)]\rangle. \quad \text{(A8)}$$

Here the terms in $\lambda_1^2$ and $\lambda_2^2$ have been incorporated into $\mathcal{H}_A'$ and $\mathcal{H}_C'$ respectively. For the particular system considered in the text, the terms in $\lambda_1^2$ will serve to broaden the nuclear resonance via the Suhl-Nakamura[14,15] indirect interaction between the nuclear spins via the indirect exchange of spin waves. The terms in $\lambda_2^2$ will serve to renormalize the phonon dispersion relation, having the effect of mixing in magnon modes.

This method is, of course, quite general and can be applied to a variety of problems. The virtue of this representation is the fact that the coupling is expressed in terms of an exact correlation function, which then hopefully could be empirically verified.

## APPENDIX B

In this Appendix,[16] we give a simple semiclassical derivation of the effective nuclear spin-phonon interaction in the absence of external magnetic fields. The normal uniform modes ($k=0$) of an uniaxial anisotropic antiferromagnetic system can be described in terms of the semiclassical picture of the magnetization precessing about the anisotropy field direction with a frequency $\omega_0=(2\omega_e\omega_A)^{1/2}$, and tracing out an elliptical orbit in the plane perpendicular to the $z$ axis. A full discussion of the different normal modes has been given by Keffer and Kittel.[17] Let us consider only one of the sublattices. The precession of the magnetization is shown in Fig. 1(a). Let us now impose an additional field on the electron magnet by straining the crystal. From the magnetostrictive term (1), we see that the field in the

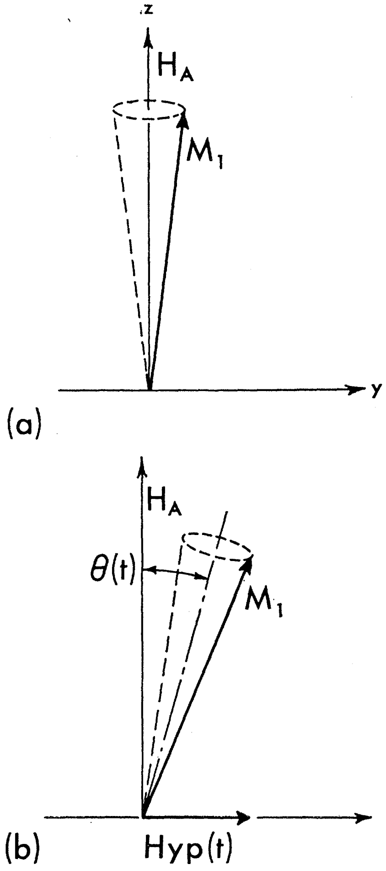

FIG. 1. Semiclassical model of the sublattice uniform mode: (a) in the absence of strain, and (b) in the presence of the additional anisotropy field due to the strain.

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[14] H. Suhl, Phys. Rev. **109**, 606 (1958).

[15] T. Nakamura, Progr. Theoret. Phys. (Kyoto) **20**, 545 (1958).

[16] The author is indebted to Professor Alan Portis for suggesting the semiclassical approach to the effective interaction.

[17] F. Keffer and C. Kittel, Phys. Rev. **85**, 329 (1952).

$y$ direction will be

$$H_{yp}(t)=GSe_{yz}(t)/\gamma_e\hbar. \qquad \text{(B1)}$$

This perpendicular field will oscillate at the frequency of the strain and will act on the magnetization as an additional anisotropy field. At a given instant of time the magnetization will precess about the new anisotropy direction, and the precessional axis will oscillate about the $z$ axis with the frequency of the impressed strain as indicated in Fig. 1(b). The assumption, of course, has been made that the precessional frequency is much greater than the phonon frequency. Let us now turn our consideration to the nucleus. We see from the isotropic form of the hyperfine interaction (2.4), that the nucleus will experience a magnetic field due to the electrons of

$$\mathbf{H}_n(t)=A\langle\mathbf{S}(t)\rangle/\gamma_n\hbar. \qquad \text{(B2)}$$

The perpendicular field component at the nucleus is then

$$H_{yn}(t)=AS\sin\theta(t)/\gamma_n\hbar\cong AS^2Ge_{yz}(t)/\gamma_n\gamma_e\hbar^2H_A. \qquad \text{(B3)}$$

Here we have taken $\sin\theta(t)\cong\theta(t)=H_{yp}(t)/H_A$. Considering the same for the $x$ direction, we obtain the net coupling of the strain to the $j$th nucleus;

$$\begin{aligned}V_{npj}(t)&=\hbar\gamma_n\mathbf{H}_{\perp j}(t)\cdot\mathbf{I}_j\\&=(AS^2G/2\hbar\omega_A)[I_j^+e_{-zj}(t)+I_j^-e_{+zj}(t)], \qquad \text{(B4)}\end{aligned}$$

which is exactly the form as derived from spin-wave theory.

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# Magnetic Resonance Studies of Unpaired Atoms in Solid $D_2$*

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We have studied the ground-state spectroscopic parameters, line shapes and breadths, relaxation times, and saturation behavior of unpaired atoms produced in samples of solid $D_2$ containing up to 1 at.% $T_2$. The D-atom electron spin resonance spectrum was found at 24 000 Mc/sec to consist of three composite lines in which the peaks of a broad component and a narrow component coincided. This result is interpreted by assuming that there are two different types of lattice sites for the unpaired atoms. The site responsible for the narrow line is tentatively identified, on the basis of linebreadth, as an interstitial located at the center of the square face of a unit cell having a $D_2$ molecule at each vertex. The other site has not been identified. The narrowline sites appear to become populated about 10 times more rapidly than the broadline sites. Linebreadths ranged from 2.2 G at 4.2°K to 44.5 G at 1.17°K. The effective spectroscopic splitting factor and hyperfine-structure interactions of the D, T, and H atoms were found to differ by only fractions of a percent from their free atomic values. The relaxation times of the D-atom spectra show little sensitivity to lattice temperature over the range from 1.2° to 4.2°. The relaxation time of the interstitial spins varies from 2 sec to 220 msec depending upon the concentration of atoms in the lattice. The relaxation time of spins in the broadline sites is in the neighborhood of 220 msec. From the presence of strong diagonal relaxation it is argued that the mechanism which relaxes the broadline D atoms has a correlation time of about $10^{-8}$ sec. The behavior of the interstitial spin relaxation is interpreted in terms of a model in which spin polarization from these atoms diffuses by the Bloembergen mechanism to the broadline sites, where relaxation takes place. The model clarifies quantitatively the differences between the relaxation behavior of D atoms on the one hand and the far less numerous T and H atoms on the other. The resonance lines are homogeneously broadened as a rule. Inconsistencies between the results of saturation studies and the measured relaxation times are shown to be due to an anomalous line narrowing and intensification after the onset of saturation. The anomaly appears to be characteristic only of the narrow line component.

## INTRODUCTION

SEVERAL years ago we undertook a series of investigations intended to demonstrate the feasibility of producing an isotopically pure target of polarized deuterium nuclei for use with medium and high-energy particle accelerators. The advantages of a polarized $D_2$ target are apparent; it serves as a source of both polarized protons and polarized neutrons, and it is without the background scattering from heavy, unpolarized nuclei produced from polarized targets of polyethylene or of the complex rare earth salt, $(La,Nd)_2Mg_3(NO_3)_{12}\cdot 24H_2O$, with which the Berkeley group has had such success.[1] With these attractive features in mind, we sought to develop techniques for producing unpaired electron spins within a solid $D_2$ matrix, whose polariza-

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[1] T. J. Schmugge and C. D. Jeffries, Phys. Rev. Letters 9, 268 (1962).