plane as that of the impurity. The probability that the diffusing ion will exchange sites with a vacancy in an adjacent plane is then larger than that of the impurity-vacancy exchange in the same basal plane. One may thus understand why the diffusion of gold in the parallel direction is faster than that in the perpendicular direction.

If the diffusion in the perpendicular direction were entirely due to the nonbasal jumps of the gold tracer, then one may expect $D_{\parallel}/D_{\perp}\cong 5.2$ for zinc. The ratio of the diffusion coefficients $D_{\parallel}/D_{\perp}$ in the temperature range of the experiment is approximately 3.3 within $\pm 10\%$. This suggests that both types of the jumps are probably contributing to the perpendicular diffusion.

ACKNOWLEDGMENTS

I wish to express my sincere thanks to Professor H. B. Huntington for his kind advice and many stimulating discussions and to A. P. Batra for his help in some of the measurements. I should also like to express my gratitude to the University of Bombay, India, for the award of the Sardar Bhimrao Ramrao Akbarnavis Scholarship and to the United States Educational Foundation in India for the Fulbright Travel Grant.

PHYSICAL REVIEW VOLUME 131, NUMBER 1 1 JULY 1963

Spin Waves and Nuclear Magnetic Resonance Enhancement in NiF_2 Domain Walls*

DAVID I. PAUL
Department of Physics, University of California, Los Angeles, California

(Received 25 February 1963)

We have obtained the allowed magnetic resonance modes or spin waves in the canted antiferromagnet NiF_2 in the presence of a Bloch wall. Our formulation includes the anisotropy and exchange energies of the crystal together with characteristics of the wall such as its stiffness, mass, and viscosity. From the dispersion equations, we show that there exists a bound wall excitation branch having a lower excitation energy than the free spin wave excitation branch. Further, we have calculated the effective nuclear magnetic resonance field enhancement due to the bound wall excitation branch as a function of the parameters of the crystal and the Bloch wall and shown that our results are equivalent to those obtained experimentally. Finally, we compare this enhancement with that of a pure antiferromagnet—demonstrating that the canting is essential for this process.

I. INTRODUCTION

IN this paper, we investigate the effect of a Bloch wall on the spin wave excitation spectra in a canted antiferromagnet such as NiF_2. In this type of substance, the canting arises from the spin-orbit coupling under the effect of the crystalline electric field. In Sec. V we obtain the allowed normal magnetic resonance modes and the dispersion equations for the bound wall excitations and the free spin wave excitations. The analogous ferromagnetic and antiferromagnetic cases have been considered by Boutron,[1] Winter,[2] and the author.[3] In Sec. VI, we calculate the effective enhancement of the nuclear magnetic resonance signal caused by the bound wall excitations. This is similar to the enhancement factor obtained by Portis and Gossard[4] for ferromagnetic substances and experimentally by Shulman[5] for NiF_2.

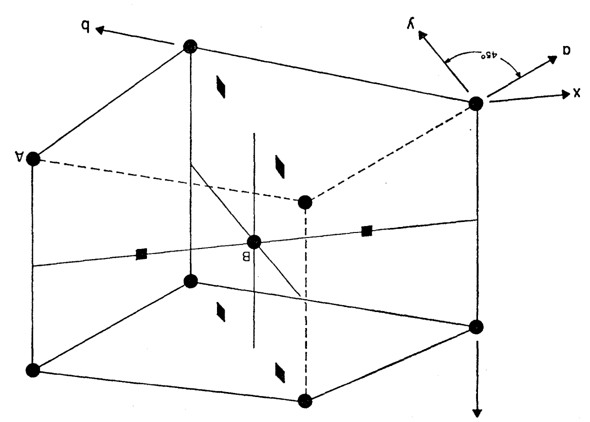

FIG. 1. Crystal structure of NiF_2. The circles and the squares represent the nickel and the fluorine ions, respectively.

II. FORMULATION OF THE PROBLEM

The substance, NiF_2, has a rutile-type crystal structure with both corner and body-center cation sites. We consider the magnetic corner cation sites as being on sublattice A with index j and the magnetic body-center sites as being on sublattice B with index k as shown in Fig. 1. The magnetic properties of NiF_2 have been con-

---

* This research was supported in part by the Office of Naval Research.

[1] Mlle. F. Boutron, Compt. Rend. **252**, 3955 (1961).
[2] J. M. Winter, Phys. Rev. **124**, 452 (1961).
[3] D. I. Paul, Phys. Rev. **126**, 78 (1962).
[4] A. Portis and A. Gossard, Suppl. J. Appl. Phys. **31**, 205S (1960).
[5] R. G. Schulman, Suppl. J. Appl. Phys. **32**, 126S (1961).

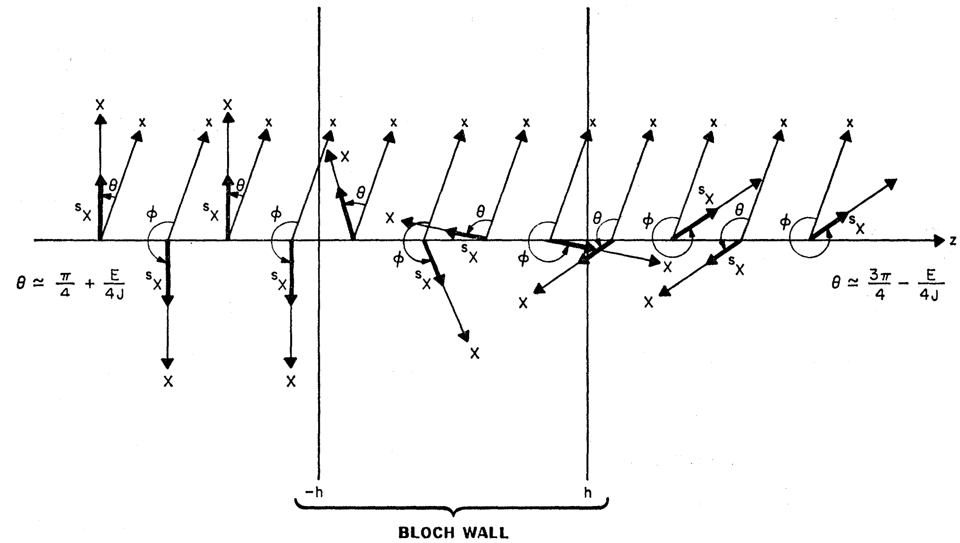

FIG. 2. Diagram showing the varying X axis, the fixed z axis, and the angles of deviation θ and ϕ of the different sublattice spins within and outside the Bloch wall.

sidered in detail by Moriya.[6] Using the spin Hamiltonian

$$\mathcal{H}=J\sum_{j,k}\mathbf{S}_j\cdot\mathbf{s}_k+\sum_j\{D(S_j^z)^2-E[(S_j^x)^2-(S_j^y)^2]\}$$
$$+\sum_k\{D(s_k^z)^2+E[(s_k^x)^2-(s_k^y)^2]\}\quad(1)$$

(where J, the exchange energy is large compared to D, the anisotropy energy, and E, the canting term), Moriya has shown, among other things, that under static conditions and below the Néel temperature, the spins align in the plane perpendicular to the c axis and are approximately along the a or b axis. There is a net magnetic moment caused by a small canting of the different sublattice spins to each other in this plane.

We postulate the existence of a Bloch wall (either from magnetostatic energy considerations or from lattice defects such as dislocations[3,7] and consider the dynamic situation in the presence of such an environment. As in references 3 and 6, we assume that the Bloch wall has a finite width determined from minimum energy considerations between the magnetic anisotropy and exchange energies of the crystal—the angle between adjacent spins changing slowly. Let θ and ϕ be the angles between the x axis and the static magnetization on sublattices A and B, respectively, and let us choose a new system of axes, X, Y, and z, where X is the spin direction for the static magnetization and X and Y vary from atom to atom while z is not changed (see Fig. 2). Then the Hamiltonian becomes

$$\mathcal{H}=J\sum_{j,k}[(S_j^Xs_k^X+S_j^Ys_k^Y)\cos(\phi_k-\theta_j)$$
$$+(S_j^Xs_k^Y-S_j^Ys_k^X)\sin(\theta_j-\phi_k)+S_j^zs_k^z]$$
$$+\sum_j\{D(S_j^z)^2-E[(S_j^X)^2-(S_j^Y)^2]\cos2\theta_j\}$$
$$+\sum_k\{D(s_k^z)^2+E[(s_k^X)^2-(s_k^Y)^2]\cos2\phi_k\}.\quad(2)$$

[6] T. Moriya, Phys. Rev. **117**, 635 (1960).
[7] I. Jacobs and C. Bean, J. Appl. Phys. **29**, 537 (1958).

III. STATIC CASE

Our unperturbed energy or ground state is determined by placing S_Y, S_z, s_Y, and s_z equal to zero, and S_X and s_X equal to S. Moriya has minimized the Hamiltonian given by Eq. (1) as a function of the angle between the two different magnetic spins, (assumed, however, to be on the same lattice site). He obtains his Eq. (5.3), i.e.,

$$\tan(\phi-\theta)=-(E/4J)\sin(\phi+\theta).$$

For E/J small, this reduces to

$$\phi=\theta+\pi+(E/4J)\sin2\theta.\quad(3)$$

Thus, substituting for ϕ_k and expanding θ_k about the position j, we get for the ground-state energy,

$$\mathcal{H}_0=\sum_i\{-8JS^2+4JS^2a^2(\partial\theta/\partial z)^2$$
$$-(E^2S^2/4J)\sin^22\theta\},\quad(4)$$

where the summation, i, is now over all lattice sites and where a is one-half the unit cell lattice distance in the z direction. Upon minimizing Eq. (4) with respect to θ, we obtain the useful relation,

$$(\partial\theta/\partial z)^2\approx(E/4Ja)^2\cos^22\theta.\quad(5)$$

For a 90° wall, this equation integrates to

$$\sin2\theta=-\tanh(2hz),\quad(6)$$

where $h=E/4Ja$ and is the inverse of the wall thickness in agreement with Moriya's results.

IV. EQUATIONS OF MOTION

When the Bloch wall is subject to perturbations, it exhibits stiffness, inertia, and viscosity caused by both the interaction of the wall with imperfections in the material and by magnetic effects of the material itself.

As shown in references 2 and 3, these additional energy contributions for the stiffness and inertia can be represented by the terms

$$K'[\sum_j (S_j^Y)^2+\sum_k (s_k^Y)^2] \tag{7}$$

and

$$M[\sum_j (S_j^z)^2+\sum_k (s_k^z)^2], \tag{8}$$

respectively, while the viscosity may be represented phenomenologically as

$$\hbar(d\mathbf{S}_j/dt)_{\text{visc}}=-\Gamma_1 S_j^Y \mathbf{e}_Y-\Gamma_2 S_j^z \mathbf{e}_z$$

and

$$\hbar(d\mathbf{s}_j/dt)_{\text{visc}}=-\Gamma_1 s_k^Y \mathbf{e}_Y-\Gamma_2 s_k^z \mathbf{e}_z. \tag{9}$$

The equations of motion are given by the formulas

$$i\hbar(d\mathbf{S}_j/dt)=[\mathbf{S}_j,\mathcal{H}], \tag{10a}$$

$$i\hbar(d\mathbf{s}_k/dt)=[\mathbf{s}_k,\mathcal{H}], \tag{10b}$$

where $\mathcal{H}$ is the total Hamiltonian given by Eqs. (2), (7), and (8) after placing the linear terms equal to zero by the minimization condition. [We add Eqs. (9) directly to Eqs. (10) to obtain complete expressions.] If, in Eq. (10a), we expand $\mathbf{s}_k$ about the position j and, in Eq. (10b), we expand $\mathbf{S}_j$ about the position k, and keep only second-order terms (valid for long wavelengths), we get, using Eq. (5) and the commutation relations,

$$dS_Y/dt=(8JS+4JSa^2\nabla^2)s_z-\Gamma_1 S_Y \\ +(8JS+2DS+2MS+2ES\cos 2\theta)S_z, \tag{11a}$$

$$ds_Y/dt=(8JS+4JSa^2\nabla^2)S_z-\Gamma_1 s_Y+[8JS+2DS \\ +2MS-2ES\cos 2\theta+(SE^2/J)\sin^2 2\theta]s_z, \tag{11b}$$

$$dS_z/dt=(8JS+4JSa^2\nabla^2)s_Y-\Gamma_2 S_z \\ -(8JS+4ES\cos 2\theta+2K'S)S_Y, \tag{11c}$$

$$ds_z/dt=(8JS+4JSa^2\nabla^2)S_Y-\Gamma_2 s_z-[8JS+2K'S \\ -4ES\cos 2\theta+(2SE^2/J)\sin^2 2\theta]s_Y. \tag{11d}$$

Neglecting small terms and recognizing that K', the stiffness, is small compared to the anisotropy D, Eqs. (11) can be solved for S_Y.

We recognize, from the excitation spectra in the absence of a Bloch wall obtained by Moriya[6] and by the author,[3] that there will be two excitation spectra—one of high energy ($w^2\approx DJ$) and one of low energy ($w^2\approx K'J$ or E^2). For the high-energy case, Eqs. (11) yield the approximate relation

$$[(w_1w_2)^2-32S^2J(D+M)(w_1w_2+64J^2S^2a^2\nabla^2) \\ +128w_1w_2J^2a^2S^2\nabla^2]S_Y=0. \tag{12a}$$

In this case, the energy of the excitations is sufficiently high so that we have been able to neglect the additional trigonometric terms coming from the presence of the Bloch wall without appreciably altering the energy level of the excitations. The solutions can be written immediately, i.e.,

$$S_Y=S_Y^0\exp[i(k_xx+k_yy+k_zz)] \tag{13a}$$

and

$$w_1w_2\approx 32JS^2(D+M)+64J^2S^2k^2a^2, \tag{14a}$$

where

$$w_1=\hbar w-i\Gamma_1,$$

$$w_2=\hbar w-i\Gamma_2.$$

For the more interesting low-energy case, we obtain the equation

$$(w_1w_2+16E^2S^2\cos 4\theta-32K'JS^2 \\ +64J^2S^2a^2\nabla^2)S_Y=0. \tag{12b}$$

In the next section, we consider the solutions to this low-energy case.

V. SOLUTIONS

If we substitute $u=-\sin 2\theta$ in Eq. (12) and let

$$S_Y=S_Y(z)\exp[i(k_xx+k_yy)], \tag{13b}$$

we get the associated Legendre equation

$$(1-u^2)(d^2S_Y/du^2)-2u(dS_Y/du) \\ +[2-(m^2/[1-u^2])]S_Y=0,$$

where

$$w_1w_2\approx 32JK'S^2+16E^2S^2(1-m^2)+64J^2S^2k_1^2a^2 \tag{14b}$$

and

$$k_1^2=k_x^2+k_y^2.$$

Thus, the solutions to Eq. (12b) are

$$S_Y(z)=S_Y^0P_1^m(u), \tag{15}$$

which for a 90° wall can be written as

$$S_Y(z)=S_Y^0e^{2mhz}[\tanh(2hz)-m]. \tag{16}$$

The only regular solutions with regular derivatives occur when m^2 is equal to one, or is equal to or less than zero.

(*a*) *$m^2=1$:* Then, $S_Y(z)$ equals $S_Y^0\cos 2\theta$. For a 90° wall, θ varies from approximately 45° at $z=-\infty$ to 135° at $z=\infty$, almost all of the change occurring within the region $|z|<h^{-1}$. Thus, this is a bound or wall excitation mode—its amplitude being essentially zero outside of the wall. The dispersion relations are obtained by putting m^2 equal to one in Eqs. (14b). We note that when the stiffness, K', is equal to zero, the excitation branch given by Eq. (14b) has a wall resonance of zero energy. The solutions corresponding to Eq. (14b) for m^2 equal to one represent translations, Δz, of the Bloch wall.

(*b*) *$m^2\leq 0$:* For m equal to zero, our solution for $S_Y(z)$ is $S_Y^0\sin 2\theta$. This wave function has its maximum values outside the Bloch wall at $\theta=45°$ and 135° and goes to zero at the center of the wall, corresponding to the first free spin wave state of the system. The dispersion relation is obtained by putting m equal to zero in Eq. (14b). All other solutions, represented by m^2 being less than zero, form, together with m equal to zero, a free spin wave excitation branch. For the dispersion relation given by Eq. (14b), the bottom of the free spin wave excitation branch is higher than the wall excitation branch due to the extra term $16S^2E^2$. As we would expect, it is easier to excite the modes corresponding to a translation of the wall than the free spin wave modes. For the higher energy expression given by Eq. (14a), the difference between the bound and wall excitation spectra is small. These results are shown graphically in Fig. 3.

Further, knowing S_Y, we can obtain our spin coordinate wave functions from Eqs. (11), (12), and (14). For the more interesting lower resonance frequency given by Eq. (14b), we get, for our normal resonance modes, the relations

$$s_Y=\left[1+\frac{E\cos 2\theta}{2J}+\frac{K'}{4J}+\frac{E^3\cos 2\theta\sin^2 2\theta}{2J^2(3E\cos 2\theta+D+M)}\right]S_Y,$$

$$iw_2S_z=\left[-\frac{E^2S}{J}\left(\cos^2 2\theta-\frac{7E\cos 2\theta+D+M}{3E\cos 2\theta+D+M}\sin^2 2\theta\right)-4JSa^2k_\perp^2\right]S_Y,$$

$$iw_2s_z=\left[\frac{E^2S}{J}\left(\cos^2 2\theta-\frac{7E\cos 2\theta+D+M}{3E\cos 2\theta+D+M}\sin^2 2\theta\right)-4K'S-4JSa^2k_\perp^2\right]S_Y. \quad (17)$$

We note that, for this resonance branch, the z components of the spin are very much smaller than the Y components while the major difference between S_Y and s_Y arises from the canting constant E.

VI. EXTERNAL MAGNETIC FIELD

We now calculate the amount of excitation of the bound Bloch wall resonance mode by an external nuclear magnetic resonance signal. This excitation, corresponding to motion of the Bloch wall, will act as an effective field on the nuclei through the nuclear hyperfine interaction, causing an apparent enhancement of the applied field. The major part of the effective field acting on the nuclei from the hyperfine interaction

$$\mathcal{H}_n=A\mathbf{I}\cdot\mathbf{S}, \quad (18)$$

corresponding to the nuclear magnetic resonance signal, is given by the term S_Y or s_Y which yield fluctuations in the hyperfine interaction perpendicular to the X or static spin direction. Thus, for a given nuclear magnetic

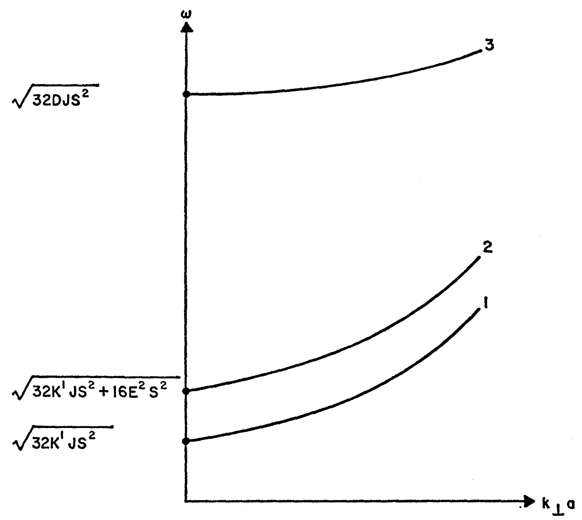

FIG. 3. Graph of allowed spin wave excitation branches for NiF_2 in the presence of a 90° Bloch wall. Curve 1 is the bound wall state, while curve 2 represents the lowest value for the free spin wave state for the lower energy excitation branch of Eq. (14b). Curve 3 is the approximate excitation spectrum for the high-energy mode given by Eq. (14a).

resonance signal, $H\cos\omega_0 t$, the effective field acting on the Y component of the nuclear magnetic moment, $\hbar\gamma_n I_Y$, is

$$H_{\mathrm{eff}}=A\,\mathrm{Re}[S_Y]/\hbar\gamma_n. \quad (19)$$

Noting that the hyperfine interaction constant, $(AS=\hbar w_0)$, has a frequency of 51.2 Mc/sec,[5] we get $H_{\mathrm{eff}}\simeq 2.5\times 10^4 S_Y$.

To calculate S_Y under the application of an external nuclear magnetic resonance signal, we apply the formulas

$$(d\mathbf{S}/dt)_{\mathrm{ext}}=\gamma_e(\mathbf{S}\times\mathbf{H}),$$
$$(d\mathbf{s}/dt)_{\mathrm{ext}}=\gamma_e(\mathbf{s}\times\mathbf{H}), \quad (20)$$

where $\mathbf{H}$, the external resonance field, shall be in the y direction, i.e.,

$$\mathbf{H}=(H\sin\theta\mathbf{e}_X+H\cos\theta\mathbf{e}_Y)\exp(iw_0t), \quad (21a)$$

for sublattice A, and

$$\mathbf{H}=(H\sin\phi\mathbf{e}_X+H\cos\phi\mathbf{e}_Y)\exp(iw_0t), \quad (21b)$$

for sublattice B. Then, using Eq. (3), our fundamental Eqs. (11c) and (11d) are modified to read

$$dS_z/dt=(8JS+4JSa^2\nabla^2)s_Y-\Gamma_2S_z-(8JS+2K'S+4ES\cos 2\theta)S_Y-\gamma_eSH\sin\theta\exp(iw_0t), \quad (11e)$$

$$ds_z/dt=(8JS+4JSa^2\nabla^2)S_Y-\Gamma_2s_z-[8JS+2K'S-4ES\cos 2\theta+(2SE^2/J)\sin^2 2\theta]s_Y+\gamma_eSH[\sin\theta+(E/4J)\cos\theta\sin 2\theta]\exp(iw_0t), \quad (11f)$$

while Eqs. (11a) and (11b) remain the same.

Following the methods used in Secs. IV and V, this set of inhomogeneous equations yields for S_Y

$$(1-u^2)\frac{d^2S_Y}{du^2}-2u\frac{dS_Y}{du}+\left(2-\frac{m_0^2}{1-u^2}\right)S_Y = \frac{f(\theta)\hbar\gamma_e H}{16E(1-u^2)}, \quad (22)$$

where

$$m_0^2 \approx [(\Gamma_1+iw_0\hbar)(\Gamma_2+i\hbar w_0)+16E^2S^2 +32K'JS^2]/16E^2S^2, \quad (23)$$

and

$$f(\theta)=3\sin 3\theta-\sin\theta. \quad (24)$$

We are interested in the excitation of the uniform bound wall mode given by $S_Y=S_Y^1P_1^1(u)$, where u equals $-\sin 2\theta$, $P_1^1(u)$ equals $\cos 2\theta$, and θ varies from 45° to 135°, (u varying from -1 to 1). Thus, we expand S_Y in terms of the normal modes of the system,

$$\textstyle\sum_m S_Y^m P_1^m(u).$$

(We note that any other terms needed to form a complete set will have very small amplitudes since the driving force, H, is small—therefore, essentially, exciting only the resonance modes.) Substituting for S_Y in Eq. (22), we get

$$\sum_m S_Y^m(m^2-m_0^2)\frac{P_1^m(u)}{1-u^2}=\frac{f(u)}{1-u^2}. \quad (25)$$

Using the orthogonality relationship,

$$\int_{-1}^{1}\frac{P_1^mP_1^n(u)}{1-u^2}du=\frac{1}{m}\frac{(1+m)!}{(1-m)!}\delta_n^m, \quad (26)$$

the excitation of the bound state, $P_1^1(u)$, is given by the equation

$$S_Y^1=\frac{\hbar\gamma_e H}{32E(1-m_0^2)}\int_{-1}^{1}\frac{f(u)P_1^m(u)}{1-u^2}du. \quad (27)$$

Substituting Eqs. (23) and (24) into Eq. (27) and integrating, we obtain for the amplitude of the bound state excitation

$$S_Y^1=-\frac{(2)^{3/2}\hbar\gamma_e HES^2}{32K'JS^2+(\Gamma_1+i\hbar w_0)(\Gamma_2+i\hbar w_0)}. \quad (28)$$

(19), the effective nuclear magnetic resonance field as seen by the nuclei in the Bloch wall, is

$$H_{\text{eff}}\approx(5\times10^{-18}/K')H_{\text{ext}}. \quad (29)$$

The stiffness parameter, K', is structure sensitive. Values between 10^{-18} and 5×10^{-20} erg/atom do not appear incompatable with data[2,8] for iron powder and nickel oxide. Thus, in this case, the nuclear magnetic resonance enhancement factor $H_{\text{eff}}/H_{\text{ext}}$ may vary from 5 to 100. The experimental value of approximately 50 observed by Shulman[5] falls within this range.

The effect of the bound excitation spectrum on the nuclear magnetic resonance linewidths is similar to that calculated by the author[9] for pure antiferromagnets.

VII. ANTIFERROMAGNETS WITHOUT CANTING

Finally, we show that an antiferromagnet without canting does not yield any enhancement of the external nuclear magnetic resonance signal. That this is not obvious stems from the fact than an antiferromagnetic substance is not magnetically inert in the presence of an external magnetic field—at least one of the sublattices being in an unfavorable energy position, and that the energy of the bound wall state is one of the same order of magnitude as that for the canted NiF_2.

The normal resonance modes for the free spin wave and bound wall excitations in the presence of a 180° Bloch wall have been calculated by the author[3] for a pure antiferromagnetic crystal possessing orthorhombic magnetic spin symmetry—the two types of spins being on two interpenetrating sublattices. Using Eqs. (20) and (21) above and Eqs. (10) and (11) of reference 3 [corresponding to our Eqs. (11)], we find that it is not possible to excite (to first order) the low-energy wall excitation given by Eq. (18) of this reference, [equivalent to our Eq. (14b) with m^2 equal to one]. Instead, only the high-energy wall excitation given by Eq. (22) [equivalent to our Eq. (14a)] is excited. The equation for S_Y is, therefore, of the form

$$S_Y^1\approx(\hbar\gamma_e/12J)H_{\text{ext}}. \quad (30)$$

We note that S_Y^1 for the antiferromagnetic case is less than that for the canted spin arrangement by the factor, K'/E, which is less than 0.01. Thus, the magnetic field enhancement is dependent on the canting of the spins.

ACKNOWLEDGMENTS

The author wishes to thank Professor A. Portis and Professor R. Orbach for bringing this problem to his attention, the U. S. Office of Naval Research for their support of this research, and the Physics Department of the University of Illinois for their hospitality during the summer months.

[8] W. L. Roth and G. A. Slack, J. Appl. Phys. **31**, 3525 (1960).
[9] D. I. Paul, Phys. Rev. **127**, 455 (1962).