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Correlations in Magnetic Exchange-Lattice Relaxation

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At sufficiently low temperatures, the bottleneck in magnetic relaxation can be between the exchange system and the lattice for substances with an exchange interaction of the same order of magnitude as the Zeeman interaction. We extend Griffiths' original theory by including correlations between different pairs of spins in a calculation of the exchange-lattice relaxation rate. A density-matrix approach is used in which the exchange and lattice systems are each assumed to possess a temperature. Results are restricted to temperatures for which Curie's law holds. Variation of exchange interaction with interatomic spacing is assumed to be the dominant source of relaxation, and single- and two-phonon processes are analyzed as well as atomic diffusion with a slow jumping rate. For linear chains with nearest-neighbor interactions, correlations have a marked effect on the phonon relaxation rate at temperatures well below the Debye θ. Two-phonon processes give a T^9 temperature dependence instead of the T^7 dependence found by Griffiths, and the relaxation rate for the direct process is less than that calculated by Griffiths by a factor of the order of $(\hbar J/k\theta)^2$. This could be of more than academic interest, since a number of paramagnetic materials in which exchange-lattice relaxation might be observable appear to have linear chain structures as far as magnetic properties are concerned. In three-dimensional magnetic lattices the correction to Griffiths' formula is about 20% for the two-phonon processes. If the source of lattice motion is atomic diffusion with a jumping frequency $1/\tau_c$ much less than the exchange frequency, then correlations are shown to be negligible. In this instance Garwin and Landesman's result $T_{\mathrm{EL}} \approx \tau_c$ is reestablished.

I. INTRODUCTION

At low temperatures, Zeeman energy is often most efficiently converted to lattice energy by first being transformed into exchange energy. This two-stage magnetic relaxation process, in which the exchange system acts as an intermediate reservoir, is shown schematically and discussed in Fig. 1. It has been used to explain temperature-independent relaxation times in paramagnetics with strong exchange interactions[1] and more recently has been applied[2–6] to solid He^3. The latter example is particularly interesting since in He^3 it has been possible to observe the second stage, exchange-lattice, of the relaxation process,[4–6] and thus there is renewed interest in theoretical treatments of exchange-lattice relaxation. The existing theory is due to Griffiths[7] who showed that variation of exchange interaction J with interatomic spacing couples exchange quanta to lattice phonons and thereby is an effective relaxation mechanism. Garwin and Landesman[4] have extended Griffiths' ideas to the case where J is modulated by atomic diffusion.

A major assumption of the Griffiths' theory (and the work of Garwin and Landesman) is that correlations between different pairs of spins may be ignored. Each pair of exchange-coupled spins is assumed to relax independently so that to compute relaxation of the total exchange Hamiltonian

$$\mathcal{H}_0 = \hbar \sum_{i<j} J_{ij} \mathbf{I}_i \cdot \mathbf{I}_j \tag{1}$$

it is sufficient to study the relaxation of any neighboring pair of spins $\mathbf{I}_i$ and $\mathbf{I}_j$ (it being assumed that $J_{ij} = J$, independent of i and j, if i and j are nearest neighbors and zero otherwise). In this paper, however, we are able to include correlation effects by use of a density matrix. As in Griffith's work, the exchange system is assumed to have internal equilibrium throughout the course of relaxation so that an exchange temperature may be used, and the calculation is restricted to temperatures well above the Néel point. These two simplifications enable us to treat correlations in a straightforward manner and in much the same spirit as Griffiths' method of summing transition probabilities.

We treat the three cases examined previously[4,7]: conversion of exchange energy to lattice energy by (1) single-phonon processes, (2) two-phonon processes, and (3) atomic diffusion in which the jumping frequency is

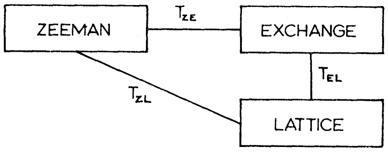

FIG. 1. Three-bath model for magnetic relaxation in substances with strong exchange interaction. At low temperatures the direct Zeeman-lattice relaxation time T_{ZL} becomes much longer than T_{ZE}, the Zeeman-exchange relaxation time, so relaxation proceeds from the Zeeman to the exchange system. If $C_{\mathrm{Z}}/T_{\mathrm{ZE}} \ll C_{\mathrm{E}}/T_{\mathrm{EL}}$ where C_{Z} and C_{E} are the respective Zeeman and exchange heat capacities, then the observed relaxation time T_1 for the longitudinal component of magnetization is T_{ZE}. But if $C_{\mathrm{Z}}/T_{\mathrm{ZE}} \gg C_{\mathrm{E}}/T_{\mathrm{EL}}$, exchange-lattice relaxation is the bottleneck and $T_1 = [(C_{\mathrm{Z}}/C_{\mathrm{E}})+1]T_{\mathrm{EL}}$. This paper is concerned with the later situation and gives a calculation of the relaxation rate $\eta = T_{\mathrm{EL}}^{-1}$.

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[1] N. Bloembergen and S. Wang, Phys. Rev. **93**, 72 (1954).

[2] H. A. Reich, Phys. Rev. **129**, 630 (1963).

[3] S. R. Hartmann, Phys. Rev. **133**, A17 (1964).

[4] R. L. Garwin and A. Landesman, Phys. Rev. **133**, A1503 (1964).

[5] R. L. Garwin and H. A. Reich, Phys. Rev. Letters **12**, 354 (1964).

[6] B. T. Beal, R. P. Giffard, J. Hatton, M. G. Richards, and P. M. Richards, Phys. Rev. Letters **12**, 393 (1964).

[7] R. B. Griffiths, Phys. Rev. **124**, 1023 (1961).

much less than J. In case (3) we show that correlations may be neglected so that the result obtained by Garwin and Landesman remains valid; but correlations can have a noticeable effect on the phonon processes. For three-dimensional lattices, the correction to Griffiths' formula is about 20%; and for linear chains the relaxation is markedly altered at temperatures well below the Debye temperature. The two-phonon processes give a T^9 instead of T^7 dependence of the relaxation rate on temperature T, and the single-phonon relaxation rate (proportional to T) is less than that calculated by Griffiths by a factor of the order of $(\hbar J/k\theta)^2$, where θ is the Debye temperature and k is Boltzmann's constant. Since the magnetic moments in a number of paramagnetic materials,[8] including organic free radicals, to which the theory was originally applied,[7] appear to form linear chains, this effect might in principle be observable at sufficiently low temperatures.

II. CALCULATION OF RELAXATION RATE FROM EQUATION OF MOTION FOR DENSITY MATRIX

Relaxation of a system with Hamiltonian $\mathcal{H}_0$ coupled to a lattice with Hamiltonian $\mathfrak{F}$ which commutes with $\mathcal{H}_0$ may be derived from the equation of motion for the density matrix ρ of the combined system in a manner described in the text by Abragam[9]:

$$\frac{d}{dt}\rho^*(t)=-\frac{1}{\hbar^2}\int_0^\infty [\mathcal{H}'(t),[\mathcal{H}'(t-\tau),\rho^*(t)]]d\tau\,, \quad (2)$$

where $\mathcal{H}'$ is the Hamiltonian which expresses coupling between $\mathcal{H}_0$ and $\mathfrak{F}$, and

$$\mathcal{H}'(t)=\exp[(i/\hbar)(\mathcal{H}_0+\mathfrak{F})t] \times\mathcal{H}'(0)\exp[(-i/\hbar)(\mathcal{H}_0+\mathfrak{F})t]\,, \quad (3)$$

$$\rho^*(t)=\exp[(i/\hbar)(\mathcal{H}_0+\mathfrak{F})t] \times\rho(t)\exp[(-i/\hbar)(\mathcal{H}_0+\mathfrak{F})t]\,. \quad (4)$$

The above equation of motion (2) treats $\mathcal{H}'$ as a perturbation, assumes that the integrand is appreciable only for times much less than t, and neglects a term in $[\mathcal{H}'(t),\rho(0)]$, which is expected to give zero on the average. For a discussion of the derivation and underlying assumptions of Eq. (2) the reader is referred to Ref. 9. It should be noted that both the system $\mathcal{H}_0$ and the lattice $\mathfrak{F}$ are treated quantum mechanically so that all time dependence of $\mathcal{H}'$ is expressed by the exponential factors appearing in (3).

To make progress with (2) we assume that each of the systems may be described by a temperature so that

$$\rho=\exp(-\beta_x\mathcal{H}_0)\exp(-\beta\mathfrak{F})/\mathrm{tr}\rho\,, \quad (5)$$

where β_x and β are $1/kT_x$ and $1/kT$, respectively, with T_x and T the respective "exchange" (or whatever $\mathcal{H}_0$ may be identified as) and lattice temperatures. The lattice heat capacity is assumed to be infinite; so the time dependence of ρ is governed by that of β_x. If we assume $\beta_x\mathcal{H}_0\ll 1$ for all matrix elements which make an appreciable contribution to the integrand in (2), then, upon multiplying both sides of (2) by $\mathcal{H}_0$ and taking a trace over the states both of $\mathcal{H}_0$ and of $\mathfrak{F}$, we obtain

$$d\beta_x/dt=\eta(\beta-\beta_x)\,, \quad (6)$$

where the relaxation rate η is given by

$$\eta=\int_0^\infty d\tau\,\mathrm{tr}(\mathcal{H}_0[\mathcal{H}'(0),[\mathcal{H}'(-\tau), \times\mathcal{H}_0\exp(-\beta\mathfrak{F})]])/\hbar^2\,\mathrm{tr}\mathcal{H}_0{}^2\exp(-\beta\mathfrak{F})\,. \quad (7)$$

In deriving (6) we have noted that $\beta_x=\beta$ in (5) is a steady-state solution[9] to (2) so that ρ may be replaced by $\rho-\rho(\beta)$ in (2), where $\rho(\beta)$ is the value of ρ for $\beta_x=\beta$. The integral in (7) is independent of t as a consequence of invariance properties of the trace. The above equation for the rate at which exchange temperature approaches lattice temperature is of the same form as derived by Hartmann[3] for Zeeman-exchange relaxation, provided $\mathcal{H}_0$ and $\mathfrak{F}$ are properly interpreted (in the case of Ref. 3, $\mathcal{H}_0$ would be the Zeeman Hamiltonian and $\mathfrak{F}$ the exchange Hamiltonian).

We now write the perturbation $\mathcal{H}'$ as

$$\mathcal{H}'(t)=\hbar\sum_{i<j}\Delta_{ij}(t)A_{ij}(t)\,, \quad (8)$$

where $\Delta_{ij}(t)$ is a function only of the lattice variables and hence

$$\Delta_{ij}(t)=\exp(i\mathfrak{F}t/\hbar)\Delta_{ij}(0)\exp(-i\mathfrak{F}t/\hbar) \quad (9)$$

and the dynamical variables of A_{ij} are all associated with $\mathcal{H}_0$, so A_{ij} commutes with $\mathfrak{F}$ and Δ_{ij}, and we have

$$A_{ij}(t)=\exp(i\mathcal{H}_0t/\hbar)A_{ij}(0)\exp(-i\mathcal{H}_0t/\hbar)\,. \quad (10)$$

Here, as in Griffiths' work, we will have

$$A_{ij}=\mathbf{I}_i\cdot\mathbf{I}_j\,, \quad (11)$$

$$\Delta_{ij}=J_{ij}(\mathbf{r}_{ij})-J_{ij}\,, \quad (12)$$

where $J_{ij}(\mathbf{r}_{ij})$ is the exchange interaction frequency between spins $\mathbf{I}_i$ and $\mathbf{I}_j$ when they are separated by a distance $\mathbf{r}_{ij}$, and J_{ij}, as in (1), means $J_{ij}(\mathbf{r}_{ij}{}^0)$ where $\mathbf{r}_{ij}{}^0$ is the equilibrium separation. If dipole-dipole interactions were to be included, we would find that $\mathcal{H}'$ can be written as a linear combination of terms[10] such as appearing in (8). Griffiths has shown that the dipole-dipole interaction makes a negligible contribution to the relaxation rate so we will not consider it in the specific cases to be treated. However, it is worth noting that results of this

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[8] D. D. Thomas, H. Keller, and H. M. McConnell, J. Chem. Phys. **39**, 2321 (1963); H. Kobayashi, T. Haseda, E. Kanda, and S. Kanda, J. Phys. Soc. Japan **18**, 349 (1963).

[9] A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University Press, New York, 1961), Chap. 8, pp. 276–289.

[10] See Ref. 9, p. 289.

section apply to dipole-dipole or any other perturbation which can be expressed in a manner similar to (8).

When (8) is inserted in (7) and the lattice part of the trace is performed, we obtain terms of the form $\langle\Delta_{ij}(0)\Delta_{kl}(-\tau)\rangle$ and $\langle\Delta_{kl}(-\tau)\Delta_{ij}(0)\rangle$ where the triangular brackets indicate a thermal equilibrium average with respect to the lattice variables:

$$\langle\mathcal{O}\rangle=\mathrm{tr}\exp(-\beta\mathcal{F})\mathcal{O}/\mathrm{tr}\exp(-\beta\mathcal{F}) \tag{13}$$

for any operator $\mathcal{O}$ which is a function of the lattice variables. In the high-temperature approximation we may take these two averages to be equal since, insofar as their contribution to the relaxation rate (7) is concerned, their difference is of the order of $\beta\mathcal{H}_0$. With this simplification, we then obtain, upon using (8) in (7)

$$\eta=\int_0^\infty \frac{B(\tau)d\tau}{\{\mathcal{H}_0{}^2\}} \tag{14}$$

where

$$B(\tau)=-\hbar^2\sum_{i<j}\sum_{k<l}\langle\Delta_{ij}(0)\Delta_{kl}(-\tau)\rangle \times\{A_{ij}(0)(d^2A_{kl}(-\tau)/d\tau^2)\} \tag{15}$$

in which the curly brackets are defined by

$$\{\mathcal{O}\}=\mathrm{tr}\mathcal{O}/\mathrm{tr}(1) \tag{16}$$

for any operator $\mathcal{O}$ which is a function of the spin variables, ($\{\mathcal{O}\}$ is the average value of $\mathcal{O}$ at infinite temperature). In deriving (14) we have made use of invariance properties of the trace together with (10) to express the commutators involving $\mathcal{H}_0$ as $d^2A_{kl}(-\tau)/d\tau^2$.

Since

$$\left|\left\{A_{ij}(0)\frac{d}{d\tau}A_{kl}(-\tau)\right\}\right|_{\tau=0}$$

is zero for the spin operators normally encountered, we may integrate (15) by parts to obtain

$$\int_0^\infty B(\tau)d\tau=-\hbar^2\sum_{i<j}\sum_{k<l}\int_0^\infty d\tau \times\left\langle\Delta_{ij}(0)\frac{d^2}{d\tau^2}\Delta_{kl}(-\tau)\right\rangle\{A_{ij}(0)A_{kl}(-\tau)\} -\hbar^2\sum_{i<j}\sum_{k<l}\left|\left\langle\Delta_{ij}(0)\frac{d}{d\tau}\Delta_{kl}(-\tau)\right\rangle\right|_{\tau=0} \times\{A_{ij}(0)A_{kl}(0)\}. \tag{17}$$

Equations (17) and (14) are particularly useful for discussing effects of correlations upon the relaxation rate. To neglect correlations is to assume that only terms for which $i=k$, $j=l$ contribute to (17). It is generally the case that

$$\{A_{ij}(0)A_{kl}(0)\}=\{A_{ij}(0)A_{ij}(0)\}\delta_{ij,kl}, \tag{18}$$

so correlations do not affect the second term on the right-hand side of (17). Thus, the question becomes one of analyzing the autocorrelation function $\{A_{ij}(0)A_{kl}(-\tau)\}$ for nonzero τ. It is instructive to consider first the conventional case of relaxation of Zeeman energy in systems for which exchange energy is much less than Zeeman energy. Then $\mathcal{H}_0$ is simply the Zeeman Hamiltonian whose eigenstates are known and $\mathcal{H}'$ is the dipole-dipole Hamiltonian which, analogously to (8), may be written[3,10] as

$$\mathcal{H}_{\mathrm{dip}}'=\hbar\sum_{M=-2}^{2}\Delta_{ij}{}^{(M)}A_{ij}{}^{(M)} \tag{19}$$

with suitable definitions for $\Delta_{ij}{}^{(M)}$ and $A_{ij}{}^{(M)}$ in terms of lattice and spin variables, respectively, and where $A_{ij}{}^{(M)}$ has matrix elements only between those eigenstates of $\mathcal{H}_0$ with energies E_m and $E_{m'}$ for which $E_m-E_{m'}=M\hbar\omega_r$ where ω_r is the angular resonance frequency. Because of this, we then have

$$\{A_{ij}{}^{(M)}(0)A_{kl}{}^{(M')}(-\tau)\} =e^{iM'\omega_r\tau}\{A_{ij}{}^{(M)}(0)A_{kl}{}^{(M')}(0)\} \tag{20}$$

which is zero unless i and j are the same spins as k and l (and also, of course, unless $M'=-M$). Thus correlations do not contribute to the relaxation rate (7) for ordinary Zeeman-lattice relaxation with negligible exchange interaction. The assumption (5) of a spin-temperature eliminates correlations at the outset; only a more detailed description[11] of the density matrix can show the effect of correlations in this case.

If, however, $\mathcal{H}_0$ contains the exchange Hamiltonian, whose eigenstates are not easily determined, we do not have simple selection rules such as in (19) and (20) for determining the time dependence of $\{A_{ij}(0)A_{kl}(-\tau)\}$. A common device in problems of this nature is to assume a gaussian dependence. In this case we would say

$$\{A_{ij}(0)A_{kl}(-\tau)\}=\{A_{ij}(0)A_{kl}(0)\}e^{-\lambda^2\tau^2} \tag{21}$$

and thus conclude, once again, that correlations have no effect since Eq. (21) says that if two pairs i, j and k, l are uncorrelated at time $\tau=0$ they remain uncorrelated for all future times. This latter statement is easily seen to be false, and we show in the next section that "later time correlations" can make an important contribution to exchange-lattice relaxation by phonon processes. On the other hand, if lattice motion is primarily one of atomic diffusion characterized by a jumping frequency much less than the exchange frequency, then we show in Sec. IV that the second term on the right-hand side of (17) is much greater than the first term so that correlations are not important in this instance.

III. PHONON PROCESSES

A. Phonon Correlation Functions

The phonon contribution to the relaxation rate is determined by computing the correlation function

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[11] P. S. Hubbard, Phys. Rev. **109**, 1153 (1958).

$\langle\Delta_{ij}(0)\Delta_{kl}(-\tau)\rangle$ for the case in which the lattice is described by noninteracting phonon states. We show in the Appendix that Eqs. (14) and (17) reduce in the proper limits to those used by Griffiths; and since Griffiths has discussed this part of the calculation in some detail, we will only outline the treatment here.

The quantity Δ_{ij} is given by (12) and for small departures of $\mathbf{r}_{ij}$ from equilibrium, we write

$$\Delta_{ij}=\sum_s \frac{\partial J_{ij}(\mathbf{r}_{ij})}{\partial x_{ij}^s}u_{ij}^s+\tfrac{1}{2}\sum_{r,s}\frac{\partial^2 J_{ij}(\mathbf{r}_{ij})}{\partial x_{ij}^r\partial x_{ij}^s}u_{ij}^r u_{ij}^s+\cdots, \qquad (22)$$

where, in the same notation as used by Griffiths, $\mathbf{r}_{ij}$ has Cartesian components $x_{ij}^s(s=1,2,3)$ and u_{ij}^s is the sth component of $\mathbf{r}_{ij}-\mathbf{r}_{ij}^0$. The displacement from equilibrium u_{ij}^s is next written in terms of phonon creation and annihilation operators, and the matrix elements needed for $\langle\Delta_{ij}(0)\Delta_{kl}(-\tau)\rangle$ are computed. The u_{ij}^s are assumed to be small so that the first term in (22) gives the dominant contribution to single-phonon processes, ones for which the matrix elements $(n_q|\Delta_{ij}|n_q\pm 1)$ are nonzero—where $|n_q)$ is the state containing n_q phonons with wave vector $\mathbf{q}$. The summation over phonon states is replaced by an integration and a simple Debye spectrum is assumed for which phonon velocity is independent of direction of propagation and polarization. The contribution of single-phonon processes-denoted by the subscript "sp"- to $\langle\Delta_{ij}(0)\Delta_{kl}(-\tau)\rangle$ is then found to be

$$\langle\Delta_{ij}(0)\Delta_{kl}(-\tau)\rangle_{\mathrm{sp}}=K_{ij,kl}\frac{\hbar V}{4\pi^2 mNv^3}\times\int_0^{\omega_0}\omega d\omega f_{ij,kl}(q)[\bar{n}_q e^{i\omega\tau}+(\bar{n}_q+1)e^{-i\omega\tau}], \qquad (23)$$

where v is the velocity of sound in the crystal, V the volume, N the number of atoms, m the atomic mass, ω_0 the Debye frequency, ω the angular frequency of a phonon with wave vector $\mathbf{q}$ and

$$\bar{n}_q=(e^{\beta\hbar\omega}-1)^{-1} \qquad (24)$$

is the thermal equilibrium occupation number of the qth phonon mode. The quantity $f_{ij,kl}(q)$ is defined by

$$f_{ij,kl}(q)=\frac{\sin qr_{ik}}{qr_{ik}}+\frac{\sin qr_{jl}}{qr_{jl}}-\frac{\sin qr_{jk}}{qr_{jk}}-\frac{\sin qr_{il}}{qr_{il}}, \qquad (25)$$

and

$$K_{ij,kl}=\sum_s\frac{\partial J}{\partial x_{ij}^s}\frac{\partial J}{\partial x_{kl}^s}. \qquad (26)$$

In a similar manner we compute the two-phonon contribution to $\langle\Delta_{ij}(0)\Delta_{kl}(-\tau)\rangle$. Here we consider only those matrix elements which describe absorption of one phonon and emission of another since these are the processes which utilize the whole phonon spectrum. Static terms are also neglected since they obviously do not contribute to (17). The result is

$$\langle\Delta_{ij}(0)\Delta_{kl}(-\tau)\rangle_{\mathrm{tp}}=\frac{\hbar^2V^2}{32\pi^4m^2N^2v^6}L_{ij,kl}\times\int_0^{\omega_0}\omega d\omega f_{ij,kl}(q)\int_0^{\omega_0}\omega' d\omega' f_{ij,kl}(q')\times[(\bar{n}_q+1)\bar{n}_{q'}e^{i(\omega'-\omega)\tau}+\bar{n}_q(\bar{n}_q'+1)e^{-i(\omega'-\omega)\tau}] \qquad (27)$$

where the subscript "tp" stands for "two-phonon" and

$$L_{ij,kl}=\sum_{r,s}\frac{\partial^2 J_{ij}}{\partial x_{ij}^r\partial x_{ij}^s}\frac{\partial^2 J_{kl}}{\partial x_{kl}^r\partial x_{kl}^s}. \qquad (28)$$

Insertion of (23) or (27) into (17) and (14) gives the relaxation rate for single- or two-phonon processes, respectively. The methods used in evaluating the integrals are the same as employed by Griffiths, in which the central assumption is that the spin correlation function $\{A_{ij}(0)A_{kl}(-\tau)\}$ becomes negligible in a time of the order of $1/J$.

B. Two-Phonon Relaxation Rate

Since the two-phonon case actually turns out to be simpler, it will be treated first. According to the above assumption, when Eq. (27) is used in (17) we need only consider frequencies ω and ω' in (27) such that $|\omega'-\omega|\gtrsim J$. But since the integrands in (27) go to zero as ω and ω' go to zero, these integrands will be most significant for ω and ω' of the order of $kT/\hbar$. And then, since by assumption $\hbar J\ll kT$, we may set $\omega'=\omega$ (and $q'=q$) in (26). Insertion of (26) in (17) and (14) then yields

$$\eta_{\mathrm{tp}}\{\mathcal{H}_0^2\}=\frac{\hbar^4V^2}{16\pi^4m^2N^2v^6}\times\sum_{i<j}\sum_{k<l}L_{ij,kl}\int_0^{\infty}\Omega^2F_{ij,kl}(\Omega)d\Omega\times\int_0^{\omega_0}\omega^2d\omega[f_{ij,kl}(q)]^2\bar{n}_q(\bar{n}_q+1), \qquad (29)$$

where η_{tp} is the two-phonon contribution to the relaxation rate and where

$$F_{ij,kl}(\Omega)=2\int_0^{\infty}\{A_{ij}(0)A_{kl}(-\tau)\}e^{i\Omega\tau}d\tau \qquad (30)$$

is identical to the quantity $F(\Omega)$ used by Griffiths when $i,j=k,l$. In the derivation of (29), the variable $\Omega=\omega-\omega'$ is introduced, it is assumed that $F(-\Omega)=F(\Omega)$, and the upper limit is extended to ∞ in the integral over $d\Omega$ since we assume that $F(\Omega)$ is negligible for frequencies much greater than J. The second term on the right-hand side of (17) is seen to be zero under the assumption that $n_q = n_{q'}$ in (27).

As noted by Griffiths,

$$\int_0^\infty \Omega^2 F_{ij,kl}(\Omega)d\Omega = -\pi \left| \frac{d^2}{d\tau^2}\{A_{ij}(0)A_{kl}(-\tau)\} \right|_{\tau=0} \tag{31}$$

from the definition (30), and thus the contribution of the spin-correlation function may be computed exactly. An important feature and simplification is that the form (31) of this contribution is independent of $f_{ij,kl}(q)$ and n_q. This is *not* the case with the single-phonon relaxation rate, as will be seen.

Evaluation of the trace (31) is performed with the help of (1), (10), and (11); and when the summation indicated by (29) is carried out, we obtain

$$\begin{aligned}\eta_{\mathrm{tp}}\{\mathcal{H}_0^2\} = (2/9)I^3(I+1)^3 \frac{\hbar^4 V^2}{16\pi^3 m^2 N^2 v^6} \\ \times \sum_{i,j,k}{}' [(J_{ij}^2 - J_{ij}J_{ik})Q_{jk,jk} - (J_{ij}^2 - J_{ij}J_{jk})Q_{ik,jk} \\ + J_{ij}J_{jk}(Q_{ij,ik} - Q_{ij,jk})],\end{aligned} \tag{32}$$

where

$$Q_{ij,kl} = L_{ij,kl} \int_0^{\omega_0} \omega^2 d\omega [f_{ij,kl}(q)]^2 \bar{n}_q(\bar{n}_q + 1) \tag{33}$$

and where all three indices i, j, k must be different as indicated by the prime on the summation sign in (32).

We now investigate the relaxation rate (32) in various lattices for nearest-neighbor interactions. For temperatures well below the Debye θ, the integral in (33) is evaluated by using the long-wavelength approximation for $f_{ij,kl}(q)$ (25). The result of most interest is that the summand in (32) is identically zero for the linear chain under these conditions.

For nearest-neighbor interactions, we write

$$J_{ij} = J\Lambda_{ij} \tag{34}$$

where Λ_{ij} is unity if spins i and j are nearest neighbors and zero otherwise. The expression for $L_{ij,kl}$ is in general rather complicated. For simplicity we assume that $J_{ij}(\mathbf{r}_{ij})$ is a function only of the magnitude r_{ij}, and, consistent with the neglect of other than nearest-neighbor interactions, we assume $J'' \gg J'/a$ where the primes denote differentiation and a is the nearest-neighbor separation. In this case we have

$$L_{ij,ij} = J''^2 \Lambda_{ij}, \tag{35a}$$

$$L_{ij,jk} = J''^2 \Lambda_{ij}\Lambda_{jk} \cos^2\theta_{ijk} \tag{35b}$$

where θ_{ijk} is the angle (i,j,k). In the long wavelength approximation, we find

$$f_{ij,ij}(q) = \tfrac{1}{3}q^2a^2 \tag{36a}$$

$$f_{ij,jk}(q) = -\tfrac{1}{3}q^2a^2 \cos\theta_{ijk}. \tag{36b}$$

Thus (32) becomes

$$\begin{aligned}\eta_{\mathrm{tp}}\{\mathcal{H}_0^2\} = (2/9)I^3(I+1)^3 \\ \times \frac{\hbar^4 V^2 J^2 J''^2 a^4}{16\times 9\pi^3 m^2 N^2 v^{10}} \int_0^{\omega_0} \omega^6 d\omega \bar{n}_q(\bar{n}_q+1) \\ \times \sum_{i,j,k}{}' (\Lambda_{ij}\Lambda_{jk} - \Lambda_{ij}\Lambda_{ik}\Lambda_{jk})(1-\cos^4\theta_{ijk}).\end{aligned} \tag{37}$$

For the linear chain it is evident that (37) predicts a zero relaxation rate since $\theta_{ijk} = 0$ or π for any set of spins along the chain. Hence we must expand $f_{ij,kl}(q)$ to a higher power of q to get a finite relaxation time. As a result, the relaxation rate is proportional to T^9 for $T \ll \theta$ instead of T^7 as it would be in the absence of correlations (neglect of the $\cos^4\theta_{ijk}$ term). [For $T \ll \theta$ the upper limit of the integral in (37) may be extended to ∞, and thus the temperature dependence of η_{tp} is determined by the power of ω appearing in the integrand.] The final result for the linear chain at temperatures well below θ is given by

$$\eta_{\mathrm{tp}}\{\mathcal{H}_0^2\} \approx \frac{12\pi^5 I^3(I+1)^3}{5m^2\omega_0^3}\left(\frac{Na^3}{V}\right)^2 8!NJ^2J''^2\hbar^4\left(\frac{T}{\theta}\right)^9, \tag{38}$$

where we have used the relation

$$\omega_0 = (6N\pi^2/V)^{1/3}v \tag{39}$$

for the simple Debye spectrum.

At temperatures of the order of θ and higher, the integral in (33) may be evaluated by using the high-temperature approximation $\bar{n}_q = kT/\hbar\omega$ together with the exact expression for $f_{ij,kl}(q)$. Griffiths has done this for the case of no correlations [See Appendix B of Ref. 7]. If we call his result for the relaxation rate (proportional to T^2) I_1 and the complete figure, including correlations, I_2, then

$$\frac{I_2}{I_1} = \int_0^{\omega_0 a/v} \left[4\left(1-\frac{\sin x}{x}\right)^2 - \left(1+\frac{\sin 2x}{2x} - 2\frac{\sin x}{x}\right)^2\right]dx \Big/ 4\int_0^{\omega_0 a/v}\left(1-\frac{\sin x}{x}\right)^2 dx \tag{40}$$

for the linear chain. In a simple cubic lattice, we have $I_2/I_1 \approx \frac{1}{3}$. (We are thinking here of a three-dimensional lattice whose magnetic ions are grouped together in linear chains.)

The T^9 two-phonon relaxation rate is a property of nearest neighbor interactions as well as of the linear chain. If *both* nearest-neighbor and next-nearest-neighbor interactions are included on the linear chain, a nonzero T^7 relaxation rate results. Vanishing of the T^7 term is not, however, dependent on the simplified form (35) for $L_{ij,kl}$ since the complete expression gives qualitatively the same result.

TABLE I. Correction factor I_2/I_1 for two-phonon relaxation rate in various lattices other than the linear chain [see Eq. (41)].

Lattice	I_2/I_1
Square array	$\frac{2}{3}$
Simple cubic	$\frac{4}{5}$
bcc	0.846
fcc (or hcp)	0.523

For lattices other than the linear chain, Eq. (37) does give a nonzero T^7 relaxation rate. If, once again, we call I_2/I_1 the ratio of our more complete results to Griffiths', then evidently

$$I_2/I_1 = \sum_{i,j,k}{}' (\Lambda_{ij}\Lambda_{jk} - \Lambda_{ij}\Lambda_{ik}\Lambda_{jk}) \times (1-\cos^4\theta_{ijk}) \Big/ \sum_{i,j,k}{}' \Lambda_{ij}\Lambda_{jk}\,. \quad (41)$$

Since an explicit expression for η_{tp} in the absence of correlations may be found either in Griffiths' work (for $T \gtrless \theta$) or in Ref. 4 (for $T \ll \theta$),[12] it will not be repeated here. The correction factors (41) for various lattices are given in Table I. We note that the term $\Lambda_{ij}\Lambda_{ik}\Lambda_{jk}$ is zero unless two adjacent spins have nearest neighbors in common. It appears even when there are no correlations, but was neglected by Griffiths for simplicity. Among the lattices studied here, it is nonzero only for fcc (or hcp). Thus the difference of close to a factor of 2 between our result and Griffiths' in the fcc lattice is not due so much to correlations as it is to the fact that, for this structure, on four of 11 sites for which $\Lambda_{ij}\Lambda_{jk}(i \neq j \neq k)$ is unity, we also have $\Lambda_{ij}\Lambda_{ik}\Lambda_{jk}(i \neq j \neq k)$ equal to unity.

C. Single-Phonon Relaxation Rate

The single-phonon relaxation rate is computed by using (23) in (17) and (14). As in the two-phonon case we assume that only those values of ω in (23) for which $\omega \gtrsim J$ need be included; so we may use the high-temperature ($\hbar\omega \ll kT$) approximation for $\bar{n}_q$ in (23) to obtain

$$\eta_{\text{sp}}\{\mathcal{H}_0{}^2\} = \frac{\hbar^2 VT}{4\pi^2 m N v^3} \sum_{i<j} \sum_{k<l} K_{ij,kl} \times \int_0^\infty F_{ij,kl}(\omega) f_{ij,kl}(q)\omega^2 d\omega \quad (42)$$

or the single-phonon relaxation rate η_{sp}. In the above $F_{ij,kl}(\omega)$ is defined as in (30) and, as in (29), we have extended the upper limit to ∞ in the $d\omega$ integration. There are two basic differences between η_{sp} and η_{tp} as may be seen by comparing (42) with (29): (i) The temperature dependence of η_{sp} (linear in T) is independent of $f_{ij,kl}(q)$, but (ii) the trace which must be taken *does* depend on $f_{ij,kl}(q)$. In the long wavelength approximation $f_{ijkl}(q)$ is proportional to $q^2 = \omega^2/v^2$; so we must compute $|\{A_{ij}(0)(d^4 A_{kl}(-\tau)/d\tau^4)\}|_{\tau=0}$ which is a considerably more complicated trace than (31). Griffiths has computed η_{sp} for the linear chain, square array, and simple cubic lattice neglecting correlations, and we shall not give explicit expressions here. We do, however, demonstrate below that, as in the two-phonon case, η_{sp} vanishes in the long-wavelength approximation for linear chains with nearest neighbor interactions.

Confining our attention to nearest-neighbor interactions along a linear chain, Eq. (42) becomes, in the long wavelength approximation,

$$\eta_{\text{sp}} \propto \sum_{i,k} K_{i,i+1;k,k+1}(r_{ik}{}^2 + r_{i+1,k+1}{}^2 - r_{i+1,k}{}^2 - r_{i,k+1}{}^2) \times \left| \left\{ \frac{d^4}{d\tau^4} A_{i,i+1}(0) A_{k,k+1}(-\tau) \right\} \right|_{\tau=0}, \quad (43)$$

where we have left out constants of proportionality for simplicity and have used (25) together with a relation similar to (31). We observe, however, that

$$K_{i,i+1;k,k+1} = J'^2 \quad (44)$$

for the linear chain, and also

$$(r_{ik}{}^2 + r_{i+1,k+1}{}^2 - r_{i+1,k}{}^2 - r_{i,k+1}{}^2) = -2a^2 \quad (45)$$

so that the coefficient of

$$\left| \left\{ \frac{d^4}{d\tau^4} A_{i,i+1} A_{k,k+1}(-\tau) \right\} \right|_{\tau=0}$$

in (43) is independent of i and k. Thus we have

$$\eta_{sp} \propto \left| \frac{d^4}{d\tau^4} \operatorname{tr} \sum_{i<j,\text{nei}} \sum_{k<l,\text{nei}} A_{ij} \exp(-i\mathcal{H}_0\tau/\hbar) \times A_{kl} \exp(i\mathcal{H}_0\tau/\hbar) \right|_{\tau=0} \quad (46)$$

where "nei" means that the summations are restricted to nearest neighbors. But since $\mathcal{H}_0 = J \sum_{\text{nei}} A_{ij}$ and the trace is invariant with respect to cyclic permutations, we see that (46) reduces to

$$\eta_{sp} \propto \left| \frac{d^4 \operatorname{tr}\mathcal{H}_0{}^2}{d\tau^4} \right|_{\tau=0} \quad (47)$$

and this is zero since $\operatorname{tr}\mathcal{H}_0{}^2$ is, of course, independent of τ. Hence, we have a rather general proof, which could equally well be applied to the two-phonon case, for the vanishing of the relaxation rate in linear chains with nearest neighbor interactions when the long wavelength approximation is used. The proof hinges upon the fact that $f_{i,i+1;k,k+1}(q)$ is independent of i and k. This is a property unique to the linear chain and long wavelength approximation. If terms in q^4 are included, then we see

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[12] Garwin and Landesman's expression for η_{tp} should be multiplied by 3 to account for an error in transcribing Griffith's equations (private communications between P. M. Richards and R. L. Garwin and H. A. Reich).

that $f_{ij,kl}(q)$ does depend on i and k and hence there is a finite relaxation rate.

By making the next approximation for $f(q)$ we bring in an additional factor of ω^2a^2/v^2. Then since we expect the major contribution of the integral in (42) to be for ω of the order of J and since ω_0 is of the order of v/a, the single-phonon relaxation rate for the linear chain should be less than that calculated by Griffiths by a factor of the order of $(J/\omega_0)^2=(\hbar J/k\theta)^2\ll 1$.

IV. RELAXATION BY ATOMIC DIFFUSION

We now examine the situation in which the dominant lattice motion is one of atomic diffusion. Garwin and Landesman showed that if the correlation time τ_c associated with lattice motion is much longer than $1/J$, then the exchange-lattice relaxation time is of the order of τ_c. This result will be rederived here in the present formalism, and we will show that correlations may in fact be neglected.

Since we expect $\{A_{ij}(0)A_{kl}(-\tau)\}$ to be significant only for times of the order of $1/J$ or less, the first term on the right-hand side of (17) may be roughly approximated by

$$\int_0^\infty d\tau\left\langle\Delta_{ij}(0)\frac{d^2}{d\tau^2}\Delta_{kl}(-\tau)\right\rangle\{A_{ij}(0)A_{kl}(-\tau)\}$$

$$\approx\left|\left\langle\Delta_{ij}(0)\frac{d^2}{d\tau^2}\Delta_{kl}(-\tau)\right\rangle\right|_{\tau=0}\{A_{ij}(0)A_{kl}(0)\}/J$$

$$\approx\langle\Delta_{ij}(0)\Delta_{kl}(0)\rangle\{A_{ij}(0)A_{kl}(0)\}/J\tau_c^2 \qquad (48)$$

while the second term will be of the order of

$$\langle\Delta_{ij}(0)\Delta_{kl}(0)\rangle\{A_{ij}(0)A_{kl}(0)\}/\tau_c$$

if we give a classical description to atomic diffusion in the manner of Torrey.[13] Thus the second term in (17) will be greater than the first term by a factor of the order of $J\tau_c\gg 1$ so that with (14) we have

$$\eta_d\{\mathcal{H}_0^2\}\approx-\hbar^2\sum_{i<j}\sum_{k+l}\left|\left\langle\Delta_{ij}(0)\frac{d}{d\tau}\Delta_{kl}(-\tau)\right\rangle\right|_{\tau=0}$$

$$\times\{A_{ij}(0)A_{kl}(0)\} \qquad (49)$$

for η_d, the "slow diffusion" relaxation rate. The quantity $\{A_{ij}(0)A_{kl}(0)\}$ is zero unless i, $j=k$, l, and hence correlations do not contribute to this relaxation rate. Performing the trace gives

$$\eta_d\{\mathcal{H}_0^2\}=-\tfrac{1}{3}\hbar^2I^2(I+1)^2$$

$$\times\sum_{i<j}\left|\left\langle\Delta_{ij}(0)\frac{d}{d\tau}\Delta_{ij}(-\tau)\right\rangle\right|_{\tau=0}. \qquad (50)$$

We evaluate $\langle\Delta_{ij}(0)\Delta_{ij}(-\tau)\rangle$ as follows. For nearest-neighbor interactions the complete Hamiltonian of the system is written as

$$\mathcal{H}=\hbar J\sum_{i<j}\alpha_{ij}(t)\Lambda_{ij}A_{ij}, \qquad (51)$$

where A_{ij} is given by (11) as before but now Λ_{ij} is a quantity which is unity if the lattice *sites* i and j are nearest neighbors and zero otherwise and $\alpha_{ij}(t)$ is unity if the *sites* i and j are both occupied by spins at time t and zero otherwise. The perturbation $\mathcal{H}'$ is the difference between $\mathcal{H}$ and its thermal equilibrium value, and thus, comparing (51) with (8) and (12), we have

$$\Delta_{ij}(t)=J[\alpha_{ij}(t)-\langle\alpha_{ij}\rangle]\Lambda_{ij}, \qquad (52)$$

where $\langle\alpha_{ij}\rangle$ is the thermal equilibrium expectation value of α_{ij}. The correlation function $\langle\Delta_{ij}(0)\Delta_{ij}(-\tau)\rangle$ then becomes

$$\langle\Delta_{ij}(0)\Delta_{ij}(-\tau)\rangle=J^2\Lambda_{ij}(\langle\alpha_{ij}(0)\alpha_{ij}(\tau)\rangle-\langle\alpha_{ij}\rangle^2), \qquad (53)$$

where we have assumed symmetry in τ and $-\tau$ and noted that

$$\langle\alpha_{ij}\rangle\langle\alpha_{ij}(\tau)\rangle=\langle\alpha_{ij}\rangle^2. \qquad (54)$$

At least for short times, we may write

$$\langle\alpha_{ij}(0)\alpha_{ij}(\tau)\rangle=\langle\alpha_{ij}^2\rangle[1-P(\tau)], \qquad (55)$$

where $P(\tau)$ is the probability that a jump has occurred in a time τ which leaves either one or both of the sites i and j unoccupied given that they were both occupied at time $\tau=0$. Since we are interested in $P(\tau)$ for short times we need consider only nearest-neighbor jumps. Following Torrey, we define $P_1(\tau)$ as the probability that a spin makes a single jump onto a neighboring site in a time τ. We also understand $P_1(\tau)$ to have the thermal equilibrium distribution of vacancies built into it—that is, $P_1(\tau)$ represents the probability of jumping onto a neighboring site only if the probability of that site's being vacant is the thermal equilibrium probability. We have

$$P_1(\tau)=(\tau/\tau_c)e^{-\tau/\tau_c} \qquad (56)$$

for a Poisson distribution, thus defining τ_c. If there are Z nearest-neighbor sites, then

$$P(\tau)=2(Z-1)P_1(\tau) \qquad (57)$$

for $\tau\ll\tau_c$ where the factor of 2 comes from the fact that either the spin at i or the spin at j may jump, and we have $Z-1$ since we are given that one of the Z neighbors is occupied at $\tau=0$.

Using (56) and (57) in (50) and (53) together with (55) then yields

$$\eta_d\{\mathcal{H}_0^2\}\approx\tfrac{1}{3}\hbar^2I^2(I+1)^2J^2(Z-1)NZ/\tau_c \qquad (58)$$

as long as the number of vacancies is sufficiently small that $\langle\alpha_{ij}\rangle\approx 1$. But since

$$\{\mathcal{H}_0^2\}=\tfrac{1}{6}\hbar^2I^2(I+1)^2JNZ \qquad (59)$$

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[13] H. C. Torrey, Phys. Rev. **92**, 962 (1953).

under the same approximation, we obtain finally

$$\eta_d = 2(Z-1)/\tau_c. \tag{60}$$

SUMMARY

Magnetic exchange-lattice relaxation has been investigated well above the Néel point under the assumption that the exchange and lattice systems may each be described by a temperature. Correlations between different pairs of spins were handled by a density matrix formalism whereas these correlations were neglected in Griffiths' treatment. The most striking effect of correlations is in linear chains with nearest neighbor interactions at temperatures much less than the Debye θ. The relaxation rate for single-phonon processes is less than that computed by Griffiths by a factor of the order of $(\hbar J/k\theta)^2$, and the two-phonon processes give a T^9 dependence instead of the normal T^7 term. In three-dimensional lattices, correlations have about a 20% effect which, though not dramatic, is at least of academic interest when one considers that correlations are rigorously negligible in Zeeman-lattice relaxation if a spin temperature is assumed.

When the frequency of lattice motion is much less than J, correlations can be neglected. Garwin and Landesman's result that the relaxation time is of the order of τ_c, the correlation time characterizing diffusion jumps, is therefore justified.

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APPENDIX: EQUIVALENCE WITH GRIFFITHS' FORMALISM

If the lattice average in (17) is expressed as a sum over the eigenstates $|\mu\rangle$ of the lattice Hamiltonian, we obtain the following equation for the relaxation rate.

$$\eta\{\mathcal{H}_0^2\} = \sum_{i<j}\sum_{k<l}\sum_{\mu>\nu} W_{\mu\to\nu}(ij,kl)(E_\mu - E_\nu)^2 P_\mu, \tag{A1}$$

where

$$W_{\mu\to\nu}(ij,kl) = 2(\mu|\Delta_{ij}|\nu)(\nu|\Delta_{kl}|\mu) \times \int_0^\infty d\tau e^{i\omega_{\mu\nu}\tau}\{A_{ij}(0)A_{kl}(-\tau)\} \tag{A2}$$

is the transition probability per unit time that the lattice changes from the state $|\mu\rangle$ to $|\nu\rangle$—and thereby loses energy $E_\mu - E_\nu = \hbar\omega_{\mu\nu}$—due to coupling with the spin pairs i, j and k, l; and

$$P_\mu = e^{-\beta\hbar\omega_\mu} / \sum_\lambda e^{-\beta\hbar\omega_\lambda} \tag{A3}$$

is the thermal equilibrium probability that the state $|\mu\rangle$ is occupied. In writing (A1) we have taken the second term on the right-hand side of (17) to be zero, as is the case for the phonon processes above the Nèel point [see Eqs. (23) and (27)]. Equation (A1) reduces to that used by Griffiths if one neglects correlations so that $W_{\mu\to\nu}(ij,kl)$ is zero unless $i=k$, $j=l$ and assumes nearest neighbor interactions only. [Compare (A1) with, for example, Eqs. (8), (13), or (22) of Ref. 7.] It is also of the same form as that used by Hebel and Slichter.[14]

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[14] L. C. Hebel and C. P. Slichter, Phys. Rev. **113**, 1504 (1959).