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Effects of self-consistency on spin-lattice relaxation*

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We propose a new quadrupolar T_1 spin-lattice relaxation process that is independent of both magnetic field strength and temperature, and yields exponential decay in both laboratory and rotating-frame experiments with comparable decay rates. Numerical estimates indicate that this process may be dominant at low temperatures in nuclear spin systems with $I > 1/2$ that are reasonably free from paramagnetic impurities. It may also be the dominant process in the relaxation of certain paramagnetic ions in systems with concentrations of ions that are not too small and where inhomogeneous broadening is minimal. The process depends upon the fact that the lattice vibrations which relax the spins acquire an enhanced spectral density arising from thermal spin fluctuations. It bears some resemblance to phonon-induced spin-spin coupling or virtual phonon mechanisms. It is further shown that this effect of the spins on the lattice vibrations can be expressed exactly in terms of the time-dependent correlation functions for the spins.

I. INTRODUCTION

It is well known that nuclear spins with $I>\frac{1}{2}$ can relax to thermal or lattice equilibrium because of the interaction of the nuclear electric quadrupole moment with the electric field gradients generated by thermal fluctuations of the lattice.[1] The relaxation can take place via the direct spin-phonon Hamiltonian which is first order in the elastic strains or lattice coordinates, or via the Raman spin-phonon Hamiltonian that is second order in the elastic strains or lattice coordinates.[2-5] Furthermore, the important thermal fluctuations of the lattice may be the intrinsic thermal fluctuations of a perfectly harmonic lattice or may arise from the effects of anharmonicity on the lattice vibrations.[5] It is also well known[6-8] that acoustic waves or lattice vibrations are damped because of their interaction with nuclear spins of $I>\frac{1}{2}$. This latter process usually goes by the name of nuclear acoustic resonance. Similar phenomena described with a different vocabulary and notation, but much the same physics, occur with electronic spins.[9]

In this paper, we propose a new quadrupolar mechanism for the relaxation of nuclear (or electronic) spins to thermal equilibrium via the direct or first-order spin-phonon interaction. In the present case, the important thermal lattice fluctuations are induced by the spins themselves. That is, the lattice vibrations at spin-resonance frequencies are enhanced because of the transverse fluctuations of the spins, and this enhancement leads to an increased relaxation rate of the spins to thermal or lattice equilibrium. Thus, the relaxation rate obtained is proportional to the fourth power of the spin-phonon coupling constant and is linear in the density of spins. Although the process depends on the existence of many interacting spins, it is a true T_1 of spin-lattice relaxation process, and is not equivalent to the effects of an indirect spin-spin interaction. As part of the derivation of the effect, we obtain some exact (though not startling) results for the effect of spins on harmonic phonons.

Although the magnitude of the process which we propose is not large, neither is it hopelessly small. Numerical estimates of T_1 arising from the relaxation mechanism range from about 10^5 to 10^2 sec for typical nuclear spin systems. Since this is much faster than nuclear spin relaxation arising from the direct absorption or emission of harmonic phonons, one might conclude that our mechanism must eventually dominate the relaxation of nuclear spins with $I>\frac{1}{2}$ at low temperatures since relaxation via the Raman or second-order interaction and direct relaxation via anharmonic phonons vanishes as T^7 at low temperatures.[5] However, virtually all materials contain some paramagnetic impurities and the nuclear spins can relax to thermal equilibrium via interactions with them[10,11] Nevertheless relaxation via our mechanism should be distinguishable from relaxation via paramagnetic impurities because of different magnetic field and temperature dependences, different ratios of T_1 in the laboratory and rotating frames, and different initial time dependences.

In the rest of this section we shall describe the notation and interactions used in the rest of the paper. Section II is subdivided into two parts. In Sec. II A we derive the effects of the spins on the phonons or lattice vibrations. It turns out that this can be done exactly. In Sec. II B we use these exact results in order to calculate the relaxation of the spins by the lattice using the usual approximations. Section III is devoted to a discussion of the results, characteristics, and numerical estimates of the process, possible previous experimental observations of the effects, and possible generalizations. The Appendix contains a derivation of some interesting exact results for the effects of a spin system on an otherwise perfect harmonic lattice.

The system of interacting spins and lattice vibrations is described by a Hamiltonian consisting of a lattice Hamiltonian $\mathcal{H}_l$, a spin Hamiltonian $\mathcal{H}_s$, and a spin-lattice Hamiltonian $\mathcal{H}_{sl}$. For the lattice we consider only the harmonic approximation and thus

$$\mathcal{H}_l = \frac{1}{2} \sum_{\vec{q},j} \{\dot{Q}(\vec{q},j)\dot{Q}(-\vec{q},j) + [\omega(\vec{q},j)]^2 Q(\vec{q},j) Q(-\vec{q},j)\} , \tag{1}$$

where $Q(\vec{q},j) = Q^\dagger(-\vec{q},j)$ is the lattice normal coordinate of wave vector $\vec{q}$ and branch j corresponding to the normal mode with frequency $\omega(\vec{q},j)$.[12] The first-order or direct spin-phonon Hamiltonian can be written[13]

$$\mathcal{H}_{sl} = N^{-1/2} \sum F_m(\vec{q},j,k) Q(\vec{q},j) A_{2,m}(\vec{l},k) e^{-\vec{q}\cdot\vec{l}} , \tag{2}$$

where the summation is over $\vec{q}$, j, m, $\vec{l}$, and k. This equation refers to a perfect lattice with N unit cells labeled by $\vec{l}$ where basis indices $\underset{\sim}{k}$ label sites within a unit cell. The quantity $A_{2,m}(\vec{l},k)$ is a second-rank (or quadrupole) spin-multipole operator[14] at the lattice site $(\vec{l},k)$, where m takes on the values ± 1, ± 2, and 0. This is the appropriate coupling for nuclear spins or electronic "real" spins, but the coupling for electronic "pseudospins" is considerably more general.[9] The quantity $F_m(\vec{q},j,k) = (-1)^m F^*_{-m}(-\vec{q},j,k)$ contains the details of the coupling and will be expressed in terms of more familiar quantities later in the paper. We do not need to express the spin Hamiltonian $\mathcal{H}_s$ since we will not make use of it explicitly.

II. DERIVATION

A. Effects of the spins on the lattice vibrations

In this subsection, we derive an exact equation for the effects of the spins on the lattice vibrations via the direct spin-phonon interaction. Although the formalism we use is rather awkward and inelegant, it is straightforward and has the further advantage that we need only assume some equilibrium ensemble. It is not necessary that both the spins and the lattice be described by the same temperature. This generality is desirable because in most T_1 experiments the spin and lattice temperatures are initially unequal. In the Appendix we present an alternative derivation that is more elegant, but requires that the whole system be described by a single temperature. In addition, this alternative derivation is used to make contact with the usual treatments of acoustic magnetic resonance.

In order to find the effects of the spins on the lattice vibrations we define a phonon correlation function as

$$D^{(+)}(\vec{q},j;\vec{q}',j';t-t') = \langle Q(\vec{q},j,t) Q^\dagger(\vec{q}',j',t')\rangle \,\Theta(t-t') , \tag{3}$$

where the angular brackets $\langle\ \rangle$ denote the thermal average of x, and Θ is the step function. Using the Heisenberg equation of motion and the commutation relations

$$[\dot{Q}(\vec{q},j), Q(\vec{q}',j')] = -i\hbar\delta(\vec{q}+\vec{q}')\delta_{jj'} , \tag{4}$$

one obtains an equation of motion for the lattice normal coordinate

$$\ddot{Q}(\vec{q},j,t) = -[\omega(\vec{q},j)]^2 Q(\vec{q},j,t) - \frac{1}{\sqrt{N}} \sum_{\vec{l},m,k} F_m(-\vec{q},j,k) A_{2,m}(\vec{l},k,t) e^{-i\vec{q}\cdot\vec{l}} . \tag{5}$$

Furthermore, by taking two time derivatives of Eq. (3), one obtains

$$\left(\frac{\partial^2}{\partial t^2}\right) D^{(+)}(\vec{q},j;\vec{q}',j';t-t') = \langle \ddot{Q}(\vec{q},j,t) Q^\dagger(\vec{q}',j',t')\rangle \Theta(t-t') + \langle \dot{Q}(\vec{q},j,t) Q^\dagger(\vec{q}',j',t)\rangle \delta(t-t') + \langle Q(\vec{q},j,t) Q^\dagger(\vec{q}',j',t)\rangle \delta'(t-t') . \tag{6}$$

By combining Eqs. (5) and (6), one obtains

$$\left(\frac{\partial^2}{\partial t^2} + [\omega(\vec{q},j)]^2\right) D^{(+)}(\vec{q},j;\vec{q}',j';t-t') = a(\vec{q},j;\vec{q}',j')\delta(t-t') + b(\vec{q},j;\vec{q}',j')\delta'(t-t') - \frac{1}{\sqrt{N}} \sum_{m,\vec{l},k} F_m(-\vec{q},j,k) e^{-\vec{q}\cdot\vec{l}} \langle A_{2,m}(\vec{l},k,t) Q^\dagger(\vec{q}',j',t')\rangle \Theta(t-t') , \tag{7}$$

where

$$a(\vec{q},j;\vec{q}',j') = \langle \dot{Q}(\vec{q},j) Q^\dagger(\vec{q}',j')\rangle, \quad b(\vec{q},j;\vec{q}',j') = \langle Q(\vec{q},j) Q^\dagger(\vec{q}',j')\rangle . \tag{8}$$

In a similar manner, an equation of motion can be obtained for the new correlation function appearing in the last term on the right-hand side of Eq. (7). The desired equation is

$$\left(\frac{\partial^2}{\partial t'^2}+[\omega(\vec{q}',j')]^2\right)[\langle A_{2,m}(\vec{l},k,t)Q^\dagger(\vec{q}',j',t')\rangle\Theta(t-t')]$$

$$=c(m,\vec{l},k\vec{q}',j')+\delta(t-t')\,d(m,\vec{l},k;\vec{q}',j')\delta'(t-t')-\frac{1}{\sqrt{N}}\sum_{m',\vec{l}',k'}F^*_{m'}(-\vec{q}',j',k')e^{i\vec{q}'\cdot\vec{l}'}G^{(+)}_{mm'}(\vec{l},k;\vec{l}',k';t-t')\ , \tag{9}$$

where

$$c(m,\vec{l},k;\vec{q}',j')=-\langle A_{2,m}(\vec{l},k)\dot{Q}^\dagger(\vec{q}',j')\rangle,\quad d(m,\vec{l},k;\vec{q}',j')=\langle A_{2,m}(\vec{l},k)Q^\dagger(\vec{q}',j')\rangle \tag{10}$$

and

$$G^{(+)}_{mm'}(\vec{l},k;\vec{l}',k';t-t')=\langle A_{2,m}(\vec{l},k,t)A^\dagger_{2,m'}(\vec{l}',k',t')\rangle\Theta(t-t')\ . \tag{11}$$

By combining Eqs. (7) and (9) it is easily seen that the phonon correlation function can be expressed exactly in terms of some static thermal averages and the exact spin-correlation function. In Sec. II B we will only want the part of the phonon correlation function that contains fluctuations arising from the spins. This part can be obtained by Fourier transforming Eqs. (7) and (9) and keeping only that part of $D^{(+)}$ that depends on $G^{(+)}$. If all time-dependent functions $f(t)$ are Fourier transformed as

$$f(\omega)=\int dt\,f(t)e^{i\omega t}\ , \tag{12}$$

then the desired result is

$$D_s^{(+)}(\vec{q},j;\vec{q}',j',\omega)$$
$$=\frac{1}{N}\sum\left(\frac{F_m(-\vec{q},j,k)}{[\omega(\vec{q},j)]^2-\omega^2}\right)\left(\frac{F^*_{m'}(-\vec{q}',j',k')}{[\omega(\vec{q}',j')]^2-\omega^2}\right)$$
$$\times G^{(+)}_{mm'}(\vec{l},k;\vec{l}',k';\omega)e^{-i\vec{q}\cdot\vec{l}}e^{i\vec{q}'\cdot\vec{l}'}\ , \tag{13}$$

where the summation is over m, $\vec{l}$, k, m', $\vec{l}'$, and k', and the subscript s on $D^{(+)}$ denotes that this is the part of $D^{(+)}$ that contains dynamical information on the spins.

At this point, in order to simplify the equations, we place a number of restrictions on the spin system. These restrictions apply to most spin resonance experiments and the consequences of lifting some of them will be discussed later in the paper. First we assume the high-temperature limit for all spins. That is, $\beta\hbar\omega_0(k)\ll 1$, where $\beta=1/kT$, $\omega_0(k)=\gamma(k)H$, H is the magnitude of an external magnetic field, and $\gamma(k)$ is the gyromagnetic ratio of the kth species of spins. We further assume that any static electric field gradients acting on the spins produce frequency shifts that are small compared to typical dipolar or other spin-spin interaction frequencies. Finally, we assume a perfect lattice of spins of each species whose gyromagnetic ratios are well separated. Under these conditions the spin-correlation function in Eq. (11) can be written

$$G^{(+)}_{mm'}(\vec{l},k;\vec{l}',k';\omega)$$
$$=G^{(+)}_{mm}(\vec{l}-\vec{l}',k,\omega)\delta_{mm'}\delta_{kk'}$$
$$=\frac{1}{N}\sum_{\vec{q}}G^{(+)}_m(\vec{q},k,\omega)\delta_{mm'}\delta_{kk'}e^{i\vec{q}\cdot(\vec{l}-\vec{l}')}\ . \tag{14}$$

Then Eq. (13) can be rewritten

$$D_s^{(+)}(\vec{q},j;\vec{q}j;\omega)$$
$$=\sum_{m,k}\left|\frac{F_m(-\vec{q},j,k)}{[\omega(\vec{q},j)]^2-\omega^2}\right|^2G^{(+)}_m(\vec{q},k,\omega)\ . \tag{15}$$

Although Eqs. (13) and (15) are exact, they can be misleading. From Eq. (15) one might conclude that $D_s^{(+)}(\vec{q},j;\vec{q}j;\omega)$ approaches infinity as $[\omega(\vec{q},j)-\omega]^2$ when ω approaches $\omega(\vec{q},j)$. In the Appendix we argue that this is not the case because $G^{(+)}_m(\vec{q},k,\omega)$ itself is a function of $D^{(+)}(\vec{q},j;\vec{q},j;\omega)$. That is, since the spins and phonons are coupled, the exact spin-correlation function must contain the exact phonon-correlation function including poles at the phonon resonances. Since the spins and phonons are not strongly coupled, $G^{(+)}_m(\vec{q},k,\omega)$ is affected by the phonon resonances only for frequencies and wavevectors for which ω and $\omega(\vec{q},j)$ are very nearly equal. We shall eventually use the expression on the right-hand side of Eq. (15) summed over all wave vectors at frequencies much much less than the Debye frequency. Thus only a negligible error will be introduced by replacing $[\omega(\vec{q},j)]^2-\omega^2$ by $\omega^2(\vec{q},j)$ and by replacing $G^{(+)}$ by the part of $G^{(+)}$ that does not include the phonon resonances. We refer the reader to the Appendix for a more rigorous discussion of this point.

B. Effects of the phonons on the spins

We cannot, of course, solve exactly for the effects of the phonons on the spins. The approximation that we shall use in this subsection is the standard one for computing direct spin-phonon relaxation. With the restrictions listed in Sec. II A, the irreducible multipole operators A_{lm} correspond closely to good normal modes of the spin system and a slight generalization of Eq. (11) of Ref. 13 yields

$$\Gamma_{10}(k,\omega)=\mathrm{Re}\,\frac{1}{N}\sum_{\vec{q},j,m}\int\frac{d\bar{\omega}}{2\pi}\,\frac{3m^2}{I(I+1)\hbar^2}\,|F_m(\vec{q},j,k)|^2 \times D^{(+)}(\vec{q},j;\vec{q},j;\bar{\omega}) \times G_m^{(+)}(k,\vec{q},\omega-\bar{\omega}) \ . \tag{16}$$

The quantity $\Gamma_{10}(k,\omega)$ is the frequency-dependent decay rate of the magnetization of the spin species k at infinite wavelength. The decay time of the magnetization $T_1(k)$ is given by $[T_1(k)]^{-1}=\Gamma_{10}(k,0)$ if the expression in Eq. (16) is constant in the frequency range from zero to several times $[T_1(k)]^{-1}$. This requires only that typical spin-spin interaction frequencies be much greater than $[T_1(k)]^{-1}$ and is almost certainly the case in all nuclear spin experiments in cold solids. Since we are interested in the self-consistent effects of the phonons on the spins, $D_s^{(+)}$ from Eq. (15) is substituted into Eq. (16) for $D^{(+)}$ yielding

$$[T_1(k)]^{-1}=\mathrm{Re}\,\frac{1}{N}\sum_{\vec{q},j,m,m',k'}\int\frac{d\bar{\omega}}{2\pi}\,\frac{3m^2}{I(I+1)\hbar^2\omega^4(\vec{q},j)} \times|F_m(\vec{q},j,k)|^2|F_{m'}(-\vec{q},j,k')|^2 \times G_m^{(+)}(k,\vec{q},-\bar{\omega})G_{m'}^{(+)}(k',\vec{q},\bar{\omega}) \ . \tag{17}$$

Under the conditions mentioned at the beginning of this subsection, the spin correlation function $G_m^{(+)}(k,\vec{q},\omega)$ is sharply peaked about the isochromats at $\omega=m\omega_0(k)$ with a width $\omega_d(k)$, a typical dipolar frequency for the spin species k. Thus, the only appreciable contributions to Eq. (17) come from terms with $k'=k$ and $m'=m$. In order to proceed further, however, one must know $F_m(\vec{q},k,j)$, $\omega(\vec{q},j)$, and $G_m^{(+)}(k,q,\omega)$.

Before discussing the results we shall try to evaluate Eq. (17) in terms of some more-familiar quantities. Since both $\omega(\vec{q},j)$ and $F_m(\vec{q},k,j)$ are proportional to $|\vec{q}|$ for long wavelengths in acoustic branches, all portions of the Brillouin zone contribute in roughly equal amounts to the $\vec{q}$ summation. However, since $\omega(\vec{q},j)$ and $F_m(\vec{q},k,j)$ are not known over the entire Brillouin zone for any substance, there is no hope for a really accurate computation. In order to obtain some idea of the magnitude of T_1, we shall assume that $F_m(\vec{q},k,j)$ is proportional to $\omega(\vec{q},j)$, with the constant of proportionality being independent of both $\vec{q}$ and j. The constant of proportionality will be obtained by averaging over directions of $\vec{q}$ at long wavelengths. This type of approximation has been used in other spin phonon calculations,[15,16] but using it to estimate magnitudes is quite uncertain. For example, an error of a factor of 2 in $F_m(\vec{q},k,j)/\omega(\vec{q},j)$ will lead to an error of $2^4=16$ in the final answer. Thus our results will certainly be no better than order of magnitude, and they could be much worse. Nevertheless, in the absence of better knowledge of $F(\vec{q},k,j)$ and $\omega(\vec{q},j)$, we proceed.

The longitudinal part of the quadrupolar spin-phonon coupling in the long-wavelength limit at a single spin site can be written[7]

$$\mathcal{H}_{sp}=\left(\frac{eQ}{2I(2I-1)}\right)\tfrac{3}{2}\,S_{11}\sum_i e_{ii}[I_i^2-\tfrac{1}{3}I(I+1)] \ , \tag{18}$$

where Q is the quadrupole moment of the spins, S_{11} is part of the S tensor, and e_{ii} is the acoustic strain

$$e_{ii}=\frac{\partial u_i}{\partial x_i} \ , \tag{19}$$

where $\vec{u}$ is the lattice displacement. By expressing $\vec{u}$ in terms of the phonon normal coordinates[12] and expressing $[I_i^2-\frac{1}{3}I(I+1)]$ in terms[13] of the irreducible spin-multipole operators A_{2m}, one obtains $F_m(\vec{q},k,j)$ in terms of more-familiar quantities. After averaging over angles, one obtains

$$\left\langle\left|\frac{F_m(q,k,j)}{\omega(q,j)}\right|^2\right\rangle=\frac{(eQS)^2(2I+3)(I+1)}{5^2\times3\times2^4I(2I-1)Mv^2b} \ . \tag{20}$$

In this formula M is the average mass per atom, v is an average acoustic velocity, S is an average S tensor, and b is the number of atoms per unit cell. Trying to specify the averages more precisely would only make the results seem more accurate then they really are. By using Eq. (20) in Eq. (17) one obtains

$$T_1^{-1}=5\omega_Q^4I(I+1)/4\omega_d(Mv^2/\hbar)^2 \ , \tag{21}$$

where ω_d is a dipolar linewidth and

$$\omega_Q=(eQS/10\hbar)[(2I+3)/I^2(2I-1)]^{1/2} \ . \tag{22}$$

The quantities S, Q, I, and ω_d in these equations all refer to the nuclear species under consideration.

Finally, we briefly consider the modifications that arise if one does not have a spin in every unit cell but where only a concentration or fraction c of the unit cells contain a spin of a given species. One would expect that the effects of the spins on the phonons to be proportional to the density of spins or proportional to c. Further, the damping of the spins by the phonons should be independent of c except insofar as the spectral intensity of lattice vibrations depends on c. This leads to the conclusion that the right hand side of Eq. (21) should be multiplied by c. In fact one can more rigorously solve the problem if one assumes an impurity spin lattice in the solid and this leads to just that factor of c. However, ω_d will usually depend on c and the concentration of spins cannot be so small that there is no spin temperature. Further, if the spin isochromats are broadened inhomogeneously by an amount ω_q that is larger than ω_d, then ω_d in Eq. (21) should be replaced by ω_q.

III. DISCUSSION

The physics of our calculation can be easily understood in two steps. First of all, because of their interaction with the spins, the lattice vibrations acquire an enhanced spectral intensity at the resonant frequencies of the spin system. This enhanced spectral intensity cannot be put into a harmonic phonon picture because it occurs for lattice vibrations of any wave vector $\vec{q}$. It can be discussed in terms of a phonon self-energy as is done in the Appendix. The relative independence of this enhancement on wavevector is, in retrospect, obvious from the existence of acoustic spin-resonance experiments which depend on matching resonance frequencies, but not on any particular frequency-wave-vector relationship. The second step consists of noting that the lattice vibrations with $\omega \approx \omega_0$ are the lattice vibrations which damp the magnetization, and these are just the ones whose spectral intensity is enhanced.

In a number of ways our calculation is suggestive of the phonon-induced spin-spin coupling or virtual phonon effects that were discussed in the literature some years ago.[17] However, this process is not the same as the one which we describe. In the first place, spin-spin interactions (real or effective) will not contribute to T_1 under the conditions assumed in Sec. II. Further, the physics of the two processes is very different. A phonon-induced spin-spin interaction or virtual phonon mechanism implies that the lattice transmits spin fluctuations passively without energy being emitted or absorbed by the lattice itself. Even the addition of retardation only changes the dispersive properties of the medium (the lattice), and does not allow for absorption. On the other hand, the phonons or lattice vibrations in our process are not virtual, but are real. There is a real buildup of spectral weight in the lattice which, in turn, can be transmitted to the spins. There is no way in which our process can be described by an effective spin-spin Hamiltonian. It is also an integral part of our calculation that the spins interact strongly enough to be describable by a spin temperature. For dilute enough concentrations of spins, especially in the presence of appreciable static electric field gradients, a spin temperature will not obtain and our calculation will not apply.

In spite of the crudeness of the approximations in going from Eq. (17) to (21), there are a number of definite characteristics of the process which we propose. Since the magnitude of T_1 predicted by Eq. (21) is quite large, estimated to be about 10^2 to 10^5 sec for typical nuclear spin systems, the process will be observable only at low temperatures where other intrinsic relaxation processes are frozen out. The primary competing mechanism will then be relaxation to paramagnetic impurities in the diffusion limited case, at least in samples that are not heavily doped. Thus the characteristics of our new process listed below are compared to the characteristics of relaxation via paramagnetic impurities[11]: (i) The new process is independent of temperature. This is rarely true for relaxation via small concentrations of paramagnetic ions where temperature independence obtains only when the relaxation time of the electronic spins, τ_c, is itself temperature independent. (ii) The new process is independent of magnetic field strength within the limits discussed in Sec. II. This field independence obtains with paramagnetic ions only if $\omega_0\tau_c \ll 1$, a highly unlikely occurrence at low temperatures and typical resonant frequencies. Further, although we have not presented calculations of angular dependence, we expect the dependence of our mechanism on magnetic field angle to be much weaker than one would expect from the equations for relaxation via paramagnetic ions. (iii) The new process yields relaxation that is exponential in time for all times. Relaxation via paramagnetic impurities, on the other hand, proceeds as $t^{1/2}$ for short times. (iv) Although we have not calculated $T_{1\rho}$ (T_1 in the rotating reference frame), the fact that T_1 does not depend on ω_0 makes it rather obvious that $T_{1\rho}$ and T_1 will be of the same order of magnitude. The ratio of $T_1/T_{1\rho}$ for relaxation via paramagnetic impurities is proportional to terms of order one plus terms of order $(1+\omega_0^2\tau_c^2)/(1+\omega_1^2\tau_c^2)$, where $\omega_1 = \gamma H_1$ and H_1 is the magnitude of the rotating magnetic field. Thus, except in the unlikely event that $\omega_0\tau_c \ll 1$, $T_1/T_{1\rho}$, due to paramagnetic impurities, will be very large at low temperatures. In fact, it is entirely possible that the new process dominates T_1 and paramagnetic impurities dominate $T_{1\rho}$ for some materials. (v) The ratios of T_1's for different isotopes of the same nuclei are quite distinct. From Eqs. (21) and (22) and the ensuing discussion, the isotopic part of $1/T_1$ is

$$cQ^4(2I+3)^2(I+1)/I^3(2I-1)^2\omega_d \quad , \tag{23}$$

where ω_d can be well approximated by the square root of the appropriate second moment.

There is some experimental evidence that the process which we propose has been observed. One prime possibility is the low-temperature T_1 and $T_{1\rho}$ data[18] of Sirovich and Norberg on ^{21}Ne. With solid polycrystalline samples of Ne enriched to about 50% ^{21}Ne, these investigators observed a T_1 of about 2×10^3 sec that was independent of temperature from about 11 to 4 K. Further, the $T_1/T_{1\rho}$ ratio was approximately two in this temperature range, and the T_1 relaxation was strictly exponential. Finally, the investigators expended a considerable effort in cleaning the samples which caused no discernible change in the data. Unfortunately, we know of no S-tensor measurements in Ne so a numerical estimate is difficult. However, by using an average velocity[19] of $v=0.8\times10^5$ cm/sec with[18] $\omega_d=10^3$ sec^{-1}, a value of $eQS/\hbar=1.0\times10^8$ sec^{-1} is needed in Eq. (21) in order to obtain $T_1=2\times10^3$ sec. This is not an unreasonable value and, in fact, this value coupled with static strains of order 3×10^{-5} would explain the $\omega_q\sim10^3$ measured by the investigators. This is also a reasonable estimate since a single Ne vacancy creates strains only of order 10^{-2} at adjacent atoms.

There is also some evidence for the process in the T_1 measurements in III-V compounds by Bridges and Clark[15] and by McNeil and Clark.[16] Using published results of velocities[20] and products of eQS/h,[21] we have estimated the magnitude of our process for the T_1's that they measured. The results are in order of magnitude agreement for ^{115}In, ^{121}Sb, and ^{123}Sb in InSb and for ^{115}In and ^{75}As in InAs. In addition, the ratio of the low temperature T_1's for ^{121}Sb and ^{123}Sb in InSb are consistent with Eq. (23). The magnitudes of the measured T_1's in GaAs and GaSb are too large to be consistent with Eq. (21) and the measurements indicated a temperature dependence in these cases.

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APPENDIX

In this appendix we pursue the question of the effects of the spins on the phonons in more detail. In order to reduce unnecessary detail, we shall assume a Bravais lattice with only one species of spin. This eliminates the basis index k. The notation and formalism in this Appendix is essentially the same as in Sec. III of Kwok's article[12] and we refer the reader to this article for some details.

The phonon and spin Green's functions are defined as

$$\begin{aligned} D(qj;q'j';t,t') &= (i/\hbar)\langle[Q(\vec{q},j,t)Q(q',j',t')]_+\rangle \quad , \\ G_{mm'}(l,l';t,t') &= (i/\hbar)\langle[A_{2m}(\vec{l},t)A_{2m'}(\vec{l}',t)]_+\rangle \quad , \end{aligned} \tag{A1}$$

where $[\ ]_+$ denotes that the operators enclosed are time ordered and $\langle\ \rangle$ denotes the thermal average of the enclosed operators. Both of the Green's functions in Eq. (A1) are functions only of $t-t'$ and they are Fourier transformed as a function of imaginary time in the usual way; that is,

$$A(\omega_\nu)=\int_0^\tau dt\,\exp[i\omega_n(t-t')]A(t) \quad , \tag{A2}$$

where $A(t)$ is any function of t and ω_n is the imaginary frequency $\omega_n=2\pi n/\tau$, $\tau=-i\beta\hbar$, and n is an integer. By using Eq. (5), one can easily derive the analog of Eqs. (7) and (9) with the Green's functions defined in Eq. (A1):

$$\{[\omega(q,j)]^2-\omega_n^2\}D(qj,q'j';\omega_n)=\delta(\vec{q}+\vec{q}')\delta_{j,j'}+\sum_{mm'}\frac{F_m(-\vec{q},\vec{j})F_{m'}(\vec{q}',\vec{j}')G_{mm'}(\vec{q},\omega_n)\delta(\vec{q}+\vec{q}')}{\{[\omega(\vec{q},j')]^2-\omega_n^2\}} \quad . \tag{A3}$$

In this equation, $G(\vec{q})$ is the spatial Fourier transform of $G(\vec{l},\vec{l}')=G(\vec{l}-\vec{l}')$.

Although Eq. (A3) is an equation for the exact-phonon Green's function in terms of the exact-spin Green's function, it is not a particularly useful equation because $G_{mm'}(\vec{q},\omega_n)$ contains the phonon resonances [poles for ω_n near $\pm\omega(\vec{q},j)$]. Although one normally thinks of spin-correlation functions containing the phonon resonances only in ordered spin systems because of large magnetoelastic coupling, this property is perfectly general. What we would really like is an equation relating $D(\vec{q},j;\vec{q},j;\omega_n)$ to $\tilde{G}_{mm'}(\vec{q},\omega_n)$, where $\tilde{G}_{mm'}(\vec{q},\omega_n)$ is the exact-spin Green's function excluding resonant-phonon effects. That is, $\tilde{G}_{mm'}(\vec{q},\omega_n)$ is the exact-spin Green's function including the coupling to all lattice vibrations except those with wave vector $\vec{q}$.

In order to derive such an equation we employ a functional derivative formalism similar to Kwok's. Thus a source function S is defined as

$$S=\left[\exp\left(\frac{i}{\hbar}\int_0^{\tau}dt'\sum_{\vec{q}'j'}J(\vec{q}',j',t')Q(\vec{q}',j',t')\right)_+\right] , \tag{A4}$$

where thermal averages are defined as

$$\langle O(t)\rangle=\mathrm{Tr}\{e^{-\beta\mathcal{H}}[SO(t)]_+\}/\mathrm{Tr}(e^{-\beta\mathcal{H}}S) . \tag{A5}$$

Here J plays the role of an external force and all thermal averages are functionals of J. After performing the desired formal manipulations, J is set equal to zero and the definition of a thermal average reverts to its usual definition. With the above definitions, the equation of motion for the normal coordinate can be written

$$\left(\frac{\partial^2}{\partial t^2}\right)\langle Q(\vec{q},j,t)=-[\omega(\vec{q},j)]^2Q(\vec{q},j,t)\rangle -\frac{1}{\sqrt{N}}\sum_{m,l}F_m(-\vec{q},j)e^{-i\vec{q}\cdot\vec{l}} \times\langle A_{2,m}(\vec{l},t)\rangle+J(-\vec{q},j,t) . \tag{A6}$$

The phonon Green's function in the presence of the source J is defined as the functional derivative

$$D(\vec{q},j;\vec{q}',j';t,t')=\frac{\delta\langle Q(\vec{q},j,t)\rangle}{\delta J(\vec{q}',j',t')} . \tag{A7}$$

This equation is entirely symmetric with respect to interchange of primed and unprimed variables and, when $J\rightarrow 0$, Eq. (A7) gives the same D as does Eq. (A1). By taking the functional derivative of Eq. (A6) with respect to $J(\vec{q}',j',t')$, one obtains

$$\left(\frac{\partial^2}{\partial t^2}+[\omega(\vec{q},j)]^2\right)D(\vec{q},j;\vec{q}',j';t,t')=\delta(q+\vec{q}')\delta_{jj}\delta(t-t')-\frac{1}{\sqrt{N}}\sum_{m\vec{l}}F_m(-\vec{q},j)e^{-\vec{q}\cdot\vec{l}}\left(\frac{\delta\langle A_{2m}(\vec{l},t)\rangle}{\delta J(\vec{q}',j',t')}\right) . \tag{A8}$$

Since $\langle A\rangle$ is a functional of J via $\langle Q\rangle$, we also have that[22]

$$\frac{\delta\langle A_{2m}(\vec{l},t)\rangle}{\delta J(\vec{q}',j',t')} =\int_0^{\tau}dt''\sum_{\vec{q}'',j''}\left(\frac{\delta\langle A_{2,m}(\vec{l},t)\rangle}{\delta\langle Q(\vec{q}'',j'',t'')\rangle}\right)\left(\frac{\delta\langle Q(\vec{q}'',j'',t'')\rangle}{\delta J(\vec{q}',j',t')}\right) \tag{A9}$$

At this point comes the only step that is not absolutely rigorous. We assume that $\delta\langle A_{2,m}(\vec{l},t)\rangle/\delta\langle Q(\vec{q}'',j'',t'')\rangle$ can be obtained by replacing $Q(q,j,t)$ in the spin-phonon Hamiltonian [Eq. (2)] by $\langle Q(\vec{q},j,t)\rangle$ when $\vec{q}=\vec{q}''$. The terms with $\vec{q}\neq\vec{q}''$ are unchanged. Then,

$$\frac{\langle\delta A_{2,m}(\vec{l},t)\rangle}{\delta\langle Q(\vec{q}'',j'',t'')\rangle} =-\frac{1}{\sqrt{N}}\sum_{m''\vec{l}''}F_m(\vec{q}'',j'')e^{i\vec{q}\cdot\vec{l}''}\tilde{G}_{mm''}(\vec{q}'';t,t'') , \tag{A10}$$

where $\tilde{G}$ is the function discussed earlier in this appendix. Further justification for this is as follows. For a macroscopic sample with a large number (N) of allowed $\vec{q}$'s, changing the spin-phonon interaction for only $\vec{q}=\vec{q}''$ cannot change any properties of the spin Green's function except the resonant coupling to the phonons with wave vector $\vec{q}$. The replacement of $Q(\vec{q}'')$ by $\langle Q(\vec{q}'')\rangle$ is saying, in effect, that the spins respond to a lattice disturbance of a single wave vector in the same way they would to an external source of that single wave vector. That is, we have made an effective field approximation for the effects of lattice vibrations of wave vector $\vec{q}$ on $G_{mm'}(\vec{q},\omega_n)$, while treating the effects of all the other lattice vibrations exactly. This point has been discussed in the literature[23] for electromagnetic interactions with very similar results to the ones which we shall obtain.

By Fourier transforming and combining Eqs. (A8), (A9), and (A10), using Eq. (A7), and then setting $J=0$ and letting $\omega_n\rightarrow\omega$, one obtains

$$\begin{aligned}\tilde{P}(\vec{q},j,\omega)&=-\sum_{mm'}F_m(-\vec{q},j)F_{m'}(q,j)\tilde{G}_{mm'}(\vec{q},\omega) ,\\ D(\vec{q},j,\omega)&=D(\vec{q},j;\vec{q},j;\omega) .\end{aligned} \tag{A11}$$

This is to be contrasted with Eq. (A3) which can be rewritten

$$\{[\omega(\vec{q},j)]^2-\omega^2\}D(\vec{q},j,\omega)=1-\frac{P(\vec{q},j,\omega)}{D_0(\vec{q},j,\omega)} ,$$

$$P(\vec{q},j,\omega)=-\sum_{m,m}F_m(-\vec{q},j)F_{m'}(\vec{q},j)G_{mm'}(\vec{q},\omega) , \tag{A12}$$

$$D_0(\vec{q},j,\omega)=\{[\omega(\vec{q},j)]^2-\omega^2\}^{-1} .$$

The effect of the resonant phonons on G can be obtained by solving for P in terms of $\tilde{P}$,

$$P=D_0^{-1}\tilde{P}/(D_0^{-1}+\tilde{P}) . \tag{A13}$$

There have been a number of treatments of the effects of spins on phonons[24] which obtain equations like (A11). However, these treatments are characterized as "first order" in the spin-phonon coupling and do not make it clear whether G or $\tilde{G}$ is to be used. In a semiclassical continuum approximation, the equations are more obvious.[8]

From Eqs. (A12) and (A13) it can easily be seen that (15) is essentially exact except for the very small fraction of phase space where $|P(\vec{q},j,\omega)| \gtrsim |[\omega(\vec{q},j)]^2-\omega^2|$. Further, in this small fraction of phase space, there is no divergence. Thus a negligible error is introduced by the procedure adopted in Sec. II leading up to Eq. (17).

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[1] R. V. Pound, Phys. Rev. 79, 685 (1950).

[2] J. Van Kranendonk, Physics (Utr.) 20, 781 (1954).

[3] K. Yosida and T. Moriya, J. Phys. Soc. Jpn. 11, 33 (1956).

[4] R. L. Mieher, Phys. Rev. 125, 1537 (1962).

[5] J. Van Kranendonk and M. B. Walker, Phys. Rev. Lett. 18, 701 (1967); Can. J. Phys. 46, 2441 (1968).

[6] S. A. Al'tshuler, B. I. Kochelaev, and A. M. Leushin, Usp. Fiz. Nauk 75, 459 (1961) [Sov. Phys.-Usp. 4, 880 (1962)].

[7] D. I. Bolef, in *Physical Acoustics*, edited by W. P. Mason (Academic, New York, 1966), Vol. 4A, Chap. 3.

[8] Peter A. Fedders, Phys. Rev. B 12, 2045 (1975).

[9] See, for example, R. Orbach and H. J. Stapleton, in *Electron Paramagnetic Resonance*, edited by S. Geschwind (Plenum, New York, 1972), Chap. 2.

[10] N. Bloembergen, Physica (Utr.) 15, 386 (1949).

[11] See, for example, I. J. Lowe and D. Tse, Phys. Rev. 166, 279 (1968), and references therein.

[12] See, for example, P. C. Kwok, Solid State Phys. 20, 213 (1967).

[13] P. A. Fedders, Phys. Rev. B 10, 4510 (1974).

[14] For a brief description of the use of spin multipole operators in magnetic resonance, see P. A. Fedders, Phys. Rev. B 11, 995 (1975).

[15] F. Bridges and W. G. Clark, Phys. Rev. 164, 288 (1967).

[16] John A. McNeil and W. Gilbert Clark, Phys. Rev. B 13, 4705 (1976).

[17] See, for example, K. Sugihara, J. Phys. Soc. Jpn. 14, 1231 (1959); L. K. Aminov and B. I. Kochelaev, Zh. Eksp. Teor. Fiz. 43, 1303 (1962) [Sov. Phys.-JETP 15, 903 (1962)]; U. Kh. Kopvillem, Sov. Phys.-Solid State 7, 1637 (1966); D. H. McMahon and R. H. Silsbee, Phys. Rev. 135, A91 (1964); R. Orbach and M. Tachiki, *ibid.* 158, 524 (1967); and references therein.

[18] B. E. Sirovich and R. E. Norberg (unpublished); B. E. Sirovich, Ph.D. thesis (Washington University, 1976) (unpublished).

[19] R. Balzer, D. S. Kupperman, and R. O. Simmons, Phys. Rev. B 4, 3636 (1971); F. Bridges and W. G. Clark, Phys. Rev. 164, 288 (1967).

[20] Gene Simmons and Herbert Wang, *Single Crystal Elastic Constants and Calculated Aggregate Properties: A Handbook*, 2nd ed. (MIT, Cambridge, Mass., 1971).

[21] R. K. Sundfors, Phys. Rev. B 10, 4244 (1974).

[22] If we had defined a source function B_m relating to A_{2m} in the same way that J relates to Q, the procedure would appear more symmetric. Then functional derivatives with one member of the set $\{Q,J,A,B\}$ varied with respect to another member would be performed with the other two members held constant.

[23] See, for example, L. P. Kadanoff and P. C. Martin, Phys. Rev. 124, 670 (1961), see in particular, pp. 679–670 and Eq. (3.33).

[24] See, for example, H. S. Bennett and E. Pytte, Phys. Rev. 155, 553 (1967); Peter A. Fedders, Phys. Rev. B 5, 181 (1972).