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Theoretical Study of Nuclear-Spin–Lattice Relaxation via Paramagnetic Centers

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The effect of paramagnetic impurities with local moments on the nuclear-spin–lattice relaxation is studied by using the method of Blume and Hubbard. An average over random impurities is taken on the equations of motion for nuclear and electron spins in the low-concentration limit. An integral equation for the electron-spin correlation function is obtained and solved self-consistently. The correlation function behaves like $\exp[-(t/\Gamma_1)^2]$ for small t, $\exp[-(t/\Gamma_2)]$ for intermediate t, and $\exp[-(t/\Gamma_3)^{1/2}]$ for large t. The nuclear-spin correlation function is calculated from the electron-spin correlation function. The dependence of the spin-lattice relaxation time on the concentration of impurities, magnetic field; and temperature is obtained. Our calculations are discussed in terms of results obtained from the phenomenological approach.

I. INTRODUCTION

In the study of nuclear-spin-lattice relaxation in a metal, the magnetization $M^z(t)$ is observed to approach the equilibrium value as $\exp[-(t/\tau)^{1/2}]$ in the diffusionless limit.[1–4] This type of relaxation is primarily caused by the presence of paramagnetic impurities. The study of the concentration c, magnetic field H_0, and temperature T dependence of the relaxation time τ is very interesting, but the contribution of the diffusive motion of the nuclear spins to the relaxation, which dominates the large-t behavior of $M^z(t)$, makes such an analysis of τ difficult.[2,5] Recent experiments[4] have overcome this difficulty and a theoretical analysis of $M^z(t)$ would be useful.

In the phenomenological explanation of the $\exp[-(t/\tau)^{1/2}]$ dependence of $M^z(t)$, a position-dependent spin-lattice relaxation time $T_1(r)$ is introduced in the Bloch equation and an average on $T_1(r)$ is taken over all impurities. There are several undesirable features in this approach. Firstly, it is not clear that the $\exp[-(t/\tau)^{1/2}]$ dependence is due to the approximation in the averaging procedure or to the Bloch equation which is valid only in the long-time limit. Secondly, $T_1(r)$ is not a well-defined quantity. If $T_1(r)$ is interpreted as T_1 of a nuclear spin at a distance r from an impurity, then the theory should predict $M^z(t)$ as a superposition of several functions $\exp[-t/T_1(i)]$, where all of the $T_1(i)$ are different.

Blume and Hubbard[6] have used the Heisenberg model to study the spin-spin correlation function from a first-principles basis. We will apply their method to a nuclear-spin system interacting with electron spins through a dipole-dipole (d-d) interaction with proper consideration of the average over random impurities. The electron spins interact through a Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction. Both the d-d and RKKY interactions behave like $1/r^3$, and it is this spatial dependence that is responsible for the time dependence of $M^z(t)$. The Blume-Hubbard formalism[6] and the average over impurities are given in Secs. II and III. New features in our calculation and a discussion of the results of McHenry, Silbernagel, and Wernick[4] are given in Sec. IV.

II. GENERAL FORMALISM

The system under consideration consists of nuclear spins $\vec{I}$ and electron spins $\vec{S}$ localized at positions $\vec{r}_i$ and $\vec{r}_j$, respectively, and coupled through a standard d-d interaction,[7]

$$H_{dd}=\sum_{i,j}\frac{\gamma_I\gamma_S}{r_{ij}^3}\left(\vec{I}_i\cdot\vec{S}_j-\frac{3(\vec{I}_i\cdot\vec{r}_{ij})(\vec{S}_j\cdot\vec{r}_{ij})}{r_{ij}^2}\right), \tag{1}$$

where $r_{ij}=|\vec{r}_i-\vec{r}_j|$ and $\gamma_I I$ and $\gamma_S S$ are the magnetic moments of $\vec{I}$ and $\vec{S}$. The magnetic energy is

$$H^z=\omega_I\sum_i I_i^z+\omega_S\sum_j S_j^z, \tag{2}$$

where $\omega_I=-\gamma_I H_0$ and $\omega_S=-\gamma_S H_0$. The magnetic energy can be eliminated from the equations of motion by transforming to a rotating frame of reference, namely, $I^\pm=I^x\pm iI^y$, and $S^\pm=S^x\pm iS^y$ are transformed to $I^\pm(t)e^{\pm i\omega_I t}$ and $S^\pm(t)e^{\pm i\omega_S t}$. The equation of motion for $\vec{I}$, the nuclear spin at r_i, is

$$\frac{d}{dt}I^\alpha(t)=i[H_{dd},I^\alpha(t)]$$

$$=\sum_j\frac{\gamma_I\gamma_S}{r_j^3}\epsilon^{\alpha\beta\gamma}\left(S_j^\beta I^\gamma-\frac{3S_j^\delta r_j^\delta r_j^\beta I^\gamma}{r_j^2}\right), \tag{3}$$

where $\vec{r}_{ij}$ has been abbreviated to $\vec{r}_j$ and a dummy-index convention has been used. In this convention the commutation relation for spins has the form $[I^\alpha, I^\beta]=i\epsilon^{\alpha\beta\gamma}I^\gamma$. The z components of $\vec{I}$ and $\vec{S}$ approach nonzero equilibrium values in the limit as $t\to\infty$. We redefine these components as $I^z(t)-\langle I^z\rangle$

and $S^z(t) - \langle S^z \rangle$, where $\langle\ \rangle$ denotes the thermodynamical-ensemble average, in order that the ensemble averages of the redefined components approach zero as $t \to \infty$.

We are interested in calculating the measured quantity $\delta I^\alpha(t)$, the relaxation function, which is defined by[8]

$$\delta I^\alpha(t) = \lim_{\epsilon \to 0} i \int_{-\infty}^{0} dt' \, [I^\alpha(t), A^z(t')] e^{+\epsilon t'} , \tag{4}$$

where $A^z(t)$ is the external disturbance that prepares the spins for the relaxation. In our problem $A^z(t) = h e^{i\omega t} I^z(t)$, where h and ω are the strength and frequency of the field. Equations (3) and (4) may be combined to give an equation of motion for $\delta I^\alpha(t)$:

$$\delta \dot{I}^\alpha(t) = \sum_j \frac{\gamma_I \gamma_S}{r_j^3} \left[\left(\epsilon^{\alpha z \gamma} \langle S_j^z \rangle - 3\epsilon^{\alpha\beta\gamma} \frac{\langle S_j^z \rangle r_j^z r_j^\beta}{r_j^2} \right) \delta I^\gamma + \left(\epsilon^{\alpha\beta\gamma} S_j^\beta - 3\epsilon^{\alpha\beta\gamma} \frac{S_j^\delta r_j^\delta r_j^\beta}{r_j^2} \right) \delta I^\gamma + \left(\epsilon^{\alpha\beta\gamma} \delta S_j^\beta(I) - \frac{3\epsilon^{\alpha\beta\gamma} \delta S_j^\delta(I) r_j^\delta r_j^\beta}{r_j^2} \right) I^\gamma \right] , \tag{5}$$

where $\delta S_j^\beta(I)$ is given by Eq. (4) with $I^\alpha(t)$ replaced by S_j^β.

Equation (5) can be rewritten as an operator equation

$$\delta \dot{I}(t) = i [h_0^* \times \delta I(t) + h_1^*(t) \times \delta I(t)] , \tag{6}$$

where h_0^* and h_1^* are the first and second terms in Eq. (5). The third term is neglected for reasons described in Appendix A. The formal solution of Eq. (6) is[6]

$$\delta I^\alpha(t) = \left[\exp_+ i \int_0^t h^*(t') dt' \, \delta I(0)\right]^\alpha , \tag{7}$$

where $h^* = h_0^* + h_1^*$ and $\exp_+$ denotes the time ordering of terms in the exponential. It follows that the normalized relaxation function is given by

$$G(t) = \langle\langle \delta I^z(t) \rangle\rangle \equiv \frac{\langle \delta I^z(t) \rangle}{\langle \delta I^z(0) \rangle} , \tag{8}$$

where $G(0) = 1$. The cumulant expansion of $\delta I(t)$ results in

$$G(t) = \exp\left\{ -\tfrac{1}{2} \int_0^t \int_0^t dt_1 \, dt_2 \, \langle\langle [h_1^*(t_1) h_1^*(t_2)]_+ \rangle\rangle_c \right\} , \tag{9}$$

where $\langle\langle\ \rangle\rangle_c$ denotes the cumulant expansion of the operator inside the brackets and subscript + means the time-ordered product is taken. In Eq. (9) we have used $\langle\langle h_0^* \rangle\rangle_c = \langle\langle h_1^* \rangle\rangle_c = 0$ and have retained only the first nonzero term in the expansion.[9] The integrand in Eq. (9) may be written

$$\begin{aligned} \langle\langle [h_1^*(t_1) h_1^*(t_2)]_+ \rangle\rangle_c &= \omega_D^2 \sum_j \left(\frac{a}{r_j}\right)^6 \left(\epsilon^{z\beta\lambda} - 3\epsilon^{z\delta'\lambda} \frac{r_j^{\delta'} r_j^\beta}{r_j^2} \right) \times \left(\epsilon^{\lambda\beta z} - 3\epsilon^{\lambda\delta z} \frac{r_j^\delta r_j^\beta}{r_j^2} \right) \langle S_j^\beta(t_1) S_j^\beta(t_2) \rangle_+ \\ &\equiv \omega_D^2 \sum_j \langle H_j(t_1) H_j(t_2) \rangle_+ , \end{aligned} \tag{10}$$

where $\omega_D = \gamma_I \gamma_S / a^3$ is the *d*-*d* interaction strength for two spins a distance a apart and a is the nearest-neighbor distance. The quantity $H_j(t_1) H_j(t_2)$ may be written in a more conventional form,[10]

$$\begin{aligned} H_j(t_1) H_j(t_2) = \frac{a^6}{r_j^6} \Big\{ &\tfrac{9}{4} |F_2|^2 \tfrac{1}{2} [S_j^+(t_1) S_j^-(t_2) e^{i\omega_S(t_1 - t_2)} + S_j^-(t_1) S_j^+(t_2) e^{-i\omega_S(t_1 - t_2)}] + 9 |F_1|^2 S_j^z(t_1) S_j^z(t_2) \\ &+ \tfrac{1}{4} |F_0|^2 \tfrac{1}{2} [S_j^+(t_1) S_j^-(t_2) e^{i\omega_S(t_1 - t_2)} + S_j^-(t_1) S_j^+(t_2) e^{-i\omega_S(t_1 - t_2)}] \Big\} , \end{aligned} \tag{11}$$

where $F_0 = 1 - 3\cos^2\theta_j$, $F_1 = \sin\theta_j \cos\theta_j e^{i\varphi_j}$, and $F_2 = \sin^2\theta_j e^{2i\varphi_j}$. In Eq. (11), we have neglected ω_I since $\omega_I / \omega_S \ll 1$. We should also point out that r_j, θ_j, and φ_j are independent of time because diffusion is neglected. Our final result for the normalized relaxation function is

$$G(t) = \exp\left(-\tfrac{1}{2} \omega_D^2 \int_0^t \int_0^t dt_2 \, dt_1 \sum_j \langle H_j(t_1) H_j(t_2) \rangle \right) . \tag{12}$$

The relaxation function for the electron spins is calculated by the same method. The electron spins are assumed to be coupled through the RKKY interaction

$$H_{\text{RKKY}} = -\tfrac{1}{2} J \sum_{i,j} \left(\frac{a}{r_{ij}}\right)^3 \vec{S}_i \cdot \vec{S}_j , \tag{13}$$

where $J \approx \frac{1}{10} E_F J_0^2 N(0)^2$ with E_F, J_0, and $N(0)$ being the Fermi energy, strength of the impurity-conduction-electron-spin interaction, and density of states at the Fermi level, respectively. Values of these parameters for the $\text{La}_{1-c}\text{Gd}_c\text{Al}_2$ system are given in Ref. 4. The result is $J \approx 1$ °K.

If we denote $\langle \delta S^z(t) \rangle / \langle \delta S^z(0) \rangle$ by $\overline{G}(t)$, then[6]

$$\overline{G}(t) = \exp\left(-\tfrac{1}{2} J^2 \int_0^t \int_0^t dt_1 \, dt_2 \sum_j \langle \overline{H}_j(t_1) \overline{H}_j(t_2) \rangle_+ \right) , \tag{14}$$

where

$$\overline{H}_j(t_1) \overline{H}_j(t_2) = \frac{a^6}{r_j^6} S^+(t_1) S^-(t_2) . \tag{15}$$

We summarize here the approximations that have been used to derive Eqs. (12) and (14). First, we have neglected the last term in Eq. (6) and have made a similar approximation in deriving Eq. (14). This approximation is discussed in Appendix A. Second, we have neglected higher-order terms in the cumulant expansion and have decoupled $h_1^*(t_1)h_1^*(t_2)$ as a sum of $H_j(t_1)H_j(t_2)$. These approximations are justified in Ref. 6 for short times. They are justified in our case for small concentrations since the neglected terms will result in higher-order terms in c.

III. IMPURITY AVERAGE

Since the electron spins are distributed randomly throughout the system, an average of $G(t)$ and $\overline{G}(t)$ over all possible configurations of the random variable $\vec{r}_j$ has to be made. We will use the so-called cumulant average in a form which is valid for small concentrations.[10] For a random variable $O_j(\vec{r}_j)$, we may write

$$\begin{aligned}\left\langle \exp\left(-\sum_{j=1}^{N_0} O_j\right)\right\rangle_{\text{av}} &\cong \prod_{j=1}^{N_0} \langle e^{-O_j}\rangle_{\text{av}} \\ &= \prod_{j=1}^{N_0} \langle 1-(1-e^{-O_j})\rangle_{\text{av}} \\ &\cong [\langle 1-(1-e^{-O_j})\rangle_{\text{av}}]^{N_0} \\ &\cong [1-\textstyle\int (d^3r/Na^3)(1-e^{-O_j})]^{N_0} ,\end{aligned} \tag{16}$$

where $\langle\ \rangle_{\text{av}}$ denotes the average over the random variable $\vec{r}_j$. The first $\cong$ sign in Eq. (16) denotes the approximation that all O_j are assumed to be independent, while the second denotes that they are all identical. The third denotes that the *a priori* probability is uniform. In the limit as $N_0 \to \infty$, we have

$$\left\langle \exp\left(-\sum_{j=1}^{N_0} O_j\right)\right\rangle_{\text{av}} = \exp\left(-c\int \frac{d^3r}{a^3}\,(1-e^{-O_j})\right) , \tag{17}$$

where $c = N_0/N$.[11]

If we apply Eq. (17) to Eq. (14), we obtain

$$\overline{G}(t) = \exp\left(-c\int_{r\geq a} \frac{d^3r}{a^3}\,(1-e^{-(a/r)^6 y_1(t)})\right), \tag{18}$$

where

$$\begin{aligned} y_1(t) &= \tfrac{1}{2}J^2\int_0^t\int_0^t dt_1\,dt_2\,[S^+(t_1)S^-(t_2)]_+ \\ &= J^2 A_T(x)\int_0^t (t-t')\,\overline{G}(t')\,dt' \end{aligned} \tag{19}$$

and

$$A_T(x) = 2\,B_S(x)/x . \tag{20}$$

The function $B_S(x)$ is the Brillouin function of the order S and argument $x = \gamma_S S H_0/T$. The derivation of Eq. (19) is given in Appendix B. A similar application of Eq. (17) to Eq. (12) gives

$$G(t) = \exp\left(-c\int_{r\geq a} \frac{d^3r}{a^3}\,[1-\exp-(a/r)^6 y_2(t,\theta,\varphi)]\right), \tag{21}$$

where

$$\begin{aligned} y_2(t,\theta,\varphi) = \omega_D^2 \int_0^t dt'(t-t')\,\overline{G}(t')\,[9|F_1|^2 A_L(x) \\ +\tfrac{1}{4}(9|F_2|^2+|F_0|^2)A_T(x)\cos\omega_S t'] \end{aligned} \tag{22}$$

and

$$A_L(x) = S^2\,\frac{\partial}{\partial x}\,B_S(x) . \tag{23}$$

The volume integral in Eq. (18) can be transformed to

$$\int_{r\geq a} \frac{d^3r}{a^3}\,(1-e^{-(a/r)^6 y(t)}) = 4\pi\,U(y(t)) , \tag{24}$$

where

$$U(y) = \frac{y^{1/2}}{6}\int_0^y \frac{dy'}{y'^{3/2}}\,(1-e^{-y'}) . \tag{25}$$

The function $U(y)$ admits the following expansions which will be used for the numerical calculations in Sec. IV: for small y,

$$U(y) = \frac{1}{6}\sum_{n=0}^{\infty}\frac{(-1)^n}{(n+1)!}\,\frac{y^{n+1}}{n+\frac{1}{2}} ; \tag{26a}$$

for large y,

$$U(y) = \frac{1}{3}\left(\pi^{1/2}-1+\frac{e^{-y}R(\frac{1}{2},y)}{1+R(\frac{1}{2},y)}\right) , \tag{26b}$$

where $R(\alpha, y)$ is the continued fraction

$$R(\alpha,y) = \cfrac{\alpha}{y+\cfrac{1}{1+\cfrac{\alpha+1}{y+\cfrac{2}{1+\cfrac{\alpha+2}{y+\cfrac{3}{1+\cdots}}}}}} . \tag{26c}$$

The volume integral in Eq. (21) is more complicated because of the angular dependence of y_2. However, if we define $y_2(t)$ as the normalized angle average of $y_2(t,\theta,\varphi)$, and write $y_2(t,\theta,\varphi) = y_2(t) + \Delta(t,\theta,\varphi)$, then the volume integral in Eq. (21) may be written

$$\begin{aligned}\int_{r\geq a} \frac{d^3r}{a^3}\left[1-\exp-\left(\frac{a}{r}\right)^6 y_2(t,\theta,\varphi)\right] \\ = 4\pi\sum_{m=0}\frac{d^m U(y_2(t))}{dy_2^m}\,\frac{\overline{\Delta}^m}{m!} .\end{aligned} \tag{27}$$

We retain just the first term in Eq. (27) since the derivative of $U(y)$ for $m \geq 2$ is small. This is equivalent to approximating $y_2(t,\theta,\varphi)$ by its normalized angle average

$$y_2(t) = \omega_D^2\int_0^t dt'(t-t')\,\overline{G}(t')\,(\tfrac{6}{5}A_L+\tfrac{7}{5}A_T\cos\omega_S t') . \tag{28}$$

Our final results for $\overline{G}(t)$ and $G(t)$ are

$$\overline{G}(t) = \exp[-4\pi c\,U(y_1(t))] \tag{29}$$

and

$$G(t) = \exp[-4\pi c\, U(y_2(t))] \;. \tag{30}$$

Equation (29) is a nonlinear integral equation for the electron-spin correlation function while Eq. (30) is an expression for the nuclear-spin correlation function which can be evaluated once $\overline{G}(t)$ is known.[12]

IV. NUMERICAL CALCULATIONS AND DISCUSSION

In this section we solve the integral equation for $\overline{G}(t)$ and evaluate the integrals of $\overline{G}(t)$ that occur in the expression for $G(t)$. A reduced time variable, $u = t/\Gamma_0$, where

$$\Gamma_0 = 3/\pi^{3/2} c J A_T(x)^{1/2} \tag{31}$$

is introduced to scale the integral equation for $\overline{G}(t)$ so that $\overline{G}(u)$ is approximately independent of c over most of the range of u. The integral equation for $\overline{G}(u)$ was solved numerically by substituting a trial solution for $\overline{G}(u)$ in Eq. (19), evaluating the integrals for $y_1(t)$, by Simpson's rule, and calculating a new trial solution from Eqs. (26) and (29). The procedure was iterated until self-consistency was achieved. The iteration sequence converged to sufficient accuracy in four or five iterations.

The numerical solutions for $\overline{G}(u)$ revealed three regions with different types of time dependence. They are the short-time region (I):

$$\overline{G}_s(u) = e^{-6u^2/\pi^2 c} \;, \quad y_1 \ll 1 \;, \quad u \gg 1 \;; \tag{32}$$

the intermediate-time region (II):

$$\overline{G}_i(u) = e^{4\pi c/3} e^{-\sqrt{2}u} \;, \quad y_1 \ll 1 \;, \quad u \gg 1 \;; \tag{33}$$

and the long-time region (III):

$$\overline{G}_l(u) = e^{4\pi c/3} \exp\left[-\left(4\,\frac{\Gamma}{\Gamma_0}(u-\overline{u})\right)^{1/2}\right], \qquad y_1 \gg 1 \;, \quad u \gg 1 \tag{34}$$

where

$$\Gamma/\Gamma_0 = \int_0^\infty \overline{G}(u)\, du \tag{35}$$

and

$$\overline{u} = \Gamma/\Gamma_0 \int_0^\infty u\, \overline{G}(u)\, du \;. \tag{36}$$

The asymptotic behavior of $\overline{G}_l$ is

$$\overline{G}_l(u) \sim e^{4\pi c/3} e^{-[4(\Gamma/\Gamma_0)u]^{1/2}} \;. \tag{37}$$

The above results for the three regions were obtained by taking the indicated limits of Eqs. (19) and (26). They are compared with the numerical solution for $\overline{G}(u)$ in Fig. 1 for $c = 0.01$. The present calculations show that solutions in regions I and III are not important in the range of u where $\overline{G}(u)$ varies from 1.0 to 0.1.

Our use of a concentration-dependent reduced-time variable has obscured the actual c dependence of $\overline{G}(t)$. The decay of $\overline{G}(t)$ is proportional to ct^2, ct, and $(ct)^{1/2}$ in regions I–III, respectively. The boundary between regions I and II is $t \cong [J^2 A_T(x)]^{-1/2}$, while the boundary between regions II and III is $ct \cong [J^2 A_T(x)]^{-1/2}$.

It should be emphasized that the results in region III are probably not a good representation of the electron-spin correlation function because of the small value of $\overline{G}(t)$ in this region. As shown in Appendix A, the validity of one of the approximations used in the derivation of the integral equation [Eq. (29)] is questionable when $\overline{G}(t) \ll 1$. The questionable behavior of $\overline{G}(t)$ in region III will not adversely affect the calculation of $G(t)$ since the small magnitude of $\overline{G}(t)$ in this region will result in a correspondingly small contribution to those integrals of $\overline{G}(t)$ needed to evaluate $G(t)$.

The nuclear-spin–lattice relaxation function $G(t)$ is calculated from $\overline{G}(t)$ according to Eqs. (26), (28), and (30). The calculation may be simplified by noting that $G(t) \approx 1$ for $t \leqslant \Gamma_0$ when $\omega_D/J \ll 1$, a condition usually satisfied. In $La_{1-c}Gd_cAl_2$, $\omega_D/J \approx 10^{-3}$. Under this condition y_2 is linear in t and its magnitude determines the time dependence of $G(t)$ through function $U(y_2)$. For $y_2 \leqslant 1$ or $t \leqslant \tau_e$, then,

$$G(t) = e^{-t/\tau_e} \;, \tag{38}$$

where

$$\tau_e^{-1} = \frac{24}{5\pi^{1/2}}\,\frac{\omega_D^2}{J}\,\frac{\Gamma}{\Gamma_0}\left(A_L + \tfrac{7}{6} A_T \frac{\Gamma(\omega)}{\Gamma}\right) A_T^{-1/2} \;, \tag{39}$$

$$\frac{\Gamma(\omega)}{\Gamma} = \int_0^\infty \overline{G}(u) \cos\omega u\, du \int_0^\infty \overline{G}(u)\, du \;, \tag{40}$$

and $\omega = \omega_s \Gamma_0$; for large y_2,

$$G(t) \approx \exp - (t/\tau)^{1/2} \;, \tag{41}$$

where

$$\tau^{-1} = \frac{8\pi^{3/2}}{5}\,\frac{\omega_D^2}{J}\, c\, \frac{\Gamma}{\Gamma_0}\left(A_L + \frac{7}{6} A_T \frac{\Gamma(\omega)}{\Gamma}\right) A_T^{-1/2} \;. \tag{42}$$

The integrals of $\overline{G}(t)$ that occur in Eqs. (39) and (42) were evaluated numerically. We find that $\Gamma/\Gamma_0 = 1 + 2.16c$ to about 1% for $c \leqslant 0.2$. A plot of $\Gamma(\omega)/\Gamma$ for $c = 0.01$ as a function of $\omega = \omega_s \Gamma_0$ is shown in Fig. 2. We find that the c dependence of the Fourier transform of $G(t)$ can be scaled according to the reduced frequency $\omega = \omega_s \Gamma_0$ for small c; departures from the curve shown in Fig. 2 for $c = 0.1$ are about 5%. The decrease of $\Gamma(\omega)/\Gamma$ with increasing ω is roughly $1/(1+\omega^2)$ in accord with the exponential behavior of $\overline{G}(u)$ in the intermediate time region which dominates the Fourier transform. Our calculations show that the expressions used in the phenomenological approaches[10] are very accurate.

To summarize our numerical results, the $\exp(-t/\tau)^{1/2}$ dependence of $G(t)$ occurs in our calculation by the Blume–Hubbard method[6] because

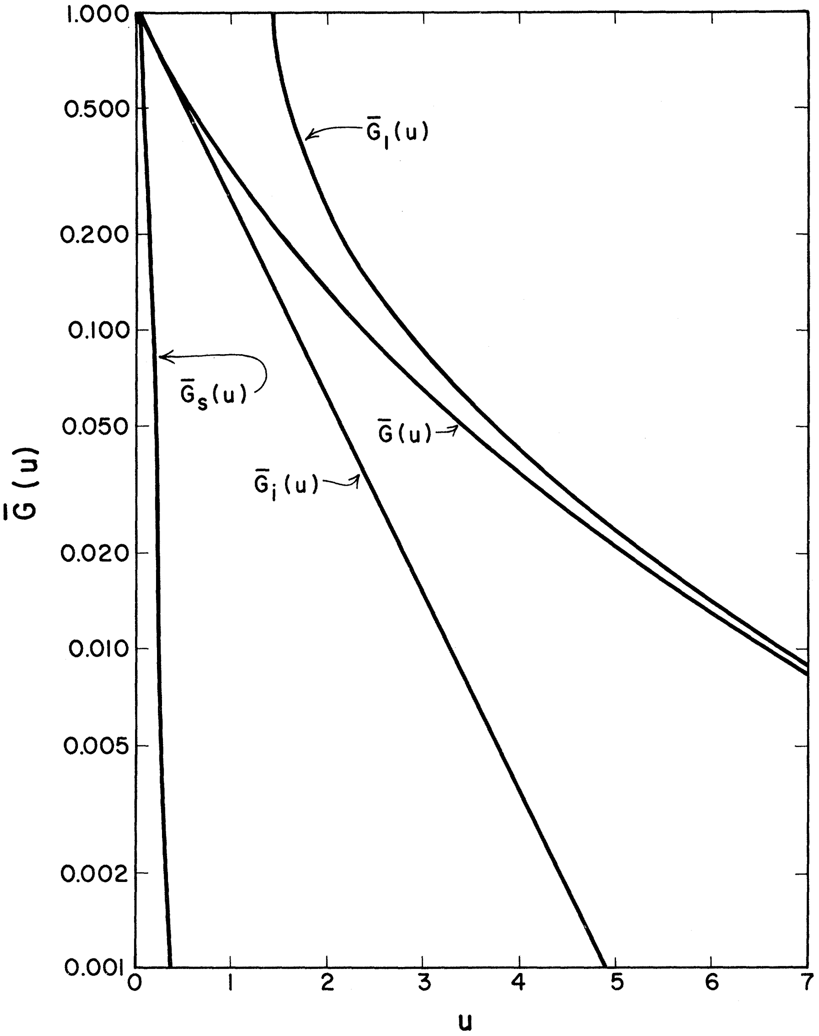

FIG. 1. Comparison of $\bar{G}(u)$ with analytic approximations in the short- ($\bar{G}_s$), intermediate- ($\bar{G}_i$), and long- ($\bar{G}_l$) time regions.

the d-d interaction has a $1/r^3$ dependence and because $\omega_D/J \ll 1$. In addition, the linear c dependence of τ in Eq. (42) is a result of $1/r^3$ dependence of RKKY interaction which also causes the exponential decay of $\bar{G}(t)$ in the intermediate-time region.

There are several experiments[1-4] where the $\exp(-t/\tau)^{1/2}$ dependence of $G(t)$ have been unambiguously identified. In the experiment by Tse and Hartmann,[2] the relaxation was observed for times corresponding to both the short-time and long-time limits. The behavior of Eq. (38), when considered as a function of $t^{1/2}$, is in qualitative agreement with the measured relaxation shown in Fig. 1 of Ref. 2, because Eq. (38) agrees with the observed result $dG(t)/dt^{1/2} \to 0$ at $t \to 0$.

The behavior of $G(t)$ at the large-t limit is studied in detail in Ref. 4. Their results can be satisfactorily summarized by an expression similar to Eq. (42), except for a factor $A_T^{1/2}$. The effect of $A_T^{1/2}$ is to reduce the change of τ as a function of x, as shown in Fig. 3. In Appendix B we discuss the origin of the factor $A_T^{1/2}$ and the possibility that it has overcorrected the expression used in Ref. 4. Our results on the second term in Eq. (42) are analogous to those of Ref. 4. When values of J and c are inserted in this term, we find it too small to explain the H_0 dependence in the experiment. We should point out, however, the second term is extremely sensitive to the numerical value of c used in the calculation.[11]

In conclusion, we have given a justification of the various time dependencies shown in Refs. 1–5.

APPENDIX A

In order to write down the formal solution for $\delta I^{\alpha}(t)$, the last term in Eq. (5) has to be neglected. An examination of the condition for the validity of this approximation is given here. Only the spin component in the z direction, S_j, is considered. We want to show that the ratio $r = \delta I_i/\delta S_j(I)$ is large at all values of t;

$$S_j(I) = (i)^2 \int_{-\infty}^{0} dt' \int_0^t dt \, \{[S_j(t) \, , \; H_{dd} + H_{\mathrm{RKKY}}], \; I_i(t')\} \, . \tag{A1}$$

We have to consider only $[S_i \, , H_{dd}]$ for r, then

$$\delta S_j(I) \lessapprox i \, \omega_D \, (a/r_{ij})^3 \int_0^t dt \int_{-\infty}^0 S_j(t) \, [I_i(t), \; I_i(t')] \, dt' \tag{A2}$$

$$\approx \omega_D \, (a/r_{ij})^3 \int_0^t dt \, S_j(t) \, \delta I_i(t) \; . \tag{A3}$$

Thus,

$$r \approx G(t) \, [\omega_D \, c \int_0^t S_j(t) \, G(t)]^{-1} \, dt \; , \tag{A4}$$

where we have used $(a/r_{ij})^3 \approx c$. Since $S_j(t)$ has the same time dependence as $\delta S_j(t)$, we can write $S_j(t) \approx \overline{G}(t) \, S_j(0)$. Then the ratio is given by

$$r \approx G(t) \, [\omega_D \, c \, S_j(0) \int_0^t G(t) \, \overline{G}(t) \, dt]^{-1}$$

$$\approx G(t) \, [\omega_D \, c \, S_j(0) \int_0^t \overline{G}(t) \, dt]^{-1} \; , \tag{A5}$$

since $G(t)$ varies much slower than $\overline{G}(t)$. For small t, $(J A_T^{1/2} t) \lessapprox 1$,

$$\int_0^t dt \, \overline{G}(t) \leqslant \frac{1}{c^{1/2} J A_T^{1/2}} \; ,$$

and

$$r \approx G(t) \, [(\omega_D / J A_T^{1/2}) \, c^{1/2} S_j(0)]^{-1} \; . \tag{A6}$$

For large t, $A_T^{1/2} c J t \geqslant 1$,

$$\int_0^t dt \, \overline{G}(t) \leqslant \frac{1}{c J A_T^{1/2}} \; ,$$

and

$$r \approx G(t) \, [(\omega_D / J A_T^{1/2}) \, S_j(0)]^{-1} \; . \tag{A7}$$

Since $\omega_D / J A_T^{1/2} \approx 10^{-3}$, r is much greater than 1 for $G(t) \geqslant 10^{-2}$. Our approximation in Eq. (5) is always valid and our result given by Eq. (42) is justified.

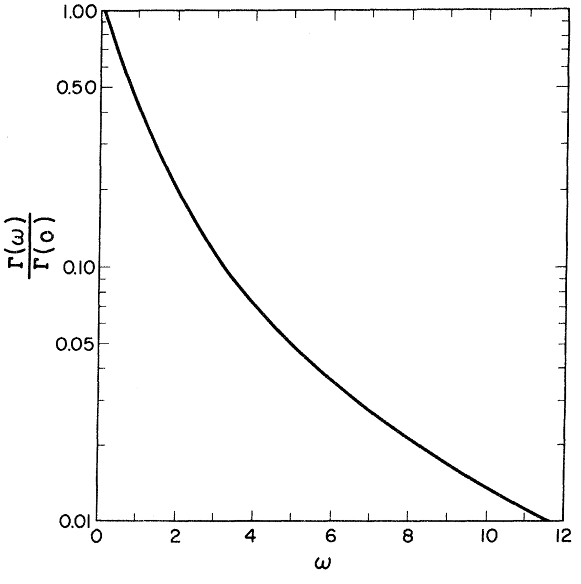

FIG. 2. Normalized Fourier transform of $\overline{G}(\omega)$ for $c = 0.01$.

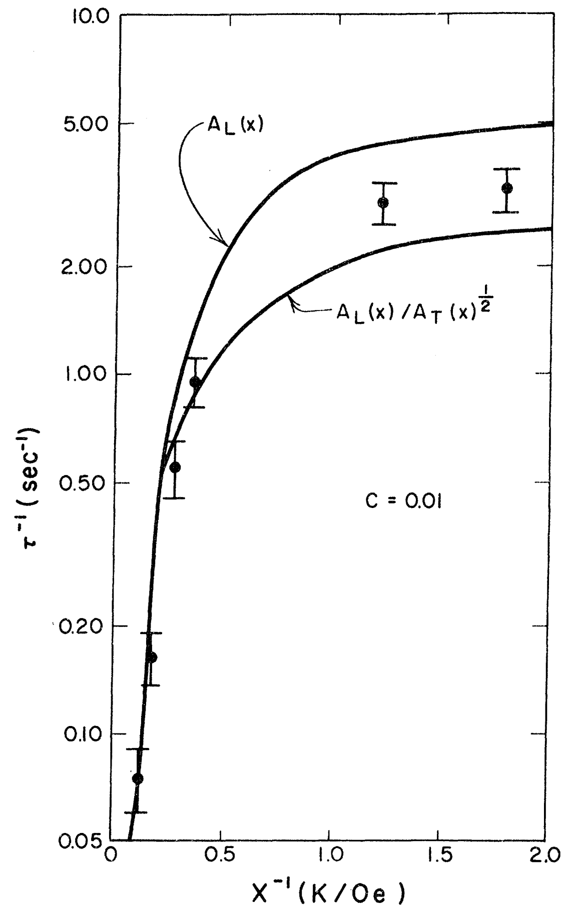

FIG. 3. Comparison of two forms for the x dependence of the relaxation time with the data of Ref. 4 for $c = 0.01$, $H_0 = 24.4$ kOe. The theoretical curves are normalized to the datum point at $x^{-1} = 0.1$.

A similar procedure can be applied to the discussion of the derivation Eq. (18), where $\delta S_j(i) = \int_{-\infty}^{0} \times \langle [S_j(t), \; S_i(t')] \rangle \, dt' \, e^{\epsilon t'}$, $i \neq j$, is neglected in comparison with

$$\delta S_i = \int_{-\infty}^{0} \langle [S_i(t) \, , \; S_i(t')] \rangle \, dt' \, e^{\epsilon t'} \; .$$

We use

$$\delta S_j(i) \approx i^2 \int_0^t dt \int_{-\infty}^{0} \langle \{ [S_j \, , H_{\mathrm{RKKY}}], S_i(t')\} \rangle \, dt' \, e^{\epsilon t'}$$

$$\approx i \, J \, (a/r_{ij})^3 \int_0^t dt \, \langle S_j(i) \int_{-\infty}^{0} [S_i(t), \; S_i(t')] \rangle \, dt' \, e^{\epsilon t'}$$

$$\approx Jc \int_0^{\infty} dt \, S_j(t) \, G(t) \, \delta S_i(0) \; . \tag{A8}$$

The ratio of δS_i and $\delta S_j(i)$ is r', where

$$r' \approx G(t) \, [S_j(0) \, c \, J \int_0^t G(t) \, dt]^{-1} \; , \tag{A9}$$

for $c J t \ll 1$, $r' \gg 1$. When $c J t \gg 1$, then

$$r' \approx G(t) \, [S_j(0) \, A_T^{1/2}]^{-1} \; , \tag{A10}$$

which seriously imposes the validity of our approximation. For the purpose of calculating $\overline{G}(t)$, we are interested only in the range that $G(t)$ is large enough to contribute to the integrals in Eq. (21) and the approximation is probably valid for this purpose. However, Eq. (A10) shows that the asymptotic behavior $G(t)$ in Eq. (37) cannot be taken seriously.

APPENDIX B

The induced magnetization $M^z(\vec{r}, t) = \gamma S^z(\vec{r}, t)$ in the presence of the external field $h(\vec{r})$ from $t = -\infty$ to 0 is[13]

$$\langle M^z(\vec{r}, t)\rangle = i\int_{-\infty}^{0} dt' \int d^3r'\, e^{\epsilon t'}\, h(\vec{r}\,') \times \langle [M^z(\vec{r}, t), M^z(\vec{r}\,', t')]\rangle$$

$$= \int \frac{d^3k}{(2\pi)^3} \int d^3r'\, h(\vec{r}\,')\, e^{i\vec{k}\cdot(\vec{r}-\vec{r}\,')} \times \int \frac{d\omega}{\pi} \frac{\chi''_{zz}(\vec{k}, \omega)}{\omega}\, e^{-i\omega(t-t')}\,, \quad (t > 0), \tag{B1}$$

where

$$\int \frac{d^3k}{(2\pi)^3} \frac{d\omega}{\pi}\, \chi''_{zz}(\vec{k}, \omega)\, e^{+i\omega(t-t')}\, e^{i\vec{k}\cdot(\vec{r}-\vec{r}\,')} = \langle [M^z(\vec{r}, t), M^z(\vec{r}\,', t')]\rangle\ .$$

Let $h(\vec{r}) = \text{const} \equiv H_0$,

$$\langle M^z(\vec{r}, 0)\rangle = H_0 \int_{-\infty}^{\infty} d\omega\, \frac{\chi''_{zz}(0, \omega)}{\pi\omega} = H_0\chi_{zz}\ ,$$

where χ_{zz} is the longitudinal static susceptibility given by

$$\chi_{zz} = \frac{\partial}{\partial H_0} \langle M^z(\vec{r}, t)\rangle\ . \tag{B2}$$

It is obvious that the Fourier transform of $\langle \delta I(\vec{r}, t)\rangle^z$ is $\chi_{zz}(\vec{r}, \omega)/\omega$ and $\langle \delta I(\vec{r}, 0)\rangle^z = \chi_{zz}$.

Define

$$\int \frac{d\omega}{\pi} M_{zz}(\vec{r}, \vec{r}\,', \omega)\, e^{-i\omega(t-t')} = \tfrac{1}{2}\langle [M^z(\vec{r}, t), M^z(\vec{r}\,', t')]_+\rangle\ ; \tag{B3}$$

then the fluctuation-dissipation theorem gives us

$$\coth(\omega/2T)\, \chi''_{zz}(\vec{r}, \vec{r}\,', \omega) = 2M_{zz}(\vec{r}, \vec{r}\,', \omega)$$

or

$$M_{zz}(\vec{r}, \vec{r}\,', t) = \tfrac{1}{2} i \frac{d}{dt}\left(\coth \frac{i}{2T} \frac{d}{dt}\right)\delta I^z(t) = T\left[\delta I^z(t) - \frac{1}{12} \frac{1}{T^2}\left(\frac{d}{dt}\right)^2 \delta I^z(t)\cdots\right]. \tag{B4}$$

The ratio of the second term to the first term is $\sim (c/10)(J^2/T^2)$ at small t, and becomes smaller as t gets larger. Substitution of the numbers $T \approx 4\,°\text{K}$, $J \approx 1\,°\text{K}$, $c \approx 0.1$ shows the ratio is indeed very small. Hence,

$$M_{zz}(\vec{r}, \vec{r}, t) = T\, \delta I^z(t) = T\, \chi_{zz}\, \overline{G}(t)\ , \tag{B5}$$

where we have neglected second terms in Eq. (B4).

When χ_{zz} is evaluated in the approximation that the spins are noninteracting, Eq. (B5) becomes

$$\tfrac{1}{2}[S_i^z(t), S_i^z(0)]_+ = S^2 \frac{\partial B(x)}{\partial x}\, \overline{G}(t)\ , \tag{B6}$$

where

$$x = \frac{S\gamma H}{T}\ ,$$

$$B(x) = \frac{2S+1}{2S} \coth \frac{2S+1}{2S}\, x - \frac{1}{2S} \coth \frac{x}{2S}\ .$$

Similarly

$$M_{+-}(\vec{r}, \vec{r}, t) = \tfrac{1}{2}\langle [M^+(\vec{r}, t)\, ,\ M^-(\vec{r}, 0)]_+\rangle = T\chi_{+-}\overline{G}(t)\ , \tag{B7}$$

where χ_{+-} is the transverse component of the static susceptibility

$$\chi_{+-} = \langle [M^+(\vec{r}, t),\ M^-(\vec{r}, t)]\rangle / H_0\ . \tag{B8}$$

Thus,

$$\tfrac{1}{2}\langle [S^+(\vec{r}, t),\ S^-(\vec{r}, t')] + [S^-(\vec{r}, t),\ S^+(\vec{r}, t')]\rangle = 2S^2 \frac{B(x)}{x}\, \overline{G}(t)\ . \tag{B9}$$

We should emphasize that an isotropic assumption is implicitly made, namely, the commutators $\langle [S^-(t), S^+(t')]\rangle$ and $\langle [S^z(t), S^z(t']\rangle$ have the same $(t - t')$ dependence. One may also make the same assumption on the anticommutators; then

$$M_{+-}(\vec{r}, \vec{r}, t) = T\, \tfrac{1}{2}\langle (S^+S^- + S^-S^+)\rangle\, \overline{G}(t) \tag{B10}$$

and

$$M_{zz}(\vec{r}, \vec{r}, t) = T\langle (S^z)^2\rangle\, \overline{G}(t)\ . \tag{B11}$$

Equation (B10) is obviously different from Eq. (B7) when x is large.[14] This problem cannot be resolved unless a set of coupled equations for M_{zz} and $M_{+-}(t)$ is solved. We use Eq. (B7) to discuss our results because it is more conventional in the literature.

An attempt was made to solve for M_{zz} and M_{+-}. Preliminary results indicate that $M_{zz}(t)$ and $M_{+-}(t)$ can be expressed as $e^{-t/\Gamma_{zz}}$ and $e^{-t/\Gamma_{+-}}$, where Γ_{zz} and Γ_{+-} are functions of A_T and A_L in the important exponential region. We find that Γ_{+-}, which should enter in Eq. (42), varies less rapidly with x than $A_T^{1/2}(x)$ as indicated in Eq. (42). Thus, the plot of $A_L(x)/A_T^{1/2}(x)$ in Fig. 3 represents too large a correction.

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Green's-Function Theory of an Induced-Moment System Containing Impurities. II. Vacancy Impurities[*]

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The bulk susceptibility of an induced-moment system containing substitutional vacancy impurities is studied in the low-impurity-concentration limit, utilizing a Green's-function method in the random-phase approximation. It is found that the variation of the inverse susceptibility with the impurity concentration is strongly temperature dependent, in contrast to the temperature-independent result predicted by the simple molecular-field theory in which the exchange interaction is merely scaled by the factor $1-c$. At low temperatures the deviation can be up to 35% for a simple cubic lattice. A further investigation shows that a refined molecular-field theory taking account of the nonuniform distribution of the magnetization in the impure crystal recovers most of the features predicted by the Green's-function theory. However, no molecular-field theory can account for the behavior of systems of small energy gap, or systems of low ordering temperature. In these systems the contribution of the collective excitations greatly alters the results at low temperatures not only quantitatively but also qualitatively.

I. INTRODUCTION

The study of the effects of impurities in an otherwise perfect crystal has been of considerable theoretical and experimental interest in recent years. In a previous paper[1] (referred to as I hereafter) we discussed the impurity modes and local susceptibilities of an induced-moment magnetic system containing a single substitutional impurity. The system was studied in the paramagnetic phase. Two singlet energy levels were assumed for all ions and explicit results were given for a simple cubic crystal lattice with nearest-neighbor-only exchange interactions. In particular, we showed that there exist two impurity modes and they are of S type. This remains true for impure induced-moment paramagnets of other geometry with only nearest-neighbor exchange interaction. As in an ordinary ferromagnet,[2] the impurity modes can become localized, appearing above the energy band and/or in the gap. Local susceptibilities on the impurity ions were also calculated and remarkable differences were found between the Green's-function results and the prediction of molecular-field theory (which ignores the collective excitations of the system).

In this paper we extend the Green's-function calculation in I to the case of vacancy impurities, that is, when the impurity ions are nonmagnetic or are actually vacancies. We still choose a two-level paramagnetic induced moment system as the host in this calculation. Instead of the local susceptibility on the impurity ion, which is zero for a vacancy impurity, we discuss the bulk susceptibility