Nuclear Dipolar Interactions in Magnetically Ordered Systems*

D. Paquette, M. Butler, and V. Jaccarino
Department of Physics, University of California, Santa Barbara, California 93106
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The dipolar coupling between nuclei in magnetically ordered systems, specifically antiferromagnets, has been studied theoretically and experimentally. In these materials, the time-averaged local fields "seen" by the nuclei may vary in magnitude and direction. This results in terms in the nuclear dipolar Hamiltonian other than the usual $I_i^z I_j^z$ and $I_i^+ I_j^-$ contributing to the dynamic width of the nuclear magnetic resonance.

The dynamic effects of the dipolar coupling of nuclear spins on the nuclear magnetic resonance is generally considered from the point of view of nuclei in "nonmagnetic" materials. We wish to show here that because the time-averaged local field may vary in direction in magnetic materials, particularly in antiferromagnets, contributions to the width of the resonance profile may involve terms in the nuclear dipolar Hamiltonian $\mathcal{H}_d$ other than the usual $I_i^z I_j^z$ and $I_i^\pm I_j^\mp$ ones. If a single uniform quantization direction is chosen for *all* spins in the system, $\mathcal{H}_d$ may conveniently be written as[1]

$$\mathcal{H}_d = \sum_{i>j} (\gamma_i \gamma_j \hbar^2 / r_{ij}^3)[A + B + C + D + E] ,$$

where
$$A = I_i^z I_j^z (1 - 3\cos^2\theta) ,$$
$$B = -\tfrac{1}{4}[I_i^+ I_j^- + I_i^- I_j^+](1 - 3\cos^2\theta) ,$$
$$C = -\tfrac{3}{2}[I_i^+ I_j^z + I_i^z I_j^+]\sin\theta\cos\theta\, e^{-i\phi} ,$$
$$D = -\tfrac{3}{2}[I_i^- I_j^z + I_i^z I_j^-]\sin\theta\cos\theta\, e^{i\phi} ,$$
$$E = -\tfrac{3}{4}[I_i^+ I_j^+ e^{-2i\phi} + I_i^- I_j^- e^{2i\phi}]\sin^2\theta ,$$

with the sum taken over all spin pairs. For nonmagnetic systems with $\gamma_i = \gamma_j$, only the terms A and B in $\mathcal{H}_d$ are secular (i.e., conserve the total energy of the system) and they alone contribute to the dynamic broadening of the resonance; the remaining terms produce satellite lines far out in the wings of the main resonance. This is a consequence of the average local field being everywhere the same in magnitude and direction when the material is nonmagnetic.

However, in some ordered systems (e.g., antiferromagnets, ferrimagnets, and spiral spin structures) the direction and magnitude of the local field may vary from site to site because of differences in hyperfine fields and the variations in the orientation of the electronic spin moments. In the particular case where the nuclear moments are all identical, terms other than A and B in $\mathcal{H}_d$ may become secular even though the magnitude of the local field at each site is everywhere the same. Such an occurrence would result in significant changes in the dipolar coupling, as the angular dependences of A and B differ from C, D, and E.

In order to illustrate this more clearly, consider a simple two-sublattice antiferromagnet of like electronic spins. The magnitude of the average local field at all the magnetic ion nuclei will be the same, provided no external field H_{ext} is present. However, the field *direction* at any given (up) sublattice site is antiparallel to that of any site on the other (down) sublattice. Choosing as a fixed quantization direction the orientation of one of the sublattices, we find the ordering of the nuclear Zeeman levels on the two different sites to be reversed with respect to each other. Hence the nuclei belonging to spins on a given sublattice will have secular interactions through the terms A and B in $\mathcal{H}_d$, while those on opposite sublattices will have secular interactions via the terms A and E as shown in Fig. 1.[2] As the operator E alone causes mutual spin flips of nuclei on opposite sublattice, it will be solely responsible for energy transfer between nuclei on the two sublattices when $\mathcal{H}_{ext} = 0$.[3]

The importance of term E as an energy transfer mechanism has been demonstrated experimentally in MnF_2, a simple two-sublattice antiferromagnet, using the F^{19} NMR. When an external field is ap-

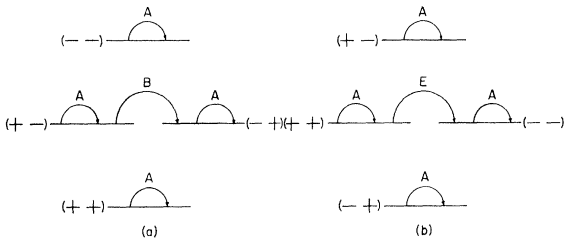

FIG. 1. Energy conserving transitions between two spin states induced by the dipolar interaction for (a) a pair of identical spins ($I = \frac{1}{2}$) on one sublattice and (b) a pair of identical spins on opposite sublattices. The states are defined by choosing a single quantization direction parallel to the hyperfine field of one of the sublattices.

plied, parallel to the direction of spontaneous alignment (c axis), it adds and subtracts, respectively, to the otherwise identical hyperfine fields at the two inequivalent F^- sites. This causes the E term in $\mathcal{H}_d$ to become nonsecular and effectively decouples the two interpenetrating, distinct F^{19} nuclear sublattices. Using conventional spin-echo techniques we have observed this decoupling by saturating the NMR of F^{19} on one sublattice and observing no change in the nuclear magnetization on the other, in a field $H_0(\|) = 4$ kOe which is much larger than the linewidth. Leaving the field fixed, we rotate the sample through 90° so that the hyperfine field and the external field are in quadrature and the effective field seen by all F^{19} is now the same. The term E in $\mathcal{H}_d$ once more becomes secular and energy transfer is possible. Since the nuclear-spin-lattice relaxation time T_1 is relatively large at low temperatures ($T_1^{19} \sim 2$ min at 4.2 °K), one can rotate the sample and restore it to its original orientation in a time $T \ll T_1$. If one resonance branch is first saturated, the rotation experiment performed, and the resonance intensity of the second branch monitored, the latter is observed to decrease to half its value *after* the rotation. Clearly, energy transfer between the two sublattices has taken place at the 90° position in a time of the order of h/E.

Further evidence of the importance of E to dynamic spin processes is obtained by comparing the transverse relaxation time $T_2(H_0 = 0)$ to $T_2(H_0 \neq 0)$. For this experiment the isostructural antiferromagnet FeF_2 was used because the low Fe^{57} abundance greatly reduces the contribution of the cation nuclei to T_2, in contrast to MnF_2 where the 100% abundant Mn^{55} nuclei play an important role.[4] The contributions of A and B to the dynamic second moment from spins on the same and opposite sublattices have previously[5] been calculated to be M_2 (same sublattice) $= 3.2 \times 10^{-45}$ erg^2, and M_2 (opposite sublattice) $= 0.16 \times 10^{-45}$ erg^2. The contribution to the second moment from E may be written

$$M_2(E) = \tfrac{3}{4}\gamma_{19}^4 \hbar^2 I(I+1) \sum_j (\sin^4\theta / r_{ij}^6)$$
$$= 1.64 \times 10^{-45} \text{ erg}^2 .$$

Assuming the homogeneous line shape to be Gaussian as is appropriate for a dense system of like dipoles, we calculate $T_2(H_0 = 0) = 0.82 T_2(H_0 \neq 0)$. T_2 was measured using conventional spin-echo techniques. While our sample was quite pure, significant inhomogeneous broadening still existed; $\delta\nu = 40$ kHz. Because of this, it is required that the rf field strength satisfy the inequality $\gamma^{19} H_1 > \delta\nu$ to obtain a $\pi/2$ pulse for all the spins in the inhomogeneously broadened line. Doing this, we find $T_2(H_0 = 0) \simeq 0.9 T_2(H_0 \neq 0)$ with an exponential decay for the echo envelope, implying the homogeneous line profile is Lorentzian. Despite this discrepancy in line shape caused by the inhomogeneous broadening, we feel this demonstrates the importance of term E when considering dynamic nuclear spin processes in antiferromagnets.

Just as E becomes important in antiferromagnets, one can see that terms C and D may become important for spiral spin structures. Here the mixing of two spin states, caused by differing directions of average local field, can make these terms, at least, partially secular.

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[1] A. Abragam, *The Principles of Nuclear Magnetism* (Oxford U. P., London, 1961), Chap. 4.

[2] Perhaps a conceptually simpler situation to understand, that is isomorphic to the antiferromagnet, is an identical nonmagnetic lattice with the nuclei on different sublattices having oppositely signed gyromagnetic factors ($\gamma_a = -\gamma_b$). Hence in any external field all nuclei in the sample would have the same resonance frequency, but only the terms A and E would cause secular interactions between nuclei with opposite signs to their moments and again E alone would be responsible for energy transfer between the (a) and (b) systems.

[3] Of course, all arguments made here are to first order and even for nuclei with different resonant frequencies a coupling still exists in second order reduced by the ratio (dipolar energy/Zeeman energy). Thus energy is still transferred between sublattices, albeit at a reduced rate. The only other magnetic coupling between nuclei in an ordered magnetic insulator arises from the virtual emission and reabsorption of spin waves via the hyperfine interaction – the Suhl-Nakamura interaction. [See H. Suhl, Phys. Rev. 109, 606 (1958); J. Phys. Radium 20, 333 (1959); T. Nakamura, Progr. Theoret. Phys. (Kyoto) 20, 542 (1958)]. The Suhl-Nakamura interaction is of the form $A(I_i^+ S_i^- + I_i^- S_i^+)$ and results in an effective nuclear spin Hamiltonian $\mathcal{H}_{s-n} = C(I_i^+ I_i^- + I_i^- I_i^+)$ which in an antiferromagnet only couples nuclei belonging to electronic spins on the same sublattice. Therefore it will not mediate energy transfer from one nuclear sublattice to another.

[4] N. Kaplan, P. Pincus, and V. Jaccarino, J. Appl. Phys. 37, 1239 (1967).

[5] T. Nakamura, Progr. Theoret. Phys. (Kyoto) 20, 551 (1958).