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H. Suhl

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NUCLEAR SPIN INTERACTIONS IN FERROMAGNETICS AND ANTIFERROMAGNETS

By H. SUHL,
Bell Telephone Laboratories, Murray Hill, New Jersey, U. S. A.

Résumé. — Dans un cristal ferromagnétique ou antiferromagnétique le couplage hyperfin entre élec-
trons et noyaux des ions magnétiques ou non-magnétiques se traduit par un certain élargissement de 
l'axe de résonance nucléaire. (Ce phénomène est déjà connu pour les échantillons paramagnétiques.) 
Moyennant ce couplage hyperfin, un noyau particulier excite une onde de spin virtuelle qui est réab-
sorbée par un des autres noyaux. Ce processus est équivalent à un couplage à distance entre spins 
nucléaires. Étant donné que la direction d'aimantation fournit un axe privilégié, ce couplage est anisotrope par rapport à cet axe. Ainsi on obtient une réduction de temps de 
relaxation transversal, T2. Si l'on a plusieurs espèces de noyaux dans l'échantillon examiné, 
le temps T1 est susceptible d'être réduit par le même mécanisme, ce qui rend possible le passage 
d'énergie des noyaux considérés vers les autres noyaux.

Abstract. — In a ferromagnetic or antiferromagnetic crystal the hyperfine coupling between 
the electrons and the nuclei of the magnetic or nonmagnetic ions leads to a certain broadening of the 
resonance line. (This phenomenon is already known for samples in the paramagnetic 
state.) Via the hyperfine coupling a particular nucleus excites a virtual spin wave, which is re-
absorbed by one of the other nuclei. This sequence of events is equivalent to a 
long range inter-
action between the nuclear spins. Since the direction of magnetization furnishes a preferred axis, 
this coupling is anisotropic with respect to this axis. Thus one obtains a reduction in the trans-
verse relaxation time, T2.

If there are several nuclear species in the sample under examination, the time T1 may be shor-
tened by the same mechanism, which enables energy to flow from the species under consideration 
to the other species.

Nuclear resonance experiments in magnetic 
materials have so far been confined to the non-
metallic nuclei in antiferromagnetics only; no 
successful experiments on the metallic nuclei in 
either ferro or antiferromagnets have been report-
ed to date. In a brief previous publication [1], 
nuclear resonance in magnetic substances was 
shown to be subject to a special line broadening 
mechanism which may make such observations 
more difficult or at any rate may call for different 
experimental techniques. In this paper we shall 
give a somewhat more detailed account of the 
effect.

The individual nuclear spin is coupled to the 
magnetic electrons through the hyperfine inter-
action, and, usually to a lesser extent, through the 
dipolar forces which we hereafter neglect. For the 
metal nuclei the hyperfine coupling comes about 
through configuration interaction which promotes 
a fraction of the inner s-electrons to outer orbits 
leaving behind partially filled, polarized s-shells. 
For the non-metallic nuclei it frequently comes 
about through covalency effects, as the result of 
which the wave functions of the magnetic electrons 
become admixed to those of the outer electrons of 
the non-metallic ions and conversely (The experi-
mements of Jaccarino and Shulman, discussed else-
where in this conference are a case in point). 
Clearly the hyperfine coupling can produce simulta-
neous transitions between the states of the 
nuclear spin system, and between the states of the 
electronic spin system. The nuclear spin states 
are adequately described, as a first approximation, 
by products of wave functions of the individual 
spins. On the other hand the electron spins, 
tightly coupled to each other by exchange forces, 
must be described by the appropriate collective 
states, the "spin-waves".

We begin by calculating the effective nuclear 
spin interaction in a simple cubic ferromagnet 
confining attention to the metal ions. The second 
order correction to the effective nuclear spin Hamil-
tonian due to the hyperfine interaction, 

\[ H^3 = A \sum \Omega(\mathbf{H}^1 \mathbf{1}_k) \left( \mathbf{1}_k \mathbf{H}^2 \mathbf{0} \right) \]

where \( \mathbf{0} \) is the ground state of the electronic spin 
system (i.e. the fully aligned state), and where \( \mathbf{1}_k \) is the state with one spin wave, of wavenumber \( k \), 
excited. \( \varepsilon_k \) is the energy of \( \mathbf{1}_k \) relative to that 
of the ground state, and the summation extends 
over the reciprocal lattice. To evaluate the matrix 
elements in (i) we write the hyperfine interaction 
in terms of the usual raising and lowering opera-
tors \( \mathbf{S}^+, \mathbf{S}^- \) etc...

\[ \langle \mathbf{I}, \mathbf{S} \rangle = \frac{1}{2} (\mathbf{I}_1^+ \mathbf{S}_1^- + \mathbf{I}_1^- \mathbf{S}_1^+) + \mathbf{I}_1^+ \mathbf{S}_1^- \]
and express \( S_i^+ \), \( S_i^- \) as Fourier series:

\[
S_i^+ = \frac{1}{\sqrt{N}} \sum_k \Delta S_i^+ e^{ikr_i}, \quad S_i^- = \frac{1}{\sqrt{N}} \sum_k \Delta S_i^- e^{-ikr_i}.
\]

The spin-wave states \( |k\rangle \) are related to \( |0\rangle \) by the equation

\[
|k\rangle = \frac{1}{\sqrt{\sum_k \Delta S_k}} |0\rangle.
\]

On the other hand \( S_i^+ |0\rangle = 0 \), since \( |0\rangle \) is already the fully aligned state. Using these definitions, we find that the effective nuclear interaction (i) becomes

\[
-\frac{S A^2}{2} \sum_k \left[ \left( \frac{1}{N} \sum_i e^{ikr_i} (\Delta S_i^+ + \Delta S_i^-) \right) \right]. \tag{ii}
\]

The range function

\[
R(r) = \frac{1}{N} \sum_k \frac{e^{ikr}}{\varepsilon_k}
\]

is evaluated by making the quadratic approximation to the spin wave spectrum

\[
\varepsilon_k = \hbar \omega_{\text{ex}} \frac{a}{r} \tag{iii}
\]

where \( \hbar \omega_{\text{ex}} \) is the energy of one spin in the applied d.c. field minus the steady demagnetizing field, \( \hbar \omega_{\text{ex}} = 2JS \) the exchange energy and \( a \) the lattice spacing. Demagnetizing effects due to the spin waves themselves are not taken into account in equations (ii) and (iii). They lead to additional terms in the interaction (ii) of the form \( I_i^+ I_i^- \) which give rise to satellite lines, and they also modify the spin wave energy (iii). We evaluate \( R(r) \) on the assumption that \( r \gg a \). Since most of the contribution to the linewidth does come from such distances, no serious error is thereby incurred. If \( r \gg a \), we may take the sum over \( k \) to extend to infinity and may replace it by an infinite integral.

The result is \( R(r) = \frac{1}{4\pi \hbar \omega_{\text{ex}} r} \), so the effective nuclear interaction becomes

\[
\frac{1}{\sqrt{N}} \Delta S_i^+ (|0\rangle \rangle) = \sqrt{2JN} \sum_k e^{-ikr} (\Delta S_i^+ |0\rangle \rangle) \tag{vii}
\]

where \( \Delta S_i^+ \) is the energy of one spin in the applied d.c. field minus the steady demagnetizing field, \( \hbar \omega_{\text{ex}} = 2JS \) the exchange energy and \( a \) the lattice spacing.

Since \( I_i^+ I_i^- = I(I+1) - I_i^+ (I_i^+) \), we see that the self-energy gives a shift in the effective field for nuclear resonance, and, unless \( I = 1/2 \), also a quadrupole distortion of the level spacing. Both effects are of the same order as the linewidth and therefore probably hard to resolve.

We now turn to the antiferromagnetic case. Let us first consider only the metallic ions, assuming the "up" and "down" spin ions to occupy alternate sites on a simple cubic lattice. Since the lowest excitation energy of an antiferromagnet is rather high, of order of the geometric mean of exchange and anisotropy energy, one would expect a smaller nuclear linewidth than in the ferromagnet. However, the zero-point motion of the antiferromagnetic array is more violent, and hence the numerator of \( \Delta \Omega \) in formula (i) is also greater.

In the actual calculation, since the exact elementary excitations of antiferromagnets are not known, we have to resort to the "harmonic oscillator" approximation to the spin deviations. In that approximation, the spin-raising and lowering operators \( S_i^+, S_i^- \) on sublattices (1) and (2) are expressed in terms of two sets of harmonic oscillator creation and destruction operators as follows

\[
\frac{1}{\sqrt{2N}} \Delta S_i^+ (|0\rangle \rangle) = \sqrt{2JN} \sum_k e^{-ikr} (\Delta S_i^+ |0\rangle \rangle) \tag{viii}
\]

where

\[
|\Omega_k \rangle = \cosh \theta_k |f_2 \rangle, \quad \gamma_k = - \sin \hbar \theta_k / 2,
\]

and since the "exchange like" and "dipole-like" parts of the interaction are about equal, no appreciable narrowing of the linewidth (v) is to be expected.

The case \( r_i = r_j \), which violates the assumption \( |r_i - r_j| \gg a \), is of some slight interest. It represents the self-energy of the individual nuclear spin due to its interaction with the electronic spin-wave field. In that case the upper limit \( k_{\text{max}} \), of order \( 2\pi/a \) must be taken into account explicitly, since the infinite sum would diverge. Integration up to \( k_{\text{max}} \sim 2\pi/a \) gives, for \( \omega_{\text{ex}} \ll \omega_{\text{ex}} \), the approximate result

\[
-\frac{1}{2} \sum_k \hbar \omega_{\text{ex}} \sum_i |I_i^-|^2. \tag{vi}
\]

Since \( I_i^+ I_i^- = I(i + 1) - I_i^+ (I_i^+) \), we see that the self-energy gives a shift in the effective field for nuclear resonance, and, unless \( I = 1/2 \), also a quadrupole distortion of the level spacing. Both effects are of the same order as the linewidth and therefore probably hard to resolve.

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sublattice. Nuclei on opposite lattices interact according to $I^+ I^+$ and $I^- I^-$, leading to satellite lines. On the same sublattice say 1, substitution of (vii) in (i) gives

$$\pm A^2 \sum \frac{j_1^{(1)+} j_1^{(1)+} + 1}{N} \sum \frac{\rho_1^{(1)}}{\rho_1^{(1)}}$$

Utilizing the definitions of $\rho_1$, $\rho_2$ expanding $\epsilon_0$ to second order in $ka$ to correspond to the quadratic approximation in the ferromagnetic case, we find if $\hbar \omega_a \ll \hbar \omega_{\text{ex}}$

$$H_{\text{eff}} = \frac{SA^2}{2} \sum \frac{j_1^{(1)+} j_1^{(1)+} + 1}{N} \sum \frac{\epsilon(k_0 \rho_1^{(1)} - \rho_2^{(1)})}{\hbar \omega_a + \hbar \omega_{\text{ex}} a^2 k^2}$$

just as for the ferromagnet. The only differences is that $\hbar \omega_a$ replaces $\hbar \omega_B$; that is to say the anisotropy field replaces the effective dc field, in this, as well as the subsequent moment calculation.

If the hyperfine interactions of the non-metallic ions are included the calculations become much more complex. For example in MnF$_2$, each electron spin is coupled to its own manganese ion and to the six fluorines surrounding it. Each $I_x$ in the previous calculation is now a linear sum of a manganese and six fluoride nuclear spins, and the effective interaction will thus include a coupling of fluoride and manganese nuclei. Hence if the Mn-nuclei have an adequate heat capacity, a T$_1$-type of relaxation time for the fluoride nuclei will result. The linewidth or the "T$_2$" of the fluoride nuclei will continue to be determined chiefly by the fluoride interaction, and will be of the order of magnitude calculated above, with appropriate values for $A$. (Actually for the fluorines the order of magnitude is less than the value calculated for direct dipole-dipole interaction.) There will also be some slightly interesting side-effects. For example, since each fluoride nucleus is coupled to three neighboring magnetic electrons, self-energy term will arise not only from $r = r$, as previously, but also from terms in which $r_1 r_2$ are linked through one fluoride ion. Conversely, since a particular electronic spin has more than one fluoride neighbor, terms with $r_1 = r_2$ will contribute somewhat to the linewidth as well as to the self-energy.

Finally we remark that in ferromagnetic metals, too, the same nuclear line broadening mechanism takes place, though the analysis must be reformulated to take account of the fact that the electrons are itinerant.

REFERENCES


DISCUSSION

Mr. Nagamiya. — Did you include the anisotropy for the electronic spin system? Nakamura (reported at Leiden Conference on Low Temperature Physics, June, 1958) took it into account and found that the anisotropy constant influences seriously the range and constant of the nuclear indirect coupling.

Mr. Suhl. — Yes, I did take anisotropy into account, in the form of an effective field.

Mr. de Gennes. — Would your interaction be effective in bringing out some new sort of nuclear ferro- or antiferro-magnetism?

Mr. Suhl. — The effective nuclear exchange field is of the order of at most a few hundred gauss; that is to say, small compared with the effective field at the nucleus due to the electronic sublattices. Therefore, at temperatures sufficiently low for the exchange field to become important in ordering the system, the effective field due to the sublattices will already have established essentially perfect order among the nuclear spins.

Mr. Kittel. — Could you kindly explain in another way why the indirect interaction is anisotropic?

Mr. Suhl. — The direction of magnetization provides the preferred axis, and causes the interaction to have axial rather than spherical symmetry.