Nuclear Magnetic Relaxation near the Curie Temperature

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A theoretical study is made on the nuclear spin relaxation in magnetic crystals near their Curie temperatures. The exchange narrowed hyperfine broadening of the NMR line width is shown to increase due to the slowing down of a certain part of the electron spin fluctuations as the transition point is approached, giving rise to the line width whose asymptotic value near the transition point is proportional to $[T_C/(T-T_C)]^{3/2}$ in cubic ferromagnets and to $[T_N/(T-T_N)]^{1/2}$ in cubic antiferromagnets. The spin-lattice relaxation rate is dominated by this mechanism and has the same value as the above contribution to the line width. The effect of the anisotropy and the external magnetic field on this mechanism is also discussed. The indirect nuclear spin interaction via the hyperfine interaction is treated from a general point of view by using the wavelength dependent susceptibility. The susceptibility is calculated with the use of a molecular field approximation. Since the spatial correlation between the spins becomes long ranged as the transition point is approached, the indirect nuclear spin interaction becomes long ranged at the same time. In non-cubic crystals this interaction gives rise to the line width whose asymptotic value near the transition point (both above and below T_C) is proportional to $[T_C/|T-T_C|]^{1/4}$ both in ferro- and antiferromagnets and the coefficient of this temperature factor is of the same order of magnitude as those in the first mechanism. In cubic crystals this effect vanishes or is reduced by orders of magnitude. The theory is compared with the F^{19}-resonance experiments in MnF_2 and the agreement is not unreasonable.

I. Introduction

Nuclear spin relaxation mechanisms in magnetic crystals have been studied extensively in recent years.[1]~[7] The important mechanisms may be classified into the following three: 1. hyperfine (electron spin-nuclear spin) interaction modulated by the exchange and other interactions between the electron spins and by the lattice vibrations; 2. indirect nuclear spin interaction via the hyperfine interaction; 3. nuclear dipole-dipole interaction and other mechanisms in which the electron spins do not take part. Here we are interested in the first and the second mechanisms through which we can look into the properties of magnetic crystals. The contribution from the third mechanism may easily be evaluated by standard methods.[8] Theoretical studies of the first mechanism have been made at high temperatures in the paramagnetic region and at low temperatures in ferro- and antiferromagnets where the spin wave approximation can be applied.[1],[2],[3] It was pointed out recently that at very low temperatures in certain antiferromagnets the mixing of the phonon and magnon modes is important.[6] The

second mechanism has been studied at first at 0°K in ferro- and antiferrromagnets where the virtual excitation of the spin waves due to the hyperfine interaction gives rise to the indirect nuclear spin interaction.[4],[5] This mechanism has been studied also in certain paramagnetic salts and it was pointed out that the coupling constant is inversely proportional to the square of the temperature at high temperatures.[7] The region near the transition point has not been studied theoretically so far.

·Recently several studies have been made as to the line width of the nuclear resonance in antiferromagnetic crystals near the Néel temperature. Heller and Benedek[9] as well as Baker, Lourens and Stevenson[10] studied the nuclear resonance line width of F^{19} in MnF_2 near the Néel point. They observed an anomalously sharp increase of the resonance line width as the temperature approaches the Néel point both in the paramagnetic and antiferromagnetic region. A similar phenomenon has been observed in NiF_2 by Shulman.[11] In CoO Shulman studied the nuclear resonance of Co^{59} in paramagnetic state and observed the increase of the line width as the Néel point is approached, though the temperature dependence is not so striking as in MnF_2.[12]

In this article a theoretical study is made on the first and second mechanisms particularly near the transition point in ferro- and antiferromagnets. The anomalous broadening of the line width may be expected both from the first and the second mechanisms on the following reasons: At high temperatures the line width as well as the spin-lattice relaxation rate is dominated by the electron spin motion due to the exchange and other spin-spin interactions. The motion of the electron spins is generally very rapid at high temperatures as compared with the nuclear spin motion under the hyperfine field and the hyperfine broadening is extremely narrowed by the exchange interaction. Near the transition point, however, certain modes of the electron spin motion slow down and the exchange narrowing effect will be reduced, thus giving rise to a broadening. As is known in the theory of critical scattering of neutrons, the macroscopic spin diffusion rate in a ferromagnet becomes zero at the Curie point and the decay time of the antiferromagnetic mode of the spin flucuation becomes infinity at the Néel point in an antiferromagnet. The indirect nuclear spin interaction may also give the anomalous broadening near the transition point since the correlation between two electronic spins becomes long ranged as the transition temperature is approached. It will actually be shown that the indirect nuclear spin interaction is of screened Coulomb type and the screening factor goes to zero as the temperature approaches the transition point.

In the following we shall treat the first and the second mechanisms in II and III, respectively. In order to calculate the line width and the spin-lattice relaxation time due to the first mechanism, the time dependent correlation functions of the electronic spins must be evaluated first. The spatial correlation functions are related with the wavelength dependent susceptibilities which are

calculated by a molecular field approximation. The form of the time dependence of the correlation functions has been given by the phenomenological theories[13],[14] for the long wave Fourier components of the ionic spins in a ferromagnet and for the antiferromagnetic Fourier component in an antiferromagnet. They are, however, insufficient for the present purpose. Recently Mori and Kawasaki[15] developed a microscopic theory of spin diffusion in ferromagnets by using a method in the statistical mechanics of irreversible processes developed by Kubo, Tomita[16],[17] and others. We shall here make use of their method in discussing the time correlation of the spins in ferro- and antiferromagnets. Quantitative expressions are given for the line width $1/T_2$ and the spin-lattice relaxation time T_1 near the transition point in ferro- and antiferromagnets. The influence of the external magnetic field and the anisotropy energy is discussed. The indirect nuclear spin coupling is treated from a general point of view. The coupling constants are expressed in terms of the wavelength dependent susceptibilities. The indirect nuclear spin coupling particularly near the transition point is thus calculated and the line width coming from this interaction is discussed. The anisotropy of the crystal is particularly important in this mechanism. It turns out that this mechanism of line broadening is unimportant in cubic ferro- and antiferromagnets, while it may be important in crystals with lower symmetry. Finally in IV a comparison between the theory and the available experimental data is made.

II. Effect of Hyperfine Interaction modulated by Electron Spin Motion

1. General formula

The formulas have been given earlier[1] for the nuclear resonance line shape and the spin-lattice relaxation time in magnetic crystals where the effect of the hyperfine interaction modulated by the exchange interaction is predominant. Denoting the interaction between the p-th nuclear spin and the j-th ionic spin as

$$I_p \cdot F_{pj} \cdot S_j , \tag{1}$$

where F_{pj} is a tensor, we have

$$I(\omega) = \int_{-\infty}^{\infty} \exp\ [i(\omega - \omega_0)t - \psi(t)]dt , \tag{2}$$

with

$$\psi(t) = \hbar^{-2} \int_0^t d\tau (t - \tau) \sum_{j,j'} \sum_{\nu,\nu'} \left\{ (F_{pj})_{z\nu} (F_{pj'})_{z\nu'} \right.$$

$$\left. + (1/2) \exp\ (i\omega_0\tau) \left[(F_{pj})_{x\nu} + i (F_{pj})_{y\nu} \right] \left[(F_{pj'})_{x\nu'} - i (F_{pj'})_{y\nu'} \right] \right\}$$

$$\times \langle \{\delta S_{j\nu}(\tau)\, \delta S_{j'\nu'}(0)\}\rangle, \tag{3}$$

and

$$1/T_1 = (1/2\hbar^2) \int_{-\infty}^{\infty} dt\, \cos\,(\omega_0 t) \sum_{j,j'} \sum_{\nu,\nu'} [\,(F_{pj})_{x\nu} + i\,(F_{pj})_{y\nu}]$$

$$\times [\,(F_{pj'})_{x\nu'} - i\,(F_{pj'})_{y\nu'}] \langle \{\delta S_{j\nu}(t)\, \delta S_{j'\nu'}(0)\}\rangle, \tag{4}$$

where $I(\omega)$ is the line shape function, ω_0 the nuclear resonance frequency, and T_1 the spin-lattice relaxation time. The z direction is along the average local field at the nucleus, ν and ν' represent x, y, z, and

$$\delta \boldsymbol{S}_j = \boldsymbol{S}_j - \langle \boldsymbol{S}_j\rangle. \tag{5}$$

$\langle\ \rangle$ means the thermal average and $\{AB\} = (AB + BA)/2.$

From (2), (3) and (4) we see that the line width and the spin-lattice relaxation time are expressed in terms of the correlation functions of the ionic spin components. It is convenient here to introduce the Fourier transform in space of the ionic spin variables. Let us for brevity consider the case where there is only one magnetic ion in a unit cell and define

$$\boldsymbol{S}_k = N^{-1/2} \sum_j \boldsymbol{S}_j \exp\,(i\boldsymbol{k}\cdot\boldsymbol{R}_j), \tag{6}$$

where $\boldsymbol{k}$ is a wave number vector and N the number of magnetic ions in a crystal. The correlation function between the jth and the j'th ionic spins can then be expressed as follows:

$$\langle \{\delta S_{j\nu}(t)\, \delta S_{j'\nu'}\}\rangle = N^{-1} \sum_k \langle \{\delta S_{k\nu}(t)\, \delta S_{-k\nu'}\}\rangle \exp\,[-i\boldsymbol{k}\cdot(\boldsymbol{R}_j - \boldsymbol{R}_{j'})]. \tag{7}$$

When we consider only an isotropic hyperfine interaction between the nuclear and the electronic spins, i.e. when $F_{pj} = A\delta_{pj}$, (3) and (4) are simply reduced to

$$\psi(t) = (A/\hbar)^2 \int_0^t d\tau\,(t-\tau) \Big[\langle \{\delta S_{jz}(\tau)\, \delta S_{jz}\}\rangle + (1/2) \exp\,(i\omega_0 \tau) \langle \{\delta S_{j+}(\tau)\, \delta S_{j-}\}\rangle \Big], \tag{8}$$

$$1/T_1 = (A^2/2\hbar^2) \int_{-\infty}^{\infty} dt\, \cos\,(\omega_0 t) \langle \{\delta S_{j+}(t)\, \delta S_{j-}\}\rangle. \tag{9}$$

Now let us introduce a relaxation function defined as follows:

$$(\delta S_k(t),\, \delta S_{-k}) = \int_0^\beta d\lambda \langle \delta S_k(t - i\hbar\lambda)\, \delta S_{-k}\rangle, \tag{10}$$

where

$$\delta S_k(t - i\hbar\lambda) = \exp\,(\lambda\mathscr{H})\, \delta S_k(t) \exp\,(-\lambda\mathscr{H}),$$

$$\beta = 1/k_B T,$$

$\mathcal{H}$ and k_B being the Hamiltonian of the electronic spin system and the Boltzmann constant, respectively. In the classical limit, which is a good approximation at high temperatures, the correlation function is equal to $k_B T$ times the corresponding relaxation function. We shall use this approximation in the following discussions.[*] Since the relaxation function for $t=0$ is related with the static susceptibility by a well-known relation, the correlation functions are written as follows :

$$\langle \{\delta S_{kz}(t)\,\delta S_{-kz}\}\rangle = (k_B T/g^2\mu_B^2)\,\chi_z(k)f_{kz}(t),$$

$$\langle \{\delta S_{k+}(t)\,\delta S_{-k-}\}\rangle = (k_B T/g^2\mu_B^2)\,\chi_+(k)f_{k+}(t), \tag{11}$$

with

$$f_{kz}(t) = (\delta S_{kz}(t),\ \delta S_{-kz})/(\delta S_{kz},\ \delta S_{-kz}),$$

$$f_{k+}(t) = (\delta S_{k+}(t),\ \delta S_{-k-})/(\delta S_{k+},\ \delta S_{-k-}), \tag{12}$$

where the wavelength dependent susceptibility $\chi(k)$ is defined by

$$\langle \boldsymbol{M}_k\rangle = g\mu_B\langle \boldsymbol{S}_k\rangle = \chi(\boldsymbol{k})\cdot\boldsymbol{H}_k, \tag{13}$$

$$\chi_z(\boldsymbol{k}) = \chi_{zz}(\boldsymbol{k}),\ \ \chi_+(\boldsymbol{k}) = \chi_{xx}(\boldsymbol{k}) + \chi_{yy}(\boldsymbol{k}). \tag{14}$$

$\boldsymbol{H}_k$ is the Fourier component with the wave vector $\boldsymbol{k}$ of the external magnetic field.

2. Spatial correlation above the transition point

The spatial correlation of the wavelength dependent susceptibility near the critical point can be calculated by various methods. This problem has been studied in connection with the critical scattering of neutrons from magnetic crystals. van Hove[13] gave a phenomenological theory. Elliott and Marshall[18] made a statistical mechanical calculation of the space correlation functions in ferro- and antiferromagnets. de Gennes and Villain[14] used a molecular field approximation in the same problem in ferrimagnets. Their results are qualitatively the same and are supported by a critical scattering experiment of neutrons.[19] Here we shall show the results of the molecular field calculation.

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[*] This may be justified for our purpose. For the calculation of T_1, we can easily see that the replacement of the correlation function by $k_B T$ times the corresponding relaxation function is almost exactly correct if the Curie temperature is not too low, since we have[17]

$$\int_{-\infty}^{\infty}dt\ e^{-i\omega t}\langle\{A(t),\ B\}\rangle = E_\beta(\omega)\int_{-\infty}^{\infty}dt\ e^{-i\omega t}(A(t),\ B),$$

with

$$E_\beta(\omega) = (\hbar\omega/2)\ \coth\ (\beta\hbar\omega/2),$$

and ω_0 is negligible as compared with $k_B T_C$. For the line width the high frequency components of the correlation functions are not effective either and the approximation is justified as well.

A. Cubic crystals

For a cubic crystal we have a scalar susceptibility,

$$\chi(k) = \alpha \{1 - \alpha [J(k)/g^2\mu_B{}^2]\}^{-1}, \qquad (15)$$

where α is the susceptibility per ion of the crystal when there is no interaction between the spins, i.e.

$$\alpha = g^2\mu_B{}^2 S(S+1)/3k_B T, \qquad (16)$$

and $J(k)$ is the Fourier transform

$$J(k) = J(-k) = \sum_j \exp[ik \cdot (R_j - R_{j'})] J_{jj'} \qquad (17)$$

of the exchange coupling constant defined by the following exchange coupling Hamiltonian:

$$\mathcal{H}_{ex} = -(1/2)\sum_{j,j'} J_{jj'}(S_j \cdot S_{j'}).$$

(a) Ferromagnets

For a ferromagnet $J(k)$ takes a maximum value at $k=0$ and the Curie temperature is given by

$$T_C = J(0)S(S+1)/3k_B.$$

Therefore, (15) can be rewritten as

$$\chi(k) = \frac{g^2\mu_B{}^2 S(S+1)/3k_B T_C}{[(T-T_C)/T_C] + \{1 - [J(k)/J(0)]\}}. \qquad (18)$$

For small k the second term in the denominator is expanded in the following form:

$$1 - [J(k)/J(0)] = \gamma k^2 + \xi_1 k^4 + \xi_2(k_x{}^4 + k_y{}^4 + k_z{}^4) + \cdots. \qquad (19)$$

(b) Antiferromagnets

For an antiferromagnet $J(k)$ takes a maximum value at $k=K_0$, which differs from 0. For a simple cubic lattice of magnetic ions we have

$$K_0 = (\pi/a, \pi/a, \pi/a),$$

and for a body centered cubic lattice

$$K_0 = (2\pi/a, 0, 0).$$

The Néel temperature is given by

$$T_N = J(K_0)S(S+1)/3k_B,$$

and the susceptibility is written as

$$\chi(k) = \frac{g^2\mu_B{}^2 S(S+1)/3k_B T_N}{[(T-T_N)/T_N] + \{1 - [J(k)/J(K_0)]\}}. \qquad (20)$$

The second term in the denominator can be expanded in terms of $\kappa = k - K_0$ as

$$1 - [J(k)/J(K_0)] = \gamma \kappa^2 + \xi_1 \kappa^4 + \xi_2 (\kappa_x{}^4 + \kappa_y{}^4 + \kappa_z{}^4) + \cdots, \tag{21}$$

when the spin arrangement below T_N has a cubic symmetry.

B. *Crystals with lower symmetry*

For a crystal with lower symmetry, the susceptibility $\chi(k)$ generally is a tensor. When there is only one magnetic ion in a unit cell, we get from the molecular field approximation

$$\chi(k) = [1 - \mu_B^{-2} \alpha \cdot g^{-1} \cdot \mathcal{J}(k) \cdot g^{-1}]^{-1} \cdot \alpha, \tag{22}$$

where α is the susceptibility tensor per magnetic ion of the crystal without the influence of the spin-spin interaction, g the g-tensor and $\mathcal{J}(k)$ the Fourier transform:

$$\mathcal{J}(k) = \mathcal{J}(-k) = \sum_{j} \mathcal{J}_{jj'} \exp[ik \cdot (R_j - R_{j'})], \tag{23}$$

of the spin-spin interaction tensor defined by the following spin-spin interaction Hamiltonian:

$$\mathcal{H}_{SS} = -(1/2) \sum_{j,j'} S_j \cdot \mathcal{J}_{jj'} \cdot S_{j'}. \tag{24}$$

$\mathcal{J}(k)$ is divided into two parts as

$$\mathcal{J}(k) = J(k) + \mathcal{P}(k), \tag{25}$$

where $J(k)$ is the isotropic exchange interaction constant and $\mathcal{P}(k)$ the anisotropic spin-spin interaction constant to which the dipole-dipole and the anisotropic exchange interactions contribute.

(a) *Ferromagnets*

In a ferromagnet one of the principal values of $\mathcal{J}(k)$ takes a maximum value at $k = 0$. Let us assume that the principal axes of α, g and $\mathcal{P}(0)$ coincide and denote the principal values of $\mathcal{P}(0)$ as $P_x(0)$, $P_y(0)$ and $P_z(0)$. The uniform susceptibility $\chi(0)$ has also the same principal axes and the principal values are given by

$$\chi_n(0) = \alpha_n \{1 - (\alpha_n/g_n^2 \mu_B^2) [J(0) + P_n(0)]\}^{-1}, \tag{26}$$

with $n = x, y, z$. When the single ion anisotropy energy is expressed as

$$D_x S_x{}^2 + D_y S_y{}^2 + D_z S_z{}^2, \tag{27}$$

with

$$D_x + D_y + D_z = 0,$$

the susceptibility components of an isolated magnetic ion are given by

$$\alpha_n = [g_n^2 \mu_B^2 S(S+1)/3k_B T] \{1 - (D_n/10k_B T) [4S(S+1) - 3] + \cdots\}. \tag{28}$$

Inserting (28) into (26), we see that the Curie temperature is given by the largest value of

$$T_n = [S(S+1)/3k_B][J(0)+P_n(0)] - (D_n/10k_B)[4S(S+1)-3], \qquad (29)$$

with $n=x, y, z$. In calculating $\chi(\boldsymbol{k})$ for general $\boldsymbol{k}$, let us simply assume that the principal axes x, y, z of the $\mathscr{P}(\boldsymbol{k})$ tensor are independent of $\boldsymbol{k}$. We get

$$\chi_n(\boldsymbol{k}) = \alpha_n[1 - [S(S+1)/3k_BT][J(\boldsymbol{k})+P_n(\boldsymbol{k})]\{1-(D_n/10k_BT)$$
$$\times [4S(S+1)-3]\}]^{-1}. \qquad (30)$$

For small D_n/k_BT, the above expression is written as

$$\chi_n(\boldsymbol{k}) = \frac{g_n^2\mu_B^2 S(S+1)/3k_B T_n}{[(T-T_n)/T_n]+1-\{[J(\boldsymbol{k})+P_n(\boldsymbol{k})]/[J(0)+P_n(0)]\}}. \qquad (31)$$

(b) Antiferromagnets

For an antiferromagnet we get similar expressions to those for a ferromagnet. The results are obtained by replacing $J(0)$ and $P_n(0)$ in the above expressions for a ferromagnet with $J(\boldsymbol{K}_0)$ and $P_n(\boldsymbol{K}_0)$, respectively. As a numerical example, let us consider the case of MnF_2 which has a rutile type crystal structure. The magnetic ions form a body centered tetragonal lattice and the susceptibility α has nearly tetragonal symmetry. The values of D and $P_n(\boldsymbol{K}_0)$ are[20]

$$D_\| = -2D_\perp = -0.008 \mathrm{cm}^{-1},$$

$$P_\| = P_\|(\boldsymbol{K}_0) = -2P_\perp = -2P_\perp(\boldsymbol{K}_0) = 0.21\mathrm{cm}^{-1}.$$

Inserting these values into (29), we get

$$T_N - T_\perp = [S(S+1)/3k_B]\{P_\| - P_\perp - (192/175)(D_\| - D_\perp)\} = 1.36°K. \qquad (32)$$

3. Spatial correlation below the transition point

Below the transition point it is essential to introduce an anisotropy energy or an external field which stabilizes a particular orientation in space of the ordered spin array. For brevity let us take account of only anisotropic interactions between the spins. The Hamiltonian is

$$\mathscr{H} = -(1/2)\sum_{j,j'}[J_{jj'}(\boldsymbol{S}_j \cdot \boldsymbol{S}_{j'}) + \boldsymbol{S}_j \cdot \mathscr{P}_{jj'} \cdot \boldsymbol{S}_{j'}] + g\mu_B\sum_j \boldsymbol{H}_j \cdot \boldsymbol{S}_j, \qquad (33)$$

where $\boldsymbol{H}_j$ is the external magnetic field at the j th spin. We assume as in the preceding paragraphs that all the anisotropic spin-spin interaction tensors have the same principal axes, x, y, z, and the z axis is the easy direction for the spin ordering. By using the molecular field approximation we have

$$\langle \boldsymbol{S}_j \rangle / S = B_S(g\mu_B|\boldsymbol{H}_j^{eff}|S/k_BT),$$

with

$$g\mu_B\boldsymbol{H}_j^{eff} = -\sum_{j'}(J_{jj'} + \mathscr{P}_{jj'}) \cdot \boldsymbol{S}_{j'} + g\mu_B\boldsymbol{H}_j, \qquad (34)$$

where $S_j = |\boldsymbol{S}_j|$ and $B_S(x)$ is the Brillouin function.

(a) *Ferromagnets*

The average values of the spin components are given by

$$\langle S_{jx} \rangle = - \langle S_j \rangle H_{jx}^{eff}/|\boldsymbol{H}_j^{eff}|, \text{ etc.} \tag{35}$$

The components of the effective local field are given by

$$g\mu_B H_{jz}^{eff} = [J(0) + P_z(0)] S_0 - \sum_{j'} [J_{jj'} + (\mathscr{P}_{jj'})_z] \delta S_{j'z} + g\mu_B H_{jz},$$

$$g\mu_B H_{jx}^{eff} = - \sum_{j'} [J_{jj'} + (\mathscr{P}_{jj'})_x] S_{j'x} + g\mu_B H_{jx}, \text{ etc.,}$$

where S_0 is the average value of the spin under no magnetic field and is given by

$$S_0 = S B_S [\{J(0) + P_z(0)\} S S_0/k_B T]. \tag{36}$$

Near the Curie temperature this leads to

$$S_0^2 = (20/3) \{(S+1)^2/[(2S+1)^2+1]\} (T/T_C)^2 [1 - (T/T_C)]. \tag{37}$$

Neglecting the terms in (35) which are higher than the second order with respect to δS_{jz}, S_{jx}, S_{jy}, and $\boldsymbol{H}_j$, and solving the Fourier transforms of (35) for δS_{kz}, S_{kx} and S_{ky}, we get the following expressions for the susceptibility:

$$\chi_z(\boldsymbol{k}) = \frac{g^2\mu_B^2 S(S+1)/3k_B T_C}{\{[1 - W(T)]/W(T)\} + 1 - \{[J(\boldsymbol{k}) + P_z(\boldsymbol{k})]/[J(0) + P_z(0)]\}}, \tag{38}$$

$$\chi_x(\boldsymbol{k}) = \frac{g^2\mu_B^2 S(S+1)/3k_B T_x}{[(T_C - T_x)/T_x] + 1 - \{[J(\boldsymbol{k}) + P_x(\boldsymbol{k})]/[J(0) + P_x(0)]\}}, \text{ etc.,} \tag{39}$$

where

$$W(T) = [3T_C S/(S+1) T] B_S' [\{J(0) + p_z(0)\} S S_0/k_B T]. \tag{40}$$

In this approximation the susceptibility perpendicular to the magnetization is independent of temperature while the susceptibility parallel to the magnetization decreases as the temperature is lowered. As $T \to 0$, $\chi_z(\boldsymbol{k})$ tends to 0 since $W(0) = 0$. Near the Curie point we have

$$[1 - W(T)]/W(T) \cong 2\delta/(1 - 3\delta), \tag{41}$$

with

$$\delta = (T_C - T)/T_C.$$

(b) *Antiferromagnets*

The average value of the jth spin under no external magnetic field is

$$\langle S_{jz} \rangle = S_0 \exp(i\boldsymbol{K}_0 \cdot \boldsymbol{R}_j),$$

with

$$S_0 = S B_S [\{J(\boldsymbol{K}_0) + P_z(\boldsymbol{K}_0)\} S S_0/k_B T].$$

The calculation of the susceptibility is similar to that for ferromagnets and the results are given by replacing T_C, $J(0)$ and $P_n(0)$ in the expressions (38)– (41) for a ferromagnet by T_N, $J(K_0)$ and $P_n(K_0)$, respectively.

4. Time correlation

The time dependence of the correlation functions has been calculated by a spin wave approximation at low temperatures[1)-3)] and by a moment expansion method at high temperatures.[1)] Near the transition point, however, these methods cannot be applied and the treatment becomes more or less qualitative. van Hove[13)] gave a phenomenological theory on the time dependence of the spin correlation functions in a ferromagnet on the basis of thermodynamics of irreversible precesses. He obtained for small k above T_C

$$f_k(t) = \exp(-\Lambda k^2 t)$$

with

$$\Lambda = \lambda/\chi(0),$$

where $\chi(0)$ is the uniform susceptibility of the ferromagnet and λ is a phenomenological constant. de Gennes and Villain[14)] gave a phenomenological discussion on an antiferromagnet and obtained

$$f_{K_0}(t) = \exp(-\Lambda' t),$$

where

$$\Lambda' \propto T - T_N.$$

They did not treat the k dependence of the correlation functions. These theories are insufficient for the present purpose even qualitatively. We need to know the k dependence better. A natural extension of these phenomenological theories may be to assume the following form of the time correlation function:

$$f_k(t) = \exp(-\Gamma_k t), \tag{42}$$

and expand Γ_k as follows:

$$\Gamma_k = \Lambda k^2 + \theta k^4 + \cdots \tag{43}$$

for a ferromagnet and

$$\Gamma_{K_0+k} = \Lambda' + \theta' k^2 + \cdots \tag{44}$$

for an antiferromagnet. Λ and Λ' tend to zero as the transition point is approached while θ and θ' are considered to remain finite. From the expressions (42), (43) and (44) we can draw a qualitative conclusion as to the asymptotic behavior of the NMR line width and the spin-lattice relaxation time as temperature approaches the transition point. For a quantitative purpose, however, this argument is still insufficient so long as Λ and θ are not evaluated. A calculation of $f_k(t)$ on a microscopic basis was made by de Gennes,[21)] though his theory

was confined to the high temperature limit. He employed a moment method and showed that at the high temperature limit the form (42) is reasonable for small k. It seems to be hard to extend the moment method to the temperature range near the transion point. Recently, Mori and Kawasaki[15] developed a theory of spin diffusion, or a method of calculating $f_k(t)$, on a microscopic basis. They ingeneously replaced the correlation functions of the spins with those of the torques as follows:

$$f_k(t) = 1 - \int_0^t d\tau (t-\tau) (T_{km}(\tau), T_{km}{}^*)/(S_{km}, S_{km}{}^*), \qquad (45)$$

with

$$T_{km}(t) = \frac{d}{dt} S_{km}(t), \quad m = x, y, z.$$

It was pointed out that in a ferromagnet $f_k(t)$ for small k may be approximately written in the form of (42) since the decay in time of $f_k(t)$ for small k may be slower than that of the correlation function of the corresponding torque. In the NMR relaxation problem, where $f_k(t)$ for large t is important, $f_k(t)$ may generally be approximated by (42) with

$$\Gamma_k = \int_0^\infty dt (T_{km}(t), T_{km}{}^*)/(S_{km}, S_{km}{}^*). \qquad (46)$$

Assuming a Gaussian decay of the correlation function of the torque as

$$(T_{km}(t), T_{km}{}^*)/(T_{km}, T_{km}{}^*) = \exp [-(t/\tau_k)^2], \qquad (47)$$

we obtain

$$\Gamma_k = \sqrt{\pi} \ \tau_k (T_{km}, T_{km}{}^*)/2 (S_{km}, S_{km}{}^*). \qquad (48)$$

τ_k can in principle be calculated from the second moment of the frequency spectrum of $T_{km}(t)$, though it is practically very hard. $(T_{km}, T_{km}{}^*)$ can be expressed in terms of the correlation functions of the spins by using the following relation[17]:

$$([\mathcal{H}, A], B) = -\langle [A, B] \rangle.$$

After a calculation (48) is reduced to

$$\Gamma_k = [\sqrt{\pi} \ \tau_k k_B T/\hbar^2 \chi(k)] N^{-1} \sum_q [J(q) - J(k+q)] \chi(q). \qquad (49)$$

The expressions (43) and (44) for ferro- and antiferromagnets are derived from (49) as can easily be observed.

We shall now consider a simple cubic and a body-centered cubic lattice with only nearest neighbor exchange interactions. We have

$$J(q) = 2J[\cos(q_x a) + \cos(q_y a) + \cos(q_z a)],$$

and

$$J(\boldsymbol{q}) = 8J \cos(q_x a/2) \cos(q_y a/2) \cos(q_z a/2),$$

for s.c. and b.c.c. lattices, respectively. In this model $\varGamma_k$ can be obtained in a closed form.

(a) Ferromagnet

For simple cubic and body-centered cubic lattices we have the following relation:

$$\sum_q [J(\boldsymbol{q}) - J(\boldsymbol{k}+\boldsymbol{q})]\chi(\boldsymbol{q}) = \{1 - [J(\boldsymbol{k})/J(0)]\}\sum_q J(\boldsymbol{q})\chi(\boldsymbol{q}). \tag{50}$$

From (18) we get

$$(1/Ng^2\mu_B^2)\sum_q J(\boldsymbol{q})\chi(\boldsymbol{q}) = (1+\delta) I_\delta - 1, \tag{51}$$

with

$$\delta = (T - T_C)/T_C, \tag{52}$$

and

$$I_\delta = (1/N)\sum_q \{(1+\delta) - [J(\boldsymbol{q})/J(0)]\}^{-1}. \tag{53}$$

For a simple cubic and a body-centered cubic lattice, (53) leads to

$$I_\delta(s.c.) = (2\pi)^{-3}\int\!\!\!\int\!\!\!\int_{-\pi}^{\pi} dxdydz \{(1+\delta) - [(\cos x + \cos y + \cos z)/3]\}^{-1} \tag{54}$$

and

$$I_\delta(b.c.c.) = (2\pi)^{-3}\int\!\!\!\int\!\!\!\int_{-\pi}^{\pi} dxdydz [(1+\delta) - \cos x \cos y \cos z]^{-1}, \tag{55}$$

and their numerical values for $\delta = 0$ are[15]

$$I_0(s.c.) = 1.52, \quad I_0(b.c.c.) = 1.39. \tag{56}$$

The decay costant $\varGamma_k$ is given as follows:

$$\varGamma_k = [3\sqrt{\pi}\ \tau_k k_B^2 TT_C/\hbar^2 S(S+1)][(1+\delta) I_\delta - 1]\{1+\delta - [J(\boldsymbol{k})/J(0)]\}$$
$$\times \{1 - [J(\boldsymbol{k})/J(0)]\}. \tag{57}$$

(b) Antiferromagnets

A similar calculation to that in a ferromagnet leads to the following re- results:

$$\varGamma_k = [3\sqrt{\pi}\ \tau_k k_B^2 TT_N/\hbar^2 S(S+1)][(1+\delta) I_\delta - 1]\{1+\delta - [J(\boldsymbol{k})/J(\boldsymbol{K}_0)]\}$$
$$\times \{1 + [J(\boldsymbol{k})/J(\boldsymbol{K}_0)]\}. \tag{58}$$

Here I_δ is given by (54) and (55) for a simple cubic and a body-centered cubic lattice, respectively, and

$$\delta = (T - T_N) / T_N .$$

The calculation of $\tau_k{}^\alpha$ is very difficult except for the high temperature limit where Mori and Kawasaki obtained for ferromagnets for small k

$$\tau_k{}^{-2} = 8z\xi S (S+1) J^2 / 3\hbar^2 ,$$

with

$$\xi = 1 - (39/5z^2) \{1 + [3/26S(S+1)]\} ,$$

where z is the number of nearest neighbors. We may expect, however, τ_k does not change seriously near the transition point and its order of magnitude remains to be $\sim J/\hbar$.

5. Relaxation times

For brevity let us consider the case where the isotropic hyperfine interaction is predominant in the nuclear relaxation mechanism. The line shape and the spin-lattice relaxation time can be calculated from (2), (8) and (9) by using the correlation functions for the spin components calculated in the preceding paragraphs. In this paragraph we shall neglect the influence of the external magnetic field and the anisotropy energy on the electron spin correlation functions. This effect will be discussed in the following paragraph. From (8), (9), (11) and (42) we get

$$\psi(t) = (A^2 k_B T / \hbar^2 g^2 \mu_B{}^2) N^{-1} \sum_k \left\{ \chi_z(\boldsymbol{k}) \int_0^t d\tau (t-\tau) \exp(-\Gamma'_k{}^0 |\tau|) \right.$$

$$\left. + (1/2) \chi_+(\boldsymbol{k}) \int_0^t d\tau (t-\tau) \exp(-\Gamma_k{}^+ |\tau| + i\omega_0 \tau) \right\} , \tag{59}$$

and

$$1/T_1 = (A^2 k_B T / \hbar^2 g^2 \mu_B{}^2) N^{-1} \sum_k \chi(\boldsymbol{k}) \int_{-\infty}^{\infty} dt \cos(\omega_0 t) \exp(-\Gamma_k |t|) , \tag{60}$$

where ω_0 is the nuclear resonance frequency. For a cubic crystal (59) and (60) can be written as follows:

$$\psi(t) = (2A^2 k_B T / \hbar^2 g^2 \mu_B{}^2) N^{-1} \sum_k [\chi(\boldsymbol{k}) \{\Gamma_k t - 1 + \exp(-\Gamma_k t)\} / \Gamma_k{}^2] , \tag{61}$$

and

$$1/T_1 = (2A^2 k_B T / \hbar^2 g^2 \mu_B{}^2) N^{-1} \sum_k [\chi(\boldsymbol{k}) / \Gamma_k] , \tag{62}$$

where a small effect of ω_0 is neglected. The calculation of T_1 can be carried

out and the result is

$$1/T_1 = (1/T_{1\infty}) \{[(I_0-I_\delta)/\delta^2] + [(dI_\delta/d\delta)/\delta]\}/zI_0[(1+\delta)I_\delta-1], \quad (63)$$

for a ferromagnet and

$$1/T_1 = (1/T_{1\infty}) \{[(I_0+I_\delta)/(2+\delta)^2] - [(dI_\delta/d\delta)/(2+\delta)]\}/zI_0[(1+\delta)I_\delta-1], \quad (64)$$

for an antiferromagnet, with

$$1/T_{1\infty} = 2[AS(S+1)]^2 zI_0/9\sqrt{\pi} \langle\tau_k\rangle (k_B T_C)^2. \quad (65)$$

$T_{1\infty}$ is the spin-lattice relaxation time at high temperature limit. In the above calculation we replaced τ_k with the average value $\langle\tau_k\rangle$ independent of k. The temperature dependence of the spin-lattice relaxation time is generally given by (63) and (64). For a body-centered cubic lattice, for example, I_δ is reduced to

$$I_\delta = [2/\pi^2(1+\delta)]\int_0^\pi dx K[\cos^2 x/(1+\delta)^2],$$

where $K(z)$ is the complete elliptic integral of the first kind, and T_1 can be calculated at any temperature by numerical computations. At temperatures near the transition point we can easily see that $1/T_1$ diverges as $\delta\to 0$ or $T\to T_C$. The asymptotic behaviors are expressed as

$$1/T_1 = (1/T_{1\infty})[\sqrt{z}/8\pi I_0(I_0-1)]\delta^{-3/2}$$
$$= (0.124/T_{1\infty})\delta^{-3/2} \text{ (for s.c.)},$$
$$= (0.205/T_{1\infty})\delta^{-3/2} \text{ (for b.c.c.)}, \quad (66)$$

for a ferromagnet and

$$1/T_1 = (1/T_{1\infty})[\sqrt{z}/16\pi I_0(I_0-1)]\delta^{-1/2}$$
$$= (0.062/T_{1\infty})\delta^{-1/2} \text{ (for s.c.)},$$
$$= (0.103/T_{1\infty})\delta^{-1/2} \text{ (for b.c.c.)}, \quad (67)$$

for an antiferromagnet.[*] These expressions hold for small δ which however is larger than $(\omega_0/\omega_e)^{1/2}$ in a ferromagnet and ω_0/ω_e in an antiferromagnet, ω_e being the exchange frequency. It should be noted that the temperature depen-

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[*] This asymptotic temperature dependence may easily be seen from (62), since we have for small k

$$\chi(k)/\Gamma_k = C/(\delta+\gamma k^2)^2 k^2,$$

for a ferromagnet and

$$\chi(K_0+k)/\Gamma_{K_0+k} = C/(\delta+\gamma k^2)^2,$$

for an antiferromagnet.

dences in ferro- and antiferromagnets are different. This difference is considered to come from the fact that $S(0)$ is a constant of motion while $S(K_0)$ is not. From (66) and (67) we see that the anomalous increase of the relaxation rate takes place in a very narrow temperature range. For an antiferromagnet with the Néel point at $\sim 100°$K, the anomalous increase in the relaxation rate is expected to be seen at $T-T_N<1°$K, in agreement with Heller and Benedek's observation in MnF_2. For a crystal with a low transition point this temperature range is extremely narrrow. For example, in an antiferromagnet with the Néel point at $1°$K, the anomalous increase of the relaxation rate will be seen at $T-T_N<10^{-2}$ °K.

As to the line shape and width, we may expect a Lorentzian line shape and
$$1/T_2=1/T_1 ,$$
for cubic ferro- and antiferromagnets at temperatures not too close to the transition point. For an antiferromagnet the above statement will hold in the range
$$\delta>A/J(K_0) ,$$
while in a ferromagnet the corresponding lower limit of δ will be larger than in antiferromagnets. In the extremely narrow temperature range where the above relation does not hold, the line shape will be deformed from a Lorentzian shape and the line width will become larger than $1/T_1$. The calculation of the line shape and the width in this temperature range is very complicated and we will not get into this problem here.

6. Influence of the external magnetic field and the anisotropy

We shall discuss in this paragraph the influence of the external magnetic field and the anisotropy which is important in actual experimental situations. The influence of the external field is more important in ferromagnets than in antiferromagnets, since the uniform magnetization is influenced significantly by a uniform external field while the antiferromagnetically ordered spins are little influenced by a uniform external field. As a matter of fact, an external magnetic field makes the ferromagnetic Curie point obscure, while it gives only a small shift to the Néel point in an antiferromagnet. The calculation of the correlation functions of the spins and the relaxation times can be carried out along the same line as in the preceding sections. Here only the results are described.

The time part of the correlation functions may be written as follows:
$$f_{kz}(t) =\exp(-\Gamma_k^0|t|) ,$$
$$f_{k+}(t) =\exp(i\omega_k t-\Gamma_k^+|t|) ,$$
with
$$\omega_k =g^2\mu_B^2 S_0/\hbar\chi_\perp(k) ,$$
$$\Gamma_k^0 =[\sqrt{\pi}\,\tau_k^0 k_B T/\hbar^2\chi_z(k)]N^{-1}\sum_q[J(q)-J(k+q)]\chi_\perp(q) ,$$

$$\Gamma_k{}^+ = [\sqrt{\pi}\,\tau_k{}^+ k_B T/\hbar^2 \chi_\perp(k)]N^{-1}\sum_q [J(q)-J(k+q)][\chi_z(q)+\chi_\perp(q)]/2,$$

in the first approximation. $\chi(k)$ in the above expressions is the differential susceptibility under the constant external field. S_0 is the average spin moment under the external magnetic field H_0 and is given by

$$S_0 = SB_S[\{J(0)S_0+g\mu_B H_0\}S/k_B T].$$

ω_k has been calculated from

$$i\omega_k = (\dot{S}_{k+}, S_{k+}{}^*)/(S_{k+}, S_{k+}{}^*).$$

T_1 and $\psi(t)$ are given as follows:

$$1/T_1 = (2A^2 k_B T/\hbar^2 g^2 \mu_B{}^2)N^{-1}\sum_k \chi_\perp(k)\,\Gamma_k{}^+/[(\Gamma_k{}^+)^2+\omega_k{}^2], \qquad (68)$$

$$\psi(t) = (A^2 k_B T/\hbar^2 g^2 \mu_B{}^2)N^{-1}\sum_k \{\chi_z(k)\int_0^t d\tau(t-\tau)\exp(-\Gamma_k{}^0|\tau|)$$

$$+\chi_\perp(k)\int_0^t d\tau(t-\tau)\exp(i\omega_k\tau-\Gamma_k{}^+|\tau|)\}. \qquad (69)$$

Now we shall discuss the cases of ferromagnets and antiferromagnets separately.

(a) Ferromagnets

Under a constant magnetic field H_0, the singularity in the differential susceptibility disappears. The differential susceptibiliy components of a cubic ferromagnet parallel and perpendicular to the external magnetic field are given by replacing $(T-T_C)/T_C$ in (18) with $\delta+\nu_\parallel$ and $\delta+\nu_\perp$, respectively, where

$$\nu_\parallel(H_0, T) = \{k_B T/J(0)S^2 B_S'[\{J(0)S_0+g\mu_B H_0\}S/k_B T]\}-(T/T_C),$$

and

$$\nu_\perp(H_0, T) = [g\mu_B H_0/J(0)S_0]-[(T-T_C)/T_C]. \qquad (70)$$

In the limit of small H_0, $\nu_\parallel$ and $\nu_\perp$ naturally tend to zero. For a finite value of H_0 it can easily be seen that when $\delta \gtrsim g\mu_B H_0/J(0)$, ν's are of the order of $[g\mu_B H_0/J(0)]^2$ and for smaller values of δ, ν's increase as $\delta \to 0$. The values of $\nu_\parallel$ and $\nu_\perp$ for $\delta = 0$ or $T = T_C$ are

$$\nu_\parallel(H_0, T_C) = 3\{3[S^2+(S+1)^2]/10S^2(S+1)^2\}^{1/3}[g\mu_B H_0/J(0)]^{2/3},$$

$$\nu_\perp(H_0, T_C) = \nu_\parallel/3. \qquad (71)$$

T_1 can be calculated by using the above expressions and the result is

$$1/T_1 = (1/T_{1\infty})(zI_0\gamma_+)^{-1}N^{-1}\sum_k \frac{1-[J(k)/J(0)]}{\{\delta+\nu_\perp+1-[J(k)/J(0)]\}^2[\zeta^2+\{1-[J(k)/J(0)]\}^2]}$$

with
$$\qquad (72)$$

$$\eta_+ = (1/2)\{(1+\delta+\nu_{\parallel})I_{\delta+\nu_{\parallel}} + (1+\delta+\nu_{\perp})I_{\delta+\nu_{\perp}}\} - 1,$$

and

$$\zeta = S_0 \hbar / \sqrt{\pi} \langle \tau_k^+ \rangle k_B T \eta_+ . \tag{73}$$

Since ν's are of the order of S_0^2, we see that for $\delta > \zeta$ the expressions (63) and (66) hold, i.e. the effect of the external field is unimportant. For smaller values of δ, $1/T_1$ levels off and for $\delta \to 0$ or $T \to T_C$ we get

$$(1/T_1)_{Tc} = (1/T_{1\infty})\,[\sqrt{z}\,(v_0/a^3)/4\sqrt{2}\,\pi I_0 \eta_+]\zeta^{-3/2} .$$

From this expression we may say that when $[g\mu_B H_0/J(0)]$ is larger than $\sim 10^{-2}$ no anomalous increase of the relaxation rate near T_C is expected.

The line width may be given by

$$1/T_2 = (1/2T_2') + (1/2T_1),$$

with

$$1/T_2' = (1/T_{1\infty})\,(\sqrt{z}\,/8\pi I_0 \eta_0)\,(\delta + \nu_{\parallel})^{-3/2}. \tag{74}$$

The line width, therefore, is expected to continue to increase at the temperature range $\zeta > \delta > \nu_{\parallel}$ as temperature is lowered.

The effect of the anisotropy energy is to shift the Curie point. If we define $T_{\parallel}$ and $T_{\perp}$ by the temperatures where $\chi_{\parallel}(0)$ and $\chi_{\perp}(0)$ diverge, respectively, the shifts in $T_{\parallel}$ and $T_{\perp}$ due to the anisotropy energy are of the order of $\sim E_{ans}^2/J(0)$. $1/T_1$ and $1/T_2$ may approximately be expressed by replacing δ in (72) and (74) with $(T-T_{\perp})/T_{\perp}$ and $(T-T_{\parallel})/T_{\parallel}$, respectively.

(b) Antiferromagnets

In an antiferromagnet the effect of the external magnetic field is mainly to shift the Néel temperature. Under the external magnetic field H_0 we shall define $T_{\parallel}$ and $T_{\perp}$ by the temperatures where the susceptibilities $\chi_{\parallel}(\boldsymbol{K}_0)$ and $\chi_{\perp}(\boldsymbol{K}_0)$ parallel and perpendicular to the external field diverge, respectively. After calculation we get

$$\nu_{\parallel} = (T_N - T_{\parallel})/T_N = \{9[S^2 + (S+1)^2]/40S^2(S+1)^2\}\,[g\mu_B H_0/J(\boldsymbol{K}_0)]^2,$$

$$\nu_{\perp} = (T_N - T_{\perp})/T_N = \nu_{\parallel}/3. \tag{75}$$

The susceptibilities $\chi_{\parallel}(\boldsymbol{k})$ and $\chi_{\perp}(\boldsymbol{k})$ for general $\boldsymbol{k}$ are given by replacing $(T-T_N)/T_N$ in (20) by $\delta + \nu_{\parallel}$ and $\delta + \nu_{\perp}$, respectively. The expressions for the relaxation times are

$$1/T_1 = (1/T_{1\infty})\,(\sqrt{z}\,/16\pi I_0(I_0-1))\,\delta_{\perp}^{-1/2},$$

$$1/T_2 = (1/T_{1\infty})\,(\sqrt{z}\,/16\pi I_0(I_0-1))\,(\delta_{\perp}^{-1/2} + \delta_{\parallel}^{-1/2})/2 , \tag{76}$$

for $\delta_{\parallel}, \delta_{\perp} > [A/J(\boldsymbol{K}_0)]$, with

$$\delta_{\parallel} = (T-T_{\parallel})/T_{\parallel}, \quad \delta_{\perp} = (T-T_{\perp})/T_{\perp}.$$

The effect of the anisotropy energy may also be expressed as the shift of T_x, T_y, and T_z by amounts of $\sim E_{ani}{}^2/J(\mathbf{K}_0)$. Therefore, it can make $1/T_1$ quite anisotropic while the anisotropy in the line width will not be so significant as that in $1/T_1$. Let us consider the case of a tetragonal crystal with the easy direction along the tetragonal axis. When the external field is applied parallel and perpendicular to the tetragonal axis, the line widths are given by

$$(1/T_2)_{\parallel} = (1/T_{1\infty}) [\sqrt{z}/16\pi I_0(I_0-1)] (\delta^{-1/2} + \delta_\perp^{-1/2})/2,$$

and

$$(1/T_2)_{\perp} = (1/T_{1\infty}) [\sqrt{z}/16\pi I_0(I_0-1)] (\delta^{-1/2} + 3\delta_\perp^{-1/2})/4 , \qquad (77)$$

respectively, where $\delta_\perp = (T-T_\perp)/T_\perp$. When $T-T_N$ is small, $(1/T_2)_{\parallel}$ is about twice as large as $(1/T_2)_{\perp}$.

III. Indirect Nuclear Spin Interaction

1. General formula

We shall assume that the time in which the electronic spin system attains to its thermal equilibrium is much shorter than the characteristic time of the nuclear spin motion. This assumption may always be satisfied in magnetic crystals which are not very dilute. We can then consider the free energy of the system as a function of the nuclear spin variables (adiabatic approximation). This free energy expression can be regarded as an effective Hamiltonian for the nuclear spin system. The part of the free energy which depends on the nuclear spins can be regarded as the polarization energy of the electron spin system due to the magnetic field coming from the nuclear moments. This observation makes it simple to calculate the indirect nuclear spin coupling of bilinear form. The magnetic field produced by the nuclear moments is written as

$$\mathbf{H}(\mathbf{R}) = \sum_j \mathfrak{A}(\mathbf{R},\ \mathbf{R}_j) \cdot \mathbf{I}_j, \qquad (\text{III} \cdot 1)$$

where $\mathfrak{A}(\mathbf{R},\ \mathbf{R}_j)$ is assumed to be a symmetric tensor. The polarization energy quadratic in the magnetic field is expressed by using a generalized magnetic susceptibility of the electron spin system as follows:

$$E = -(1/2) \iint \mathbf{H}(\mathbf{R}) \cdot \chi(\mathbf{R}-\mathbf{R}') \cdot \mathbf{H}(\mathbf{R}') d\mathbf{R} d\mathbf{R}', \qquad (\text{III} \cdot 2)$$

where the susceptibility $\chi(\mathbf{R}-\mathbf{R}')$ is defined by

$$\mathbf{M}(\mathbf{R}) = \int \chi(\mathbf{R}-\mathbf{R}') \cdot \mathbf{H}(\mathbf{R}') d\mathbf{R}', \qquad (\text{III} \cdot 3)$$

$\mathbf{M}(\mathbf{R})$ being the density of magnetization at $\mathbf{R}$. From (III·1) and (III·2) the indirect nuclear spin coupling between two nuclei $\mathbf{I}_1$ and $\mathbf{I}_2$ is expressed as

$$E_{12} = -\boldsymbol{I}_1 \cdot \mathfrak{G}_{12} \cdot \boldsymbol{I}_2 \,,$$

with

$$\mathfrak{G}_{12} = \iint \mathfrak{A}(\boldsymbol{R}, \boldsymbol{R}_1) \cdot \chi(\boldsymbol{R} - \boldsymbol{R}') \cdot \mathfrak{A}(\boldsymbol{R}', \boldsymbol{R}_2) \, d\boldsymbol{R} d\boldsymbol{R}' \,. \qquad (\text{III} \cdot 4)$$

Thus the calculation of the indirect nuclear spin coupling is reduced to that of the magnetic susceptibility $\chi(\boldsymbol{R})$ whose Fourier transform $\chi(\boldsymbol{k})$ has been discussed in the preceding section II. For example, when we consider only a contact type hyperfine interaction, i.e.

$$\mathfrak{A}(\boldsymbol{R}, \boldsymbol{R}') = (A/v_0)\,\delta(\boldsymbol{R} - \boldsymbol{R}') \,,$$

the range of the interaction is simply given by $\chi(R)$:

$$E_{12} = (A/v_0)^2 \boldsymbol{I}_1 \cdot \chi(\boldsymbol{R}_1 - \boldsymbol{R}_2) \cdot \boldsymbol{I}_2 .$$

Even in more general cases the calculation is straightforward. We note that the polarization energy (III·2) can also be written as

$$E = -(1/2) \sum_{\boldsymbol{k}} \boldsymbol{H}(-\boldsymbol{k}) \cdot \chi(\boldsymbol{k}) \cdot \boldsymbol{H}(\boldsymbol{k}) . \qquad (\text{III} \cdot 5)$$

The above formulas are quite general. When applied to a free electron gas with modified hyperfine interactions, they lead to the Ruderman-Kittel formula.[22] In ferro- and antiferromagnets at low temperatures, the susceptibility $\chi(\boldsymbol{k})$ or $\chi(\boldsymbol{R})$ can be calculated by a spin wave approximation and at $0°K$ (III·4) is reduced to the Suhl-Nakamura interaction.[4],[5]

2.   Magnetic susceptibility $\chi(R)$ above the transition point

$\chi(\boldsymbol{R})$ can be calculated by taking a Fourier transform of $\chi(\boldsymbol{k})$ calculated in II–2 and II–3.

A. *Behavior at high temperatures*

At high temperatures, where α is small, the expression (22) can be expanded as follows :

$$\chi(\boldsymbol{k}) = \alpha + \mu_B^{-2} \alpha \cdot g^{-1} \cdot \mathcal{J}(\boldsymbol{k}) \cdot g^{-1} \cdot \alpha + \cdots .$$

The Fourier transform of this is

$$\chi(\boldsymbol{R}) = \alpha \delta_{R,0} + \mu_B^{-2} \alpha \cdot g^{-1} \cdot \mathcal{J}(\boldsymbol{R}) \cdot g^{-1} \cdot \alpha + \cdots .$$

We may thus conclude generally that at high temperatures the R-dependent part of the susceptibility and therefore the indirect nuclear spin coupling constant is proportional to $1/T^2$. This temperature dependence has already been obtained in certain special cases.[7]

B. *Behavior near the transition point*

(a) *Cubic crystals*

The Fourier transforms of (18) and (20) can be calculated easily for large R. Since the contribution from the region for small k is important, we may take only the first term in the expansions (19) and (21). We get

$$\chi(R) = [g^2\mu_B^2 S(S+1) v_0/36\pi\gamma k_B T_C]\exp(-\lambda R)/R, \qquad (\text{III}\cdot 6)$$

with

$$\lambda = [(T-T_C)/\gamma T_C]^{1/2}, \qquad (\text{III}\cdot 7)$$

for a ferromagnet and

$$\chi(R) = [g^2\mu_B^2 S(S+1) v_0/36\pi\gamma k_B T_N]\exp(i\boldsymbol{K}_0\cdot\boldsymbol{R})\exp(-\lambda R)/R, \qquad (\text{III}\cdot 8)$$

with

$$\lambda = [(T-T_N)/\gamma T_N]^{1/2}, \qquad (\text{III}\cdot 9)$$

for an antiferromagnet. Here v_0 is the volume per magnetic ion and γ is given by

$$\gamma = J''(\boldsymbol{k}_0)/2J(\boldsymbol{k}_0), \qquad (\text{III}\cdot 10)$$

with $\boldsymbol{k}_0=0$ for a ferromagnet and $\boldsymbol{k}_0=\boldsymbol{K}_0$ for an antiferromagnet. It is seen that $\chi(R)$ is isotropic for large R and the range of interaction increases as the temperature approaches the transition point. When only the contact type hyperfine interaction is taken into account, the nuclear spin interaction is of an exchange or dot-product type and is ferromagnetic in a ferromagnet and antiferromagnetic in an antiferromagnet.

(b) Crystals with lower symmetry

Let us consider the same simplified model as in II-2-B. A similar approximation to the above is possible in calculating the Fourier transform of (31) for large R. The second term in the denominator in (31) may be expanded as follows:

$$1 - \{[J(\boldsymbol{k}) + P_n(\boldsymbol{k})]/[J(0) + P_n(0)]\} = \sum_m^{x,y,z}\gamma_{nm}k_m^2 + \cdots, \qquad (\text{III}\cdot 11)$$

where

$$\gamma_{nm} = [\{d^2[J(\boldsymbol{k}) + P_n(\boldsymbol{k})]/dk_m^2\}/2[J(\boldsymbol{k}) + P_n(\boldsymbol{k})]]_{k=0}. \qquad (\text{III}\cdot 12)$$

$\chi(\boldsymbol{R})$ for large R is written as follows:

$$\chi_n(\boldsymbol{R}) = [\alpha_n v_0 T/12\pi\gamma_n T_n]\exp(-\lambda_n\cdot R')/R', \qquad (\text{III}\cdot 13)$$

where

$$\lambda_n = [(T-T_n)/\gamma_n T_n]^{1/2},$$

$$\gamma_n = (\gamma_{nx}\gamma_{ny}\gamma_{nz})^{1/3},$$

and

$$R_x' = (\gamma_n/\gamma_{nx}) R_x, \ R_y' = (\gamma_n/\gamma_{ny}) R_y, \ R_z' = (\gamma_n/\gamma_{nz}) R_z. \qquad \text{(III·14)}$$

In an antiferromagnet we get the same expression as (III·13) except for a factor $\exp(i\boldsymbol{K}_0 \cdot \boldsymbol{R})$.

Let us consider the case of MnF_2 as an example. It is a good approximation in this crystal to take account of only the next nearest neighbor exchange interaction.[23] With the coordinate transformation:

$$R_x = R_x', \ R_y = R_y', \ R_z = (c/a) R_z', \qquad \text{(III·15)}$$

where a and c are the lattice constants for a tetragonal unit cell, we have

$$\gamma = a^2/8,$$

and the parallel and the perpendicular susceptibilities are written as

$$\chi_{\parallel}(\boldsymbol{R}) = (2a\alpha_{\parallel} T/3\pi T_N) \exp(i\boldsymbol{K}_0 \cdot \boldsymbol{R} - \lambda_{\parallel} R')/R',$$

$$\chi_{\perp}(\boldsymbol{R}) = (2a\alpha_{\perp} T/3\pi T_{\perp}) \exp(i\boldsymbol{K}_0 \cdot \boldsymbol{R} - \lambda_{\perp} R')/R', \qquad \text{(III·16)}$$

with

$$\lambda_{\parallel} = [8(T - T_N)/T_N]^{1/2}/a, \ \lambda_{\perp} = [8(T - T_{\perp})T_{\perp}]^{1/2}/a. \qquad \text{(III·17)}$$

Since $T_N - T_{\perp} = 1.36°K$, the susceptibility is quite anisotropic near T_N. At T_N, $\lambda_{\parallel}$ vanishes while $\lambda_{\perp} = 1/2.6a$.

3. Magnetic susceptibility $\chi(\boldsymbol{R})$ below the transition point

(a) Ferromagnets

Let us consider the same case as in paragraph III–2–b (II–3–a). The easy direction of the magnetization is assumed to be the z axis. Taking Fourier transforms of (38) and (39), we can easily see that $\chi_z(\boldsymbol{R})$ tends to zero as $T \to 0$, while $\chi_x(\boldsymbol{R})$ and $\chi_y(\boldsymbol{R})$ are temperature independent. Near the Curie point $\chi_z(\boldsymbol{R})$ for large R may be expressed by a similar expression to (III·13):

$$\chi_z(\boldsymbol{R}) = (\alpha_z v_0 T/12\pi \gamma_z T_C) \exp(-\sqrt{2}\lambda_z R_z')/R_z', \qquad \text{(III·18)}$$

where

$$\lambda_z = [(T_C - T)/\gamma_z T_C]^{1/2}.$$

The screening constant below the Curie point is $\sqrt{2}$ times as large as that above the Curie point. The susceptibility components perpendicular to the easy direction is expressed for large R as

$$\chi_x(\boldsymbol{R}) = (\alpha_x v_0 T/12\pi \gamma_x T_x) \exp(-\lambda_{x0} R_x')/R_x', \qquad \text{(III·19)}$$

with

$$\lambda_{x0} = [(T_C - T_x)/\gamma_x T_x]^{1/2}, \ \text{etc.}$$

This result agrees qualitatively (except for a numerical factor) with the spin wave calculation at $0°K$. We also see that $\chi_x(\boldsymbol{R})$ and $\chi_y(\boldsymbol{R})$ are continuous

through the Curie point.

(b) Antiferromagnets

The result is quite similar to that in the case of ferromagnets, except for a factor $\exp(i\boldsymbol{K}_0 \cdot \boldsymbol{R}_j)$ which gives $+$ and $-$ signs on the $+$ and $-$ sublattice points, respectively.

4. Indirect nuclear spin interaction

The indirect nuclear spin coupling constant can be calculated from (III·4) and the results of the preceding paragraphs. The coupling constant $\mathfrak{A}^{(p)}(\boldsymbol{R}, \boldsymbol{R}_j)$ between the nuclear spin $\boldsymbol{I}_j^{(p)}$ of the p th kind and the ionic spin at $\boldsymbol{R}$ consists of two parts:

$$\mathfrak{A}^{(p)}(\boldsymbol{R}, \boldsymbol{R}_j) = \mathfrak{A}_h^{(p)}(\boldsymbol{R}, \boldsymbol{R}_j) + \mathfrak{A}_d^{(p)}(\boldsymbol{R}, \boldsymbol{R}_j), \qquad (\text{III·20})$$

where the first and the second terms are the hyperfine and dipole coupling constants, respectively. They are written as

$$\mathfrak{A}_h^{(p)}(\boldsymbol{R}, \boldsymbol{R}_j) = \sum_t \mathcal{A}_{j,t}^{(p)}\, \delta_{\boldsymbol{R}, \boldsymbol{R}_j + \boldsymbol{r}_t}, \qquad (\text{III·21})$$

$$\mathfrak{A}_d^{(p)}(\boldsymbol{R}, \boldsymbol{R}_j) = -\frac{\gamma_p \hbar}{|\boldsymbol{R} - \boldsymbol{R}_j|^3}\left\{1 - 3\frac{(\boldsymbol{R} - \boldsymbol{R}_j)(\boldsymbol{R} - \boldsymbol{R}_j)}{(\boldsymbol{R} - \boldsymbol{R}_j)^2}\right\}, \quad (\text{III·22})$$

where $\mathcal{A}_{jt}^{(p)}$ is a hyperfine coupling tensor between the electronic spin on the ion centered at $\boldsymbol{R}_j + \boldsymbol{r}_t$ and the nuclear moment at $\boldsymbol{R}_j$ and γ_p is the gyromagnetic ratio of the nuclei of the p th kind. The calculation of the coupling constant between two nuclear spins $\boldsymbol{I}_j^{(p)}$ and $\boldsymbol{I}_{j'}^{(p')}$ is carried out by using (III·4) directly or by using a method of Fourier transforms. We have

$$\mathfrak{G}_{jj'}^{pp'} = \sum_{\boldsymbol{R}, \boldsymbol{R}'} \mathfrak{A}^{(p)}(\boldsymbol{R}, \boldsymbol{R}_j) \cdot \chi(\boldsymbol{R} - \boldsymbol{R}') \cdot \mathfrak{A}^{(p')}(\boldsymbol{R}', \boldsymbol{R}_{j'}), \qquad (\text{III·23})$$

or

$$\mathfrak{G}_{jj'}^{pp'} = N^{-1}\sum_k \exp\left[i\boldsymbol{k} \cdot (\boldsymbol{R}_j - \boldsymbol{R}_{j'})\right]\mathfrak{A}^{(p)}(-\boldsymbol{k}) \cdot \chi(\boldsymbol{k}) \cdot \mathfrak{A}^{(p')}(\boldsymbol{k}). \qquad (\text{III·24})$$

The largest contribution to the coupling constant $\mathfrak{G}$ comes from the term quadratic in the hyperfine coupling constant:

$$\left[\mathfrak{G}_{12}^{pp'}\right]_{hh} = \sum_t \sum_{t'} \mathcal{A}_{1t}^{(p)} \cdot \chi(\boldsymbol{R}_1 - \boldsymbol{R}_2 + \boldsymbol{r}_t - \boldsymbol{r}_{t'}) \cdot \mathcal{A}_{2t'}^{(p')}. \qquad (\text{III·25})$$

As a simple example, when there is only one magnetic ion in a unit cell the coupling constant for the nuclear spins of two magnetic ions is written as

$$\left[\mathfrak{G}_{12}\right]_{hh} = \mathcal{A} \cdot \chi(\boldsymbol{R}_1 - \boldsymbol{R}_2) \cdot \mathcal{A}.$$

For cubic crystals $\mathcal{A}$ and χ are simply scalar and the coupling is of the exchange or dot-product type. For an orthorhombic crystal the coupling is anisotropic and the principal values of the coupling constant are

$$A_n^2 \chi_n(\boldsymbol{R}_1 - \boldsymbol{R}_2), \quad (n = 1, 2, 3).$$

In crystals like MnF_2, where a fluorine nucleus has hyperfine coupling with the three neighboring Mn^{2+} ions, we need to make detailed calculation by using (III·25).

The contribution of the next importance may be the terms bilinear in the hyperfine interaction and the dipolar interaction. The magnitude of this contribution is of the order of $\gamma\hbar/v_0A$ times the first one, i.e. roughly two orders of magnitude smaller than the first one. This term, however, is always anisotropic and may be important in cubic crystals where the first contribution gives only an isotropic coupling. This contribution is treated in the Appendix.

5. Nuclear resonance line width

The contribution of the above discussed indirect nuclear spin coupling to the NMR line width may be calculated by using conventional methods. We shall here use the moment method. Let us consider a crystal with two kinds of nuclear spins. The first kind has a spin quantum number I and the coupling constant between the nuclear spins $I_j^{(1)}$ and $I_{j'}^{(1)}$ of the first kind is denoted by

$$(\mathfrak{G}_{jj'}^{(1,2)})_{xx} = G_{xx}^{jj'}, \text{ etc.} \tag{III·26}$$

The nucleus of the second kind has a spin quantum number I' and the coupling constant between the nuclear spins $I_j^{(1)}$ of the first kind and $I_p^{(2)}$ of the second kind is written as

$$(\mathfrak{G}_{jp}^{(1,2)})_{xx} = \bar{G}_{xx}^{jp}, \text{ etc.} \tag{III·27}$$

When the magnetic field is applied in the z direction, the second moment of the NMR frequency of the first kind of nuclei is given by

$$h^2\langle\nu^2\rangle = [I(I+1)/12]\sum_{j'}(G_{xx}^{jj'}+G_{yy}^{jj'}-2G_{zz}^{jj'})^2$$

$$+ [I'(I'+1)/3]\sum_p(\bar{G}_{zz}^{jp})^2. \tag{III·28}$$

As an example let us consider a crystal with only one magnetic ion in a unit cell. We further assume that only the nuclei of the magnetic ions have magnetic moments, and take account of only the hyperfine interaction between the nuclear and the electronic spins. In a cubic crystal, where the coupling constant $\mathfrak{G}$ is a scalar, the second moment (III·28) (with $\bar{G}=0$) vanishes. This means that the main contribution to the indirect coupling which is quadratic in the hyperfine interaction do not contribute to the NMR line width. In crystals with lower symmetry, the second moment does not vanish. As we have studied in III-2-B, one component of $\chi(\boldsymbol{R})$ and therefore one component of the coupling constant $\mathfrak{G}$ for a long distance is of a screened Coulomb type near T_C and the screening constant is proportional to $|T-T_C|^{1/2}$. The second moment, therefore, diverges as the transition point is approached. We shall assume that the principal axes of $\mathcal{A}$ are the x, y and z axes and the principal values are A_x, A_y and A_z. The principal axes of $\chi(\boldsymbol{R})$ are also assumed to be the same.

The second moment (III·28) then is expressed as

$$h^2\langle\nu^2\rangle = [I(I+1)/12]\sum_{R}[A_x^2\chi_x(\boldsymbol{R}) + A_y^2\chi_y(\boldsymbol{R}) - 2A_z^2\chi_z(\boldsymbol{R})]^2, \quad \text{(III·29)}$$

for $\boldsymbol{H}_0\|z$-axis, etc.

In the following we shall consider a crystal in which magnetic ions from a body-centered tetragonal lattice as in MnF_2. We assume $\chi_x(\boldsymbol{R}) = \chi_y(\boldsymbol{R}) = \chi_\perp(\boldsymbol{R})$ and $A_x = A_y = A_\perp$. Using (III·16) and neglecting the difference between $\alpha_\|$ and $\alpha_\perp$, we get

$$h^2\langle\nu^2\rangle_{H_0\|z} = 4h^2\langle\nu^2\rangle_{H_0\perp z}$$

$$= [I(I+1)/3](2a\alpha T/3\pi T_N)^2\sum_{R}[\{A_\perp^2\exp(-\lambda_\perp R')/R'\} - \{A_\|^2\exp(-\lambda_= R')/R'\}]^2. \quad \text{(III·30)}$$

The summation in (III·30) can be evaluated, by replacing it with an integral, to be

$$h^2\langle\nu^2\rangle_{H_0\|z} = (4\sqrt{2}/27\pi)I(I+1)[g^2\mu_B^2 S(S+1)/3k_B T_C]^2$$

$$\times \{(A_\|^4/\delta) - 4A_\|^2 A_\perp^2/(\delta+\delta_\perp) + (A_\perp^4/\delta_\perp)\}, \quad \text{(III·31)}$$

with $\delta = (T-T_C)/T_C$ and $\delta_\perp = (T-T_\perp)/T_\perp$. This formula is applied both for ferro- and antiferromagnets.

The contribution from the $Mn^{55}-Mn^{55}$ indirect coupling to the second moment of the NMR line of Mn^{55} in MnF_2 can be estimated from the above formula directly. The contribution from the $F^{19}-F^{19}$ indirect coupling to the F^{19}-resonance may also be estimated approximately. In MnF_2 one fluorine nucleus has a hyperfine interaction with three neighboring Mn^{++} ions of which two belong to one sublattice and one to the other in the antiferromagnetic state. The indirect coupling of this nucleus via one Mn^{++} has an opposite sign to those via the other two Mn^{++}'s when the other nucleus is not too close to this one. For a long range interaction we can consider as if one fluorine nucleus has hyperfine interaction with only one Mn^{++} out of three neighbors. The hyperfine interactions in MnF_2 are mainly isotropic and the coupling constants are given as follows[24],[25]:

$$g\mu_B A(Mn^{++}-Mn^{55}) = 0.90\times10^{-2}cm^{-1},$$

$$g\mu_B A(Mn^{++}-F^{19}) = 0.16\times10^{-2}cm^{-1}. \quad \text{(III·32)}$$

The contribution of the $Mn^{55}-Mn^{55}$ interaction to the second moment of Mn^{55}-resonance line and the contribution of the $F^{19}-F^{19}$ interaction to the second moment of F^{19}-resonance line are estimated as

$$[\langle\nu^2\rangle_{H_0\|z}]_{Mn-Mn} = 1.54\times10^{80}I'(I'+1)[g\mu_B A(Mn^{++}-Mn^{55})]^4$$

$$+ \{(1/\delta_\|) - [4/(\delta_\|+\delta_\perp)] + (1/\delta_\perp)\},$$

$$= 1.4\times10^{10}\{(1/\delta_\|) - [4/(\delta_\|+\delta_\perp)] + (1/\delta_\perp)\}, \quad \text{(III·33)}$$

and

$$[\langle \nu^2 \rangle_{H_0 \perp z}]_{\text{F-F}} = 2 \times 1.54 \times 10^{80} I(I+1) \left[g\mu_B A(\text{Mn}^{++} - \text{F}^{19}) \right]^4$$
$$\times \left\{ (1/\delta_\parallel) - [4/(\delta_\parallel + \delta_\perp)] + (1/\delta_\perp) \right\}$$
$$= 2.4 \times 10^8 \left\{ (1/\delta_\parallel) - [4/(\delta_\parallel + \delta_\perp)] + (1/\delta_\perp) \right\}, \qquad \text{(III·34)}$$

where I' is the nuclear spin quantum number 5/2 of Mn^{55}. We took account of the fact that there are twice as many fluorine ions as manganese.

Next we shall estimate the contribution from the Mn^{55}—F^{19} interaction to the second moment of the F^{19} resonance line. As is shown in (III·28) the interaction between the different kinds of nuclear spins always gives the broadening of the resonance line. In a similar approximation to the above we estimate this contribution as

$$[\langle \nu^2 \rangle_{H_0 \parallel z}]_{\text{F-Mn}} = 1.54 \times 10^{80} I'(I'+1) \left[g^2 \mu_B{}^2 A(\text{Mn}^{++} - \text{Mn}^{55}) A(\text{Mn}^{++} - \text{F}^{19}) \right]^2 / \delta_\parallel,$$
$$= 4.5 \times 10^8 / \delta_\parallel = 3.7 \times 10^9 / (T - T_N)^{1/2},$$

and

$$[\langle \nu^2 \rangle_{H_0 \perp z}]_{\text{F-Mn}} = (\delta_\parallel / \delta_\perp) [\langle \nu^2 \rangle_{H_0 \parallel z}]_{\text{F-Mn}}. \qquad \text{(III·35)}$$

Comparing the above two contributions to the second moment of the F^{19}-resonance line, we see that the F^{19}—Mn^{55} interaction is more than two orders of magnitude as effective as the F^{19}—F^{19} interaction, so that the latter contribution is negligible. Taking square roots of (III·35), we get

$$[\langle \nu^2 \rangle_{H_0 \parallel z}]^{1/2} = 6 \times 10^4 / (T - T_N)^{1/4},$$
$$[\langle \nu^2 \rangle_{H_0 \perp z}]^{1/2} = 6 \times 10^4 / (T - T_\perp)^{1/4},$$

or

$$[\langle (\varDelta H)^2 \rangle_{H_0 \parallel z}]^{1/2} = 15 / (T - T_N)^{1/4},$$
$$[\langle (\varDelta H)^2 \rangle_{H_0 \perp z}]^{1/2} = 15 / (T - T_\perp)^{1/4}. \qquad \text{(III·36)}$$

Near the Néel temperature the line width depends on the direction of the external magnetic field strongly. We have to mention here the effect of narrowing of the F^{19}-resonance line width discussed above due to the Mn^{55}—Mn^{55} interaction. This may reduce the width by a factor 5 or so.

Below the transition point, this mechanism gives a broadening of the NMR line width which is proportional to $(T_N - T)^{-1/4}$ when the external magnetic field is applied along the easy axis. The coefficient of the temperature factor is $2^{-1/4}$ times as large as that above the transition point.

IV. Comparison with Experiment

We have seen in II and III that the contributions of the two mechanisms to the NMR line width have different temperature dependence. At temperatures close to the transition point the relaxation mechanism (hyperfine interaction

modulated by exchange) gives the temperature dependence of $[(T-T_c)/T_c]^{-3/2}$ in ferromagnets and $[(T-T_N)/T_N]^{-1/2}$ in antiferromagnets, while the indirect nuclear spin coupling gives $[(T-T_c)/T_c]^{-1/4}$ both in ferro- and antiferromagnets. The numerical coefficients of the above temperature factors in the two contributions are of the same order of magnitude. Therefore, we cannot say in general which of these two contributions is more important. Though the first mechanism becomes more and more important than the second or the indirect coupling mechanism as the temperature approaches the transition point, there may be a temperature range where the indirect coupling mechanism is of significant importance. The spin-lattice relaxation is always dominated by the first mechanism and it will be interesting to measure the difference between T_1 and T_2.

The only available experimental data for the comparison with the theory are those on F^{19}-resonance in MnF_2.[9][10] The two contributions to the line width may be written as follows:

$H_0 \| c$-axis

$$(\varDelta H)_{relax} = 0.85(\varDelta H)_\infty [(T-T_N)^{-1/2} + (T-T_\perp)^{-1/2}]/2, \qquad \text{(IV·1)}$$

$$(\varDelta H)_{indirect} = 3(T-T_N)^{-1/4} \text{ gauss}, \qquad \text{(IV·2)}$$

$H_0 \perp c$-axis

$$(\varDelta H)_{relax} = 0.85(\varDelta H)_\infty [(T-T_N)^{-1/2} + 3(T-T_\perp)^{1/2}]/4, \qquad \text{(IV·3)}$$

$$(\varDelta H)_{indirect} = 3(T-T_\perp)^{-1/4} \text{ gauss}, \qquad \text{(IV·4)}$$

where $(\varDelta H)_\infty$ is the line width arising from the hyperfine interaction modulated by exchange at high temperature limit. The observed value of $(\varDelta H)_\infty$ is 43 gauss.[24] However, a fluorine ion in MnF_2 has three neighboring Mn^{++} ions and the effect of the short range order is to give a tendency for one of them to be antiparallel with the other two, so that the effective value of $(\varDelta H)_\infty$ to put into (IV. 1) and (IV. 3) may be smaller than the above value by a factor $\sim 2 \sim 3$.[*] In the expressions (IV. 2) and (IV. 4) the narrowing effect due to the Mn^{55}—Mn^{55} indirect coupling was taken into account. Since the coefficients in (IV. 1) and (IV. 3) are about one order of magnitude larger than those in (IV. 2) and (IV. 4), we may say that the indirect coupling mechanism is relatively unimportant as compared with the relaxation mechanism in the broadening of F^{19}-resonance in MnF_2.

Heller and Benedek[9] made analysis of their data by using the following empirical formula:

$$\varDelta H(T) = [K/(T-T_N)^p] + \alpha(T-T_N) + \varDelta H_0,$$

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[*] As a matter of fact the decrease of the line width in a rather high temperature range as temperature is lowered[24] may be explained by this effect of the short range order. A detailed calculation by using the present theory may be possible though we will not work it out here.

above the Néel point. The numerical values of the coefficients were determined as follows:

$$\alpha = 0.1 \text{ gauss/degree},$$

$$p = 0.85, \quad K = 9.9 \text{ gauss deg}^p, \quad \Delta H_0 = 20.2 \text{ gauss}, \text{ for } H_0 \| c,$$

$$p = 0.95, \quad K = 3\cdot0 \text{ gauss deg}^p, \quad \Delta H_0 = 19.5 \text{ gauss}, \text{ for } H_0 \| a.$$

Below the Néel point they obtained

$$\Delta\nu = K(T_N - T)^{-p},$$

with

$$K = 500 \text{ kc/sec}, \quad p = 0.53, \text{ for } H_0 \| c.$$

Baker, Lourens and Stevenson[10] obtained $(T - T_N)^{-1/3}$ dependence above T_N. The theoretical values (IV. 1) and (IV. 3) give right orders of magnitudes and qualitatively right dependence on the direction of the external magnetic field of the NMR line width. The theoretical temperature dependence gives an asymptotic form which diverges as temperature approaches the transition point in agreement with the data of Heller and Benedek and that of Baker et al. The theoretical temperature dependence, however, seems to be a little weaker than the Heller and Benedek data though weaker dependence than the latter has been reported by Baker et al. It may not be so surprising even if the theoretical temperature dependence does not give an excellent agreement with the experimental data, since in our theory the effect of the short range order may not be taken into account sufficiently. It can easily be seen that the use of Elliott and Marshall's result[18] for the space correlation functions instead of the molecular field results will not alter the asymptotic form of the temperature dependence of the relaxation times. We might need a better approximation particularly near the transition point. We might also say that at present the experimental data are rather scanty to make a full test of the present theory. Future experiments on a variety of crystals are expected.

Acknowledgments

Appendix

Let us consider here the effect of the dipole interaction between the nuclear and electronic spins on the indirect nuclear spin interaction in cubic ferro- and antiferromagnets.

(a) *Ferromagnets*

Let us for brevity consider the case where only one kind of nuclei (transition element nuclei) have magnetic moments. The hyperfine coupling constant is isotropic and we have

$$\mathfrak{A}(\boldsymbol{k}) = A + D[1 - (3/k^2)\boldsymbol{k}\boldsymbol{k}], \qquad (A\cdot 1)$$

where

$$D = 4\pi\gamma\hbar/3v_0, \qquad (A\cdot 2)$$

v_0 and γ being the volume per magnetic ion and the nuclear gyromagnetic ratio, respectively. The second term of $(A\cdot 1)$ is the Fourier transform of the dipole interaction tensor calculated approximately by replacing a summation over the lattice points with an integral over infinite space. This approximation is good for small k. In antiferromagnets where $\mathfrak{A}(\boldsymbol{K}_0)$ is important, $(A\cdot 1)$ is, of course, not a good approximation. From $(A\cdot 1)$ and $(III\cdot 24)$ we get

$$\mathfrak{G}_{12} = A^2\chi(\boldsymbol{R}) + (2AD/N)\sum_{\boldsymbol{k}}\exp(i\boldsymbol{k}\cdot\boldsymbol{R})\,\chi(\boldsymbol{k})\,[1 - (3/k^2)\boldsymbol{k}\boldsymbol{k}]$$

$$+ (D^2/N)\sum_{\boldsymbol{k}}\exp(i\boldsymbol{k}\cdot\boldsymbol{R})\,\chi(\boldsymbol{k})\,\{2 - [1 - (3/k^2)\boldsymbol{k}\boldsymbol{k}]\}, \qquad (A\cdot 3)$$

where

$$\boldsymbol{R} = \boldsymbol{R}_1 - \boldsymbol{R}_2.$$

In cubic ferromagnets $\chi(\boldsymbol{k})$ for small k is a function of $k = |\boldsymbol{k}|$ as was shown in II–2–A. Inserting (18) and (19) into $(A\cdot 3)$, we get for large R

$$\mathfrak{G}_{12} = (A^2 + 2D^2)\chi(R) + (2AD - D^2)F(R)\,[1 - (3/R^2)\boldsymbol{R}\boldsymbol{R}], \qquad (A\cdot 4)$$

with

$$F(R) = -(v_0\alpha T/4\pi\gamma T_C R)[(3/\lambda^2 R^2)\{1 - \exp(-\lambda R)\} - (3/\lambda R)\exp(-\lambda R) - \exp(-\lambda R)],$$
$$\qquad (A\cdot 5)$$

where $\chi(R)$ is given by $(III\cdot 6)$. We see that the first term of $(A\cdot 4)$ gives an isotropic or dot-product type interaction while the second term gives the dipolar type interaction with the R-dependence given by $(A\cdot 5)$. We note that both $F(R)$ and $\chi(R)$ tend to $1/R$ as the temperature approaches the Curie point.

(b) *Antiferromagnets*

The expression $(III\cdot 24)$ for the indirect nuclear spin coupling constant will be evaluated here for an antiferromagnet. In the summation in $(III\cdot 24)$ the contribution from the part of the $\boldsymbol{k}$ space near $\boldsymbol{K}_0$, the antiferromagnetic vector, is important. Expanding $\mathfrak{A}_d(\boldsymbol{k})$ around $\boldsymbol{K}_0$, we have

$$\mathfrak{A}_d(\boldsymbol{k}) = \mathfrak{A}_d(\boldsymbol{K}_0) + 0(\kappa^2), \quad \boldsymbol{\kappa} = \boldsymbol{k} - \boldsymbol{K}_0.$$

The second term is of more than the second order in κ and gives the indirect nuclear spin coupling of shorter range than the first term. Let us for brevity neglect the second term. The coupling constant then is expressed in a simple

form as follows:

$$\mathfrak{G}_{12} = [A + \mathfrak{A}_d(\boldsymbol{K}_0)] \cdot \chi(\boldsymbol{R}) \cdot [A + \mathfrak{A}_d(\boldsymbol{K}_0)]. \tag{A·6}$$

It should be noted that if the crystal has a high symmetry and there are more than one equivalent $\boldsymbol{K}_0$'s, we have to sum up the contributions from all the $\boldsymbol{K}_0$'s in (A·6). Let us first consider a simple cubic lattice consisting of magnetic ions. The antiferromagnetic spin arrangement in this case is given by $\boldsymbol{K}_0 = (\pi/a, \pi/a, \pi/a)$ where a is the lattice constant. In this case $\mathfrak{A}_d(\boldsymbol{K}_0) = 0$ and there is no dipolar contribution to the long range indirect nuclear spin coupling. The same is true for a body-centered cubic lattice with $\boldsymbol{K}_0 = (0, 0, 2\pi/a)$. For a face-centered cubic lattice we have several possible spin arrangements in the anti-ferromagnetic state. When the spin arrangement below T_N has cubic symmetry, the dipolar contribution to the long range indirect nuclear spin coupling vanishes. Let us consider the case where the spin arrangement below T_N has trigonal symmetry. There are four equivalent $\boldsymbol{K}_0$'s:

$$(a/\pi)\boldsymbol{K}_{01} = (1, 1, 1), \quad (a/\pi)\boldsymbol{K}_{02} = (-1, 1, 1),$$

$$(a/\pi)\boldsymbol{K}_{03} = (1, -1, 1), \quad (a/\pi)\boldsymbol{K}_{04} = (1, 1, -1). \tag{A·7}$$

These vectors of course represent four different spin arrangements. From Cohen-Keffer's table[26] we get

$$\mathfrak{A}_d(\boldsymbol{K}_{0\nu}) = -(3·615\gamma\hbar/v_0)[(3/|\boldsymbol{K}_{0\nu}|^2)\boldsymbol{K}_{0\nu}\boldsymbol{K}_{0\nu} - 1]. \tag{A·8}$$

Assuming that $\chi(\boldsymbol{K}_{0\nu} + \boldsymbol{\kappa})$ is a function of only $\kappa = |\boldsymbol{\kappa}|$, the coupling constant is given by

$$\mathfrak{G}_{12} = \sum_{\nu} \exp(i\boldsymbol{K}_{0\nu} \cdot \boldsymbol{R}) \chi_0(R)[A + \mathfrak{A}_d(\boldsymbol{K}_{0\nu})] \cdot [A + \mathfrak{A}_d(\boldsymbol{K}_{0\nu})], \tag{A·9}$$

where

$$\chi_0(R) = [g^2\mu_B^2 S(S+1)v_0/36\pi\gamma k_B T_C]\exp(-\lambda R)/R,$$

with

$$\lambda = [(T - T_C)/\gamma T_C]^{1/2}.$$

Now we shall take the three fundamental vectors which define the unit cell of a face-centered cubic lattice as follows:

$$\boldsymbol{a}_1 = (a/2, a/2, 0), \quad \boldsymbol{a}_2 = (0, a/2, a/2), \quad \boldsymbol{a}_3 = (a/2, 0, a/2). \tag{A·10}$$

When a vector $\boldsymbol{R} = \boldsymbol{R}_1 - \boldsymbol{R}_2$ is expressed as

$$\boldsymbol{R} = n_1\boldsymbol{a}_1 + n_2\boldsymbol{a}_2 + n_3\boldsymbol{a}_3,$$

the indirect nuclear spin coupling constant is given as follows:

$$\mathfrak{G}_{12} = [A^2 + 2(3·615\gamma\hbar/v_0)^2]\chi_0(R)(\exp i\pi n_1 + \exp i\pi n_2)(1 + \exp i\pi(n_2 + n_3))$$

$$+ [2A(-3.615\gamma\hbar/v_0) + (3.615\gamma\hbar/v_0)^2]\chi_0(R)$$

$$\times \left[\, (\exp i\pi n_1 - \exp i\pi n_2) \, \{1 + \exp i\pi \, (n_2 + n_3)\} \, (\hat{x}\hat{y} + \hat{y}\hat{x}) \right.$$

$$+ (\exp i\pi n_2 - \exp i\pi n_3) \, \{1 + \exp i\pi \, (n_3 + n_1)\} \, (\hat{y}\hat{z} + \hat{z}\hat{y})$$

$$\left. + (\exp i\pi n_3 - \exp i\pi n_1) \, \{1 + \exp i\pi \, (n_1 + n_2)\} \, (\hat{z}\hat{x} + \hat{x}\hat{x}) \right], \qquad (A \cdot 11)$$

where $\hat{x}, \hat{y}, \hat{z}$ are unit vectors in the x, y, z directions, respectively.

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