age $\partial\phi_l/\partial q$ is zero, and at $\mathbf{q}_0$ it should be large and negative. The two Herman[37] values are -2.1 and -1.2 times $\sqrt{3}a/8$. We take the total $(\partial\phi_t/\partial q)-(\sqrt{3}a/8)$ to be $-2.5\sqrt{3}a/8=-0.54a$, again with at least 30% uncertainty. All three effects contribute comparably to the linear change of plane-wave coefficient, so this uncertainty carries over in large measure to the final results in Table VII. Furthermore, the linear approximation itself should be used only with caution in an interband transition calculation, because of the proximity of the branch point connecting LA and LO.

The convergence and general behavior of the calculation was, on the average, the same as for the work of Sec. V. Calculations were made of the quantities in Table VII for the deformable ion case by assuming that no new plane waves were mixed into the interpolating function. General behavior of the calculation was as bad as in Sec. VI; in fact, the algebra is essentially identical. Moreover, the prefactor to the result includes $(\partial\phi/\partial q)-(\sqrt{3}a/8)$, which as discussed above, is rather uncertain.

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Trapping of a Resonant Phonon by a Pair of Paramagnetic Ions*

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The trapping of a resonant phonon by a pair of paramagnetic ions is studied in the limit of zero temperature with the aid of the Heitler damping formalism. The probability amplitudes of the states (spin 1 up, spin 2 down, no phonon), (spin 1 down, spin 2 up, no phonon), and (spin 1 down, spin 2 down, one phonon) are computed. Provided coherence is maintained between the two spins, the transfer of energy to the crystal lattice takes place in the time $T_{10}(1-\sin k_0r_{12}/k_0r_{12})^{-1}$. Here T_{10} is the spin-lattice relaxation time for an isolated ion at zero degrees, k_0 is the wave vector of the resonant phonon, and r_{12} is the distance between the spins. The relation of this result to the general problem of spin-lattice relaxation at low temperature is discussed.

I. INTRODUCTION

IN the standard treatment of the spin-lattice relaxation of a two-level paramagnetic spin system it is assumed that the ensemble of spins can be characterized by a temperature.[1,2] Loosely speaking, a description in terms of a spin temperature different from the lattice temperature is valid whenever the spin-spin relaxation time T_2 is less than the spin-lattice relaxation time T_1.[3] In this paper we will discuss the transfer of energy from the spin system to the lattice for a situation where the opposite condition holds, namely $T_1 \ll T_2$.

At zero degrees an isolated spin in the excited level has a lifetime T_{10}, where T_{10} is the spin-lattice relaxation time evaluated at $T=0$. We will show that the presence of a neighboring spin may greatly enhance this lifetime, provided coherence is maintained between the two spins for intervals greater than T_{10}. We identify this enhancement with the coherent trapping of the resonant phonon. Although the situation studied is somewhat artificial there is reason to believe that the results of the calculation indicate the conditions under which an analogous trapping may be present in a crystal with a large number of spins.

II. THEORY

In order to discuss this effect in detail we start with the Hamiltonian of the two-spin system ($S=\frac{1}{2}$),

$$\mathcal{H}=\omega_0(S_z^1+S_z^2)+\sum_{\mathbf{k}}\omega_k a_{\mathbf{k}}^\dagger a_{\mathbf{k}}+S_x^1\sum_{\mathbf{k}}A_k e^{i\mathbf{k}\cdot\mathbf{r}_1}\times(a_{\mathbf{k}}^\dagger+a_{-\mathbf{k}})+S_x^2\sum_{\mathbf{k}}A_k e^{i\mathbf{k}\cdot\mathbf{r}_2}(a_{\mathbf{k}}^\dagger+a_{-\mathbf{k}}). \quad (1)$$

The first term in (1) is the Zeeman interaction ($\hbar=1$), the second is the phonon Hamiltonian ($a_{\mathbf{k}}$ and $a_{\mathbf{k}}^\dagger$ are the phonon annihilation and creation operators), while the third and fourth terms couple the spins to the lattice. In the interaction terms, $\mathbf{r}_1$ and $\mathbf{r}_2$ denote the locations of the two spins and $\mathbf{k}$ is the phonon wave vector. The x components of the spins are denoted by S_x^1 and S_x^2, and A_k is a coupling constant inversely proportional to the square root of the volume of the crystal. We will assume for simplicity that $\omega_k=vk$ where v is the velocity of sound, and that A_k depends only on the magnitude of $\mathbf{k}$. Since we are interested in the limit $T_1 \ll T_2$ we have omitted the dipolar coupling. The

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[1] J. H. Van Vleck, Phys. Rev. **57**, 426 (1940).
[2] R. Orbach, Proc. Roy. Soc. **A264**, 458 (1961).
[3] A. Abragam, *The Principles of Nuclear Magnetism* (Clarendon Press, Oxford, England, 1961), Chap. V.

influence of the spin-spin interaction on the trapping will be discussed below.

In the absence of a spin-phonon interaction the eigenstates of the combined spin and lattice systems are characterized by the number of phonons present in each mode and the eigenvalues of the z components of the two spins. We will consider a certain subset of these states, namely, the states in which one spin is in the upper level, the other in the lower level, and there are no phonons present, and the states in which both spins are in the lower level and there is one phonon present in the $\mathbf{k}$th mode. Since only phonons with energies comparable to ω_0 are "on speaking terms" with the spins, the neglect of multi-phonon states is a permissible approximation as long as ω_0 is much greater than KT, the typical energy of a thermal phonon.

We indicate by $b_1(t)$ and $b_2(t)$ the wave functions of the states in which spins 1 and 2 are in the upper level, respectively. The wave function of the one-phonon state is denoted by $g_{\mathbf{k}}(t)$. We are interested in the situation where initially one of the spins is in the upper level and there are no phonons present. The evolution of the wave functions in the presence of the interaction and subject to this initial condition is described by the Heitler damping equations.[4] A straightforward application of the Heitler formalism leads to the following coupled equations for the Fourier-Laplace transforms $\bar{b}_1(E)$, $\bar{b}_2(E)$, and $\bar{g}_{\mathbf{k}}(E)$ of the previously defined wave functions:

$$(E-\omega_0+i\epsilon)\bar{b}_1(E)=1+\tfrac{1}{2}\textstyle\sum_{\mathbf{k}}e^{-i\mathbf{k}.\mathbf{r}_1}A_k\bar{g}_{\mathbf{k}}(E)\,, \tag{2}$$

$$(E-\omega_0+i\epsilon)\bar{b}_2(E)=\tfrac{1}{2}\textstyle\sum_{\mathbf{k}}e^{-i\mathbf{k}.\mathbf{r}_2}A_k\bar{g}_{\mathbf{k}}(E)\,, \tag{3}$$

$$(E-\omega_k+i\epsilon)\bar{g}_{\mathbf{k}}(E)=\tfrac{1}{2}\textstyle\sum_{\mathbf{k}}e^{i\mathbf{k}.\mathbf{r}_1}A_k\bar{b}_1(E)+\tfrac{1}{2}\sum_{\mathbf{k}}e^{i\mathbf{k}.\mathbf{r}_2}A_k\bar{b}_2(E)\,. \tag{4}$$

Here we have assumed that at $t=0^+$, $b_1=1$, and $b_2=g_{\mathbf{k}}=0$.[5]

These equations are readily solved with the result[6]

$$(E-\omega_0+i\epsilon)\bar{b}_1(E)=1+\tfrac{1}{4}\textstyle\sum_{\mathbf{k}}A_k^2(E-\omega_k+i\epsilon)^{-1}\bar{b}_1(E)+\tfrac{1}{4}\sum_{\mathbf{k}}A_k^2(E-\omega_k+i\epsilon)^{-1}e^{i\mathbf{k}.(\mathbf{r}_2-\mathbf{r}_1)}\bar{b}_2(E)\,, \tag{5}$$

$$(E-\omega_0+i\epsilon)\bar{b}_2(E)=\tfrac{1}{4}\textstyle\sum_{\mathbf{k}}A_k^2(E-\omega_k+i\epsilon)^{-1}\bar{b}_2(E)+\tfrac{1}{4}\sum_{\mathbf{k}}A_k^2(E-\omega_k+i\epsilon)^{-1}e^{i\mathbf{k}\cdot(\mathbf{r}_1-\mathbf{r}_2)}\bar{b}_1(E)\,. \tag{6}$$

In order to invert these equations and obtain closed expressions for the wave functions we will make the approximation of replacing E by ω_0 in the denominators of the terms on the right-hand side. This approximation, for an isolated spin, leads to the Wigner-Weisskopf expressions for the level shift and radiative lifetime.[7] In the two-spin problem it gives rise to a nonretarded interaction between the spins (see below). Upon inverting (5) and (6) we obtain the equations ($t>0$)

$$idb_1(t)/dt=[\omega_0-(i/2T_{10})+\Delta\omega_0]b_1(t)+f(r_{12})b_2(t)\,, \tag{7}$$

$$idb_2(t)/dt=[\omega_0-(i/2T_{10})+\Delta\omega_0]b_2(t)+f(r_{12})b_1(t)\,, \tag{8}$$

where

$$\Delta\omega_0=\tfrac{1}{4}p\textstyle\sum_{\mathbf{k}}A_k^2(\omega_0-\omega_k)^{-1} \tag{9}$$

and

$$1/2T_{10}=\tfrac{1}{4}\pi\textstyle\sum_{\mathbf{k}}A_k^2\delta(\omega_0-\omega_k) \tag{10}$$

are the well-known expressions for the level shift and width of isolated spins. Also, we have

$$f(r_{12})=\tfrac{1}{4}p\textstyle\sum_{\mathbf{k}}A_k^2(\omega_0-\omega_k)^{-1}e^{i\mathbf{k}.(\mathbf{r}_2-\mathbf{r}_1)}-\dfrac{i}{2T_{10}}\dfrac{\sin k_0r_{12}}{k_0r_{12}}, \tag{11}$$

where $k_0(=\omega_0/v)$ is the wave vector of the resonant phonon and $r_{12}=|\mathbf{r}_1-\mathbf{r}_2|$. In arriving at (9)–(11) we have made use of the symbolic identity $1/(E+i\epsilon)=p/E-i\pi\delta(E)$ where p denotes the principal value. We note that the equation for $b_1(t)$ involves the function $b_2(t)$ evaluated at the same instant of time. Strictly speaking, the interaction between the spins is retarded since the finite velocity of sound imposes a limit on the speed with which acoustic signals can propagate between the two sites. As long as the time it takes for a phonon to travel from one site to the other, r_{12}/v is short compared to T_{10} the neglect of retardation is probably not a bad approximation.[8]

Equations (7) and (8) are easily solved. We find

$$b_1(t)=\exp[-i(\omega_0+\Delta\omega_0-i/2T_{10})t]\cos f(r_{12})t\,, \tag{12}$$

$$b_2(t)=-i\exp[-i(\omega_0+\Delta\omega_0-i/2T_{10})t]\sin f(r_{12})t\,. \tag{13}$$

The corresponding probabilities for finding the spins in the upper states are given by

$$|b_1(t)|^2=[\cos^2\mathrm{Re}(f)t\cosh^2\mathrm{Im}(f)t+\sin^2\mathrm{Re}(f)t\sinh^2\mathrm{Im}(f)t]e^{-t/T_{10}}, \tag{14}$$

$$|b_2(t)|^2=[\cos^2\mathrm{Re}(f)t\sinh^2\mathrm{Im}(f)t+\sin^2\mathrm{Re}(f)t\cosh^2\mathrm{Im}(f)t]e^{-t/T_{10}}, \tag{15}$$

where $\mathrm{Re}(f)$ and $\mathrm{Im}(f)$ denote the real and imaginary parts of the function $f(r_{12})$.

With the typical values $\omega_0=1$ cm^{-1} and $v=4\times10^5$ cm/sec, we have $k_0=5\times10^5$/cm, so that the inequality $k_0r_{12}\ll1$ holds as long as the separation between the spins is less than 10^{-6} cm. Assuming this to be the case

[4] W. Heitler, *The Quantum Theory of Radiation* (Clarendon Press, Oxford, England, 1957), pp. 163–174.

[5] The symbol $+i\epsilon$ is inserted to indicate that the path of integration in the E plane is taken to be slightly above the real axis.

[6] Equations similar to these but pertaining to the exchange of optical photons have been derived in the limit $\omega_0r_{12}/v\gg1$ by Barrat [J. P. Barrat, J. Phys. Radium **20**, 541 (1959)].

[7] V. Weisskopf and E. Wigner, Z. Physik **63**, 54 (1930); **65**, 18 (1930).

[8] The effect of retardation on the exchange of resonant photons has been investigated by Hamilton [J. Hamilton, Proc. Phys. Soc. (London) **62**, 12 (1949)].

we infer the asymptotic behavior

$$|b_1(t)|^2 \sim |b_2(t)|^2 \sim \tfrac{1}{4} \exp\left[-\frac{t}{T_{10}}\left(1-\frac{\sin k_0 r_{12}}{k_0 r_{12}}\right)\right]. \quad (16)$$

This is to be compared with the probability of finding an isolated spin in the upper state, $|b_{\rm iso}(t)|^2$:

$$|b_{\rm iso}(t)|^2 = e^{-t/T_{10}}. \quad (17)$$

III. DISCUSSION

In the two-spin system the lifetime of either spin in the upper level is given by $T_{10}[1-\sin(k_0 r_{12})/k_0 r_{12}]^{-1}$. This lifetime is much greater than the lifetime of an isolated spin provided $k_0 r_{12} \ll 1$. We attribute the enhancement of the lifetime to the coherent trapping of the phonon by the two spins. A phonon emitted by one spin is captured by the other, raising it to the excited level. The second spin then emits a phonon which is recaptured by the spin that was initially excited. The exchange of excitation by the two spins leads to a decrease in the probability of a phonon "escaping" from the locality of the spins.

In this simplified picture it can be seen how the presence of dipolar coupling tends to inhibit the phonon trapping. The dipolar interaction contains terms of the form $A_{ij}(S_+{}^i S_-{}^j + S_-{}^i S_+{}^j)$ which transfer excitation from one site to another. Through the action of these terms the excitation can diffuse out of the region in which it was initially trapped.[9] The energy "leak" is expected to be particularly important when the spin-spin interaction is strong enough to lead to spin waves capable of long-range energy transfer. It should be noted that thermal phonons of energy ω_0 can also destroy the trapping. The spin in the lower state could absorb a thermal phonon, thus bringing the exchange to a halt. Alternately, one can view the action of the thermal vibrations as destroying the coherence between the spins and thus effectively isolating them from one another. When this happens the transfer of excitation from the spin system to the lattice takes place in a time characteristic of the relaxation time of an isolated spin.

The discussion we have given here has been limited to two spins. In a many-spin system we expect an analogous trapping involving not only pairs but also triples, quartets, etc., of coherently precessing spins. From the preceeding analysis we can draw several conclusions about the conditions that must hold when the coherent trapping is present:

(1) The spin-spin interactions must be sufficiently weak so that energy transfer via the spin-spin interaction is not important.

(2) The temperature of the crystal must be well below ω_0/K in order that the influence of thermal phonons can be neglected.

(3) The wavelength of the trapped phonons must be considerably greater than the typical separation between the spins ($k_0 r_{12} \ll 1$).

The stipulated conditions are extreme, but they may not be impossible to obtain with fast relaxing ions in dilute concentrations. The trapping phenomenon might be reflected in a spin-lattice "relaxation time" which rapidly increased as the temperature of the crystal fell below ω_0/K.

It should be pointed out that the trapping also affects the conditions necessary for a phonon bottleneck.[10] In the case of a bottlenecked spin system, the populations of the lattice modes on speaking terms with the spin system are greatly enhanced over their equilibrium values. Because of this, relaxation of the spin system is governed by the phonon-bath relaxation rate. The phonon trapping delays the transfer of excitation from the spin system to the lattice and thus may give the phonon-bath coupling sufficient leeway to maintain a state of thermal equilibrium in the lattice.

Finally we note that the trapping considered in this paper is analogous to the imprisonment of resonance radiation in macroscopic volumes of gas.[11,12] However, in the gas problem, as treated in Ref. 11, no assumption is made about coherence being maintained between the emitting and absorbing atoms. A resonant photon is emitted from a region of the sample, propagates some distance, and is absorbed. In the situation discussed here the radiation is trapped by adjacent atoms and thus escapes from the emitting region at a much slower rate than if only one atom were involved. In a certain sense coherent trapping is imprisonment on a microscopic scale in that it involves only a small number of atoms.

[9] There are paramagnetic salts (e.g., dysprosium ethyl sulphate) where the matrix elements of the angular-momentum ladder operators vanish within the ground doublet. The absence of first-order flip-flop processes makes these salts especially attractive candidates for coherent phonon trapping.

[10] J. H. Van Vleck, Phys. Rev. **59**, 724 (1941).
[11] T. Holstein, Phys. Rev. **72**, 1212 (1947).
[12] P. W. Anderson, Phys. Rev. **114**, 1002 (1959).