Phonon Bottleneck and Frequency Distribution in Paramagnetic Relaxation at Low Temperatures*

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The general problem of the imprisonment of resonant quanta due to reabsorption has been studied for phonons in a lattice of paramagnetic centers. Expressions for the apparent spin-lattice relaxation time T_1' and the width of lattice excitation $\Delta\nu_L$ have been derived from several points of view as functions of the spin-resonance linewidth $\Delta\nu_s$, the line shape, and the intrinsic spin-lattice relaxation time T_1. In the presence of a phonon bottleneck $T_1'>T_1$ and $\Delta\nu_L>\Delta\nu_s$. Detailed agreement is found with Holstein's theory of photon trapping in atomic gases, and inconsistencies in other treatments of phonon trapping are illuminated. The present study gives a detailed physical picture of the imprisonment process. Special attention is given to the nature of the bottleneck when the phonon interruption rate becomes comparable with the spin-resonance linewidth.

I. INTRODUCTION

PARAMAGNETIC relaxation (pmr) may occur by means of the direct process, in which energy is transferred to a narrow band of lattice modes close to the spin-resonance frequency ν. Phonons then deliver this energy to the bath by traveling to the surface of the crystal.

If the first process transfers energy rapidly, the phonons may not be able to deliver their energy to the bath sufficiently fast to prevent the lattice from warming up, at least as judged by the average energy of the lattice vibrations at the frequency ν. If delivery of energy by phonons to the bath is very slow the relaxation process will be delayed and an apparent relaxation time T_1' which is significantly longer than the intrinsic relaxation time will be observed. The temperature of the lattice modes interacting with the spins will rise to a value approaching the spin temperature. This process has become known as the *phonon bottleneck*.[1–13]

Recent experiments[7,11–13] provide strong evidence for the existence of the phonon bottleneck at helium temperatures in microwave pulse and saturation pmr measurements.[13a] The earlier pmr measurements[2] of Gorter and his colleagues using the audiofrequency susceptibility technique also provide a variety of examples of relaxation times limited by lattice bath conduction. Initial evidence suggests that 29 cm^{-1} acoustic phonons produced by $2\bar{A}\rightarrow\bar{E}$ transitions in optically pumped ruby at low temperatures may also show the bottleneck effect.[8] There has been considerable discussion[1–7,9,10] of the interpretation of the phonon bottleneck; however, the various approaches have resulted in apparent inconsistencies and some misunderstanding. The purpose of this paper is to indicate the physical processes which are responsible for phonon energy transport and the phonon bottleneck and to point out the inadequate assumptions and conclusions which are present in some treatments.

In Sec. II a simple estimate illustrates the inadequacy, in some cases, of the lattice modes near the spin resonance to act as a reservoir for the spin system. A previous estimate,[10] which purported to show that even in extreme cases the bottleneck was negligible, is shown to be numerically in error.

Section III examines the transport of phonons for the case of an inhomogeneously broadened spin resonance and it is shown that not only can diffusion not be neglected but that in fact diffusion alone may

* This work was initiated while the authors were at Columbia University, New York.

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[13a] See *Note added in proof*.

control the escape of the resonant quanta from the absorbing medium.

The theories of Holstein[14,15] and Veklenko[16] which apply to optical resonance radiation and homogeneously broadened lines are modified for low-temperature pmr. The results of their rigorous analyses, which have corroboration at optical frequencies and which should be valid for our situation, are presented in Sec. IV for comparison with our calculations.

An analysis in Sec. V which is predicated upon the coupled differential equations which describe the temporal population changes in the spin and lattice systems shows that the energy distribution in the lattice can have a spectral width which is appreciably larger than the spin-resonance width. The same result is derived by another approach as well.

In Sec. VI an approach which considers the modes more explicitly enables one to compute the spectral width of a given mode, the spectral range of lattice excitation and the spin-bath relaxation time constant for the cases of uniformly distributed loss and of loss localized at the crystal boundaries. It is shown that Holstein's treatment is equivalent to a description of the phonon bottleneck in terms of broadened lattice modes, and that furthermore the nature of the phonon decay makes a detailed consideration of spatial transport (diffusion) unnecessary for homogeneously broadened lines.

Section VII is concerned with "uncertainty" or interruption broadening and the phenomena which arise when the lattice mode interruption rate approaches the spin-resonance linewidth.

In the conclusion, Sec. VIII, we summarize our results and briefly the assumptions and results of other workers in light of our findings.

It should be emphasized that the discussion which follows should apply quite generally to the trapping of resonant quanta, be they phonons or photons.

II. SIGNIFICANCE OF THE BOTTLENECK EFFECT

We shall imagine that the spins associated with a single resonance line ($S=\frac{1}{2}$) are maintained at an average temperature T_S. If we equate the power delivered to the lattice modes within $\Delta\nu$ by the spins *to* the power which the same modes surrender to the bath we find,[17] for $h\nu \ll kT$,

$$\frac{h\nu}{2}\left(\frac{d\Delta N}{dt}\right)=\left[\frac{(h\nu)^2N}{4kT_1}\right]\left[T_P^{-1}-T_S^{-1}\right]$$
$$=\tau_{LB}^{-1}\rho(\nu)\Delta\nu k(T_P-T_B).$$

In this equation, N is the total number of spins per unit volume, T_1 the spin-lattice relaxation time, T_P is the average temperature of the modes within the bandwidth $\Delta\nu$, $\rho(\nu)=12\pi\nu^2v^{-3}$ is the density of lattice oscillators per unit bandwidth, τ_{LB} the lifetime of a phonon against absorption by the bath, and T_B is the helium bath temperature. We assume that the "direct" spin-lattice decay process is dominant and that phonon-phonon collisions are negligible[18,19] for $\nu\sim10^{10}$ cps and $T_B\sim1$–4°K. The phonon lifetime τ_{LB} is $\eta\Lambda v^{-1}$, where η is a transmission factor which can be $\gg1$ if the acoustic mismatch at the crystal-helium interface is appreciable, Λ is a measure of the phonon mean free path (the order of magnitude of a crystal dimension) and v is an average acoustic propagation velocity. We shall ignore phonon diffusion, this being correct as we shall note for spins which are well coupled to one another. Rearrangement of the above expression yields

$$(T_P-T_B)/(T_S-T_P)=(\eta\Lambda v^2h^2N)/(48\pi k^2\Delta\nu T_1T_ST_P).$$

To emphasize the inadequacy of the lattice modes as a thermal reservoir for the spins we shall assume perfect matching ($\eta=1$). This assumption appears to be reasonable for hydrated crystals.[7,12,13,20] For the fully concentrated copper ammonium Tutton salts[12] we will take $\Lambda=L$, $L=$a crystal dimension $\approx10^{-1}$ cm, $v\approx2.5\times10^5$ cm/sec, $N=3\times10^{21}$ spins/cm^3, and $\Delta\nu\approx10^9$ cps. We assume for our estimate that $\Delta\nu\approx\Delta\nu_s$, the spin-resonance width. Since it is a common practice[7,12] to record recovery times in the region $T_S\approx T_P\approx T_B$, so as to discriminate against cross-relaxation effects which might be present in the initial portion of the decay, we will take $T_B\approx1.4$°K and appropriately[12] then $T_1\leqslant7$ msec. We find that $(T_P-T_B)/(T_S-T_P)\geqslant21$, suggesting a substantial bottleneck that should be readily detected. Orbach's[10] estimate is found to be numerically in error. Apart from a concentration dependence of T_1, one might expect the same value of $(T_P-T_B)/(T_S-T_P)$ in a crystal with a spin concentration of 1% and a linewidth of 10^7 cps.

Although the above equations are valid in predicting the occurrence of a bottleneck, it will be seen from Secs. IV and V that they are not useful in calculating accurately the extent of the bottleneck. This important point which is a major concern of this paper, can be seen as follows: For an inhomogeneously broadened line the acoustic modes "on speaking terms" with the spin system are those within the spin-resonance linewidth $\Delta\nu_s$ and $\Delta\nu\approx\Delta\nu_s$. In the absence of significant lattice imperfections or impurities, phonons can escape to the crystal surface only by diffusion; the rate of transfer of energy by this mechanism under bottleneck conditions is much slower than $\tau_{LB}^{-1}\rho(\nu)\Delta\nu k(T_P-T_B)$, where

[14] T. Holstein, Phys. Rev. **72**, 1212 (1947).
[15] T. Holstein, Phys. Rev. **83**, 1159 (1951).
[16] V. A. Veklenko, Zh. Eksperim. i Teor. Fiz. **36**, 204 (1959) [English transl.: Soviet Phys.—JETP **9**, 138 (1959)].
[17] The factor $\frac{1}{2}$ is present because a change of unity in the number of phonons represents a change of two in ΔN.
[18] J. H. Van Vleck, Phys. Rev. **59**, 730 (1941).
[19] R. Orbach, doctoral dissertation, University of California, 1960 (unpublished).
[20] D. L. Mills, Phys. Rev. **133**, A876 (1964); **134**, A306 (1964).

$\tau_{LB}\sim L/v$. As a result the above equations will underestimate the magnitude of the bottleneck. On the other hand for a homogeneously broadened line it will be seen that modes in the far wings of the line play a decisive role in the relaxation under bottleneck conditions, and the effective value of $\Delta\nu$ may be much larger than $\Delta\nu_s$. As a result the above equations will overestimate the magnitude of the bottleneck.

III. DIFFUSION OF IMPRISONED PHONONS

The physical problem which is presented is that of the escape of resonant phonons from an absorbing medium of paramagnetic centers. For inhomogeneously broadened resonance lines, the career of any particular phonon is a series of rapid transits from spin to spin alternating with longer periods of imprisonment of average length T_1. The environment of a typical phonon is opaque and spatial diffusion would appear to govern the kinetics of lattice energy transport. In subsequent sections of this paper we will consider this same problem for homogeneously broadened lines where a given spin has an emission frequency which is independent of the frequency at which it absorbed.

For spatial diffusion without spectral redistribution, a simple random walk equation can provide us with a rough estimate of the spin bath or diffusion time T_1'. If our geometry is an infinite slab of thickness L, then the net distance L' which an average phonon must diffuse in order to reach the bath[21] is approximately equal to $2L/3$ and is related to T_1' through the equation $L'^2=(2\Lambda^2/3)(T_1'/T_1)$, where Λ is the phonon mean free path, T_1 is the spin-lattice relaxation time (in this case the "step" time) and T_1'/T_1 is the number of steps. Since the lattice modes are more strongly coupled to the spins than to the bath, equilibration of the spins and modes requires that $(\Delta N/T_1)\approx(2\langle n\rangle\rho(\nu)\Delta\nu/\tau_{LS})$. The modes within $\Delta\nu$ are approximately at the same temperature as the spins; the other modes which are not "on good speaking terms" with the spins remain at the bath temperature. In this equation ΔN is the net number of spins per unit volume in the lower spin state, $\langle n\rangle\approx kT/h\nu$ is the phonon occupation number, $\Delta\nu$ is the range of participating lattice modes and in this case equals $\Delta\nu_s$ which is the full width of the spin resonance. The time τ_{LS}, which is defined by the above equation, is the reabsorption time of a phonon. It is assumed that $\tau_{LS}^{-1}\ll\Delta 2\pi\nu$.

Combining the equations we find for $\Lambda=v\tau_{LS}$, $h\nu\ll kT$, and for a temperature T common to the spins and the modes, that T_1' is given by

$$T_1'=T_1\left(\frac{h\nu}{kT}\right)^4\left[\frac{1}{2\sqrt{6}}\frac{NL}{\rho(\nu)\Delta\nu_s T_1 v}\right]^2. \tag{1}$$

[21] After a small time interval the temperature distribution of an initially uniformly excited sample should be $\propto\sin(\pi x/L)$. One-half the spins are within a distance $L/3$ from the slab face. Since the transport to the bath is typically not along a path which is perpendicular to the slab face the average net-distance traveled is $\approx(2L/3)$.

If one chooses to solve the equation $\partial\Delta N/\partial t=D\partial^2\Delta N/\partial^2 x$ directly,[3] one finds[22] from $T_1'=(L^2/\pi^2 D)$ a result identical to (1) except that the factor $[1/2(\sqrt{6})]$ is replaced by $(\sqrt{3}/4\pi)$.

It may be argued however that the appeal to analogy with diffusion is faulty. Anderson[4] has pointed out the great similarity between the trapping of resonant photons in gases and that of resonant phonons in paramagnetic crystals. We shall have more to say below about this similarity, but for the present we note that the former problem has been considered by Milne[23] who examined the emission and absorption processes associated with the escape of resonant quanta for a situation in which the motions of the atoms and any radiation frequency changes were ignored. Such a treatment would apply completely to a paramagnetic lattice at zero degrees absolute. In our notation his equation for one-dimensional flow is

$$\frac{\partial}{\partial x}\left[\frac{1}{\Delta N}\frac{\partial}{\partial x}\left\{\frac{1}{\Delta N}\left(N_2+T_{10}\frac{\partial N_2}{\partial t}\right)\right\}\right]=\beta^2 T_{10}\frac{\partial N_2}{\partial t}, \tag{2}$$

where $\beta=(2/v\rho(\nu)\Delta\nu_s T_{10})$, N_2 is the upper state spin density and T_{10} is the spin-lattice relaxation time at 0°K. This differs from the standard diffusion equation only in the second term. It is a consequence of the new term that T_1' must exceed T_{10}, i.e., that no harmonic can die away at a rate faster than T_{10}^{-1}. Milne solved this equation for the photon-gas case by the appropriate assumption that $\Delta N=N_1-N_2\approx N_1\approx N$. However our interest is in the case where $N_1\approx N_2$. If we make the substitution $N_2=\frac{1}{2}(N-\Delta N)$ and perform the indicated operations in (2), we find after dropping terms which fall off faster than N^{-2}, that

$$\frac{N}{\Delta N^3}\frac{\partial^2\Delta N}{\partial x^2}+\frac{T_{10}}{(\Delta N)^2}\frac{\partial^3\Delta N}{\partial x^2\partial t}=\beta^2 T_{10}\frac{\partial\Delta N}{\partial t}. \tag{3}$$

The diffusion constant[24] D of this equation is $\frac{1}{4}(\Lambda^2/T_1)$ instead of the usual $\frac{1}{3}(\Lambda^2/T_1)$. Since our concern throughout this paper will be with the region where $\Delta N\approx\Delta N_0$, we may linearize (3) and solve the resulting equation for $h\nu\ll kT$ in the same way that Milne solved (2) for $h\nu\gg kT$. For large opacity (severe trapping) we can neglect the second term in (3). Using[24] the equation $T_{10}\approx 2(kT/h\nu)T_1$, we obtain for a slab of thickness L the result

$$T_1'=T_1\left(\frac{h\nu}{kT}\right)^4\left[\frac{NL}{2\pi\rho(\nu)\Delta\nu_s T_1 v}\right]^2. \tag{4}$$

Apart from a factor of 1.6, (4) and (1) are in agreement.

[22] A. Bronwell, *Advanced Mathematics in Physics and Engineering* (McGraw-Hill Book Company, Inc., New York, 1953), p. 261.

[23] E. A. Milne, J. London Math. Soc. **1**, 40 (1926).

[24] For this purpose it is necessary to use the relation $T_{10}=[2\langle n\rangle+1]T_1$ which is derived in Appendix A.

For marginal imprisonment we find[23]

$$T_1'=T_1\left[1+\left(\frac{h\nu}{kT}\right)^2\frac{NL}{4\rho(\nu)\Delta\nu_s T_1 v}\right]. \tag{5}$$

As expected the size dependence changes from L^2 to L when the probability of reabsorption becomes small compared to the probability of capture by the walls. Equation (5) is applicable when $[h\nu/kT]^2[NL/4\rho(\nu)\times\Delta\nu_s T_1 v]\equiv\alpha\sim 1$. The condition $\alpha\ll 1$ is a criterion for judging when diffusion can be neglected for an inhomogeneously broadened spin resonance, and is of course equivalent to the condition that $T_S-T_P\gg T_P-T_B$ as discussed in Sec. II. One factor common to our treatments has been the assumption that absorption is uniform over a breadth $\Delta\nu_s$, i.e., the spin resonance is rectangular in shape. This is a good description of a resonance whose "core" is denied access to its "wings."

For the sake of completeness we will give Milne's result for $h\nu\gg kT$. For severe and marginal trapping, respectively we have

$$T_1'=T_{10}\left[\frac{2}{\pi}\frac{NL}{\rho\Delta\nu_s v T_{10}}\right]^2 \tag{4'}$$

and

$$T_1'=T_{10}\left[1+\frac{NL}{\rho(\nu)\Delta\nu_s v T_{10}}\right]. \tag{5'}$$

IV. HOLSTEIN'S APPROACH

In addition to calling attention to the similarity between the phonon bottleneck and the trapping of resonant photons in gases, Anderson[4] has pointed to the theoretical[14,15] and experimental[25] work of Holstein *et al.* in association with the photon-gas bottleneck. As Anderson[4] has emphasized, Holstein's success in obtaining experimental verification for his calculations depends upon the rapid spectral redistribution of energy within the line. The relatively transparent "wings" play a crucial role in the release of resonance radiation, and indeed for an arbitrary line shape without cutoff in the wings, Holstein has shown[14] that it is impossible to define a mean free path for resonant quanta (photons or phonons) in an infinite medium.

The inadequacy of the standard diffusion equation led Holstein to formulate the radiative transport of resonance excitation in terms of a Boltzmann-type integrodifferential equation for the density of excited atoms. In addition to calculating the imprisonment time Holstein has found the emergent radiation spectrum to suffer self-reversal[26] which is expected for a nonuniform density of excited atoms.

If we cast Holstein's result for severe trapping [Eqs. (1.1) and (6.5), Ref. 15] into our notation, and make the necessary modification appropriate to the condition $h\nu\ll kT$, then for approximate equilibration of the spins, modes and bath at a temperature T_B we find that for a Gaussian-shaped spin resonance

$$k(\nu)=k_G\exp\left\{-\left[\frac{(\nu-\nu_0)}{(\Delta\nu_s/2)}\right]^2\ln 2\right\} \tag{6}$$

and an infinite slab of thickness L,

$$T_1'=0.22\left(\frac{h\nu}{kT_B}\right)^2\frac{NL}{\rho(\nu)\Delta\nu_s v}\times\left[\ln\left\{\frac{(\ln 2)^{1/2}}{4\sqrt{\pi}}\left(\frac{h\nu}{kT_B}\right)^2\frac{NL}{\rho(\nu)\Delta\nu_s v T_1}\right\}\right]^{1/2}. \tag{7}$$

For a Lorentzian shape

$$k(\nu)=\frac{k_L}{1+[(\nu-\nu_0)/(\Delta\nu_s/2)]^2}, \tag{8}$$

$$T_1'=0.61T_1\left[\left(\frac{h\nu}{kT_B}\right)^2\frac{N}{\rho(\nu)\Delta\nu_s T_1}\frac{L}{v}\right]^{1/2}. \tag{9}$$

(See Appendix B for derivation of k_G and k_L.) Holstein has also solved the problem for the geometry of an infinite cylinder, and has indicated that for a rectangular line shape his transport equation reduces to the standard diffusion equation. Veklenko,[16] using a more analytical approach, has considered an infinite medium, and his results differ from Holstein's by factors less than 2. Veklenko has explicitly demonstrated that the diffusion of monochromatic radiation (inhomogeneously broadened resonance) is analogous to the diffusion of particles. In all cases the enclosure walls were assumed nonreflecting.

Before proceeding to the next section we shall consider in the context of Holstein's calculations our assumption that the inverse of the radiation quantum lifetime (τ_{LS}) is less than the spectral width of the resonance.

The equation for τ_{LS} was used in Sec. III (see also Appendix B) and is $\tau_{LS}=4(kT/h\nu)^2\rho(\nu)\Delta\nu T_1 N^{-1}$. For $T\approx 1°\mathrm{K}$, $\nu\approx 10^{10}$ cps, $\rho(\nu)=12\pi\nu^2 v^{-3}$, $v\approx 2.5\times 10^5$ cm/sec, $N=3\times 10^{21}$ spins/cm^3, and $\Delta\nu\approx 10^9$ cps, $(2\pi\tau_{LS})^{-1}\approx 5\times 10^4 T_1^{-1}$. Even if T_1 were $\approx 10^{-4}$ sec, the above assumption would be valid.

However, for photons and atoms, i.e., for the case in which Holstein's agreement with experiments[25] is good, $\tau\approx(8\pi\nu^2\Delta\nu\tau_{at}/Nc^3)$ and for $\nu\approx 10^{15}$ cps, $\Delta\nu\approx 10^9$ cps, $N\approx 10^{14}$ atoms/cm^3, and $\tau_{at}\approx 10^{-7}$ sec, we find that $(2\pi\tau)^{-1}=2\times 10^{11}\gg\Delta\nu\approx 10^9$ cps, and thus that the above assumption is grossly violated.

Holstein's analysis is based upon equations which are dependent upon the Einstein A and B coefficients, and which in turn are related by among other factors,

[25] D. Alpert, A. O. McCoubrey, and T. Holstein, Phys. Rev. **76**, 1257 (1949); **85**, 985 (1952); S. Heron, R. W. P. McWhirter, and E. H. Rhoderick, Proc. Roy. Soc. (London) **234**, 565 (1956).

[26] T. Holstein, Scientific Paper 1501, Westinghouse Research Laboratories, Pittsburgh, Pennsylvania, 1950 (unpublished).

the density of radiation modes $8\pi\nu^2/c^3$. A tacit assumption then in Holstein's computations is that the radiation modes are not essentially modified by interaction with the atoms; i.e., dispersion, which should be present for strong resonant coupling is neglected. In cases of severe trapping on the other hand, the phenomenon of specular reflection of resonance radiation[27] suggests that propagating modes may in fact not even exist near the resonance frequency. The resolution of the contradiction is related to the fact that the modes which are significant in transporting photons to the gas absorption cell walls are modes which lie in the wings of the resonance; these modes are much less strongly perturbed since there the atomic system is relatively transparent.

If we once again consider the fully concentrated Tutton salts[12] (Sec. II) where a roughly Gaussian shape is dominant we find that the observed proportionality of $T_1' \propto LT_B^{-2}$ decides strongly in favor of a Holstein-type equation.

Again for completeness we shall give Holstein's results for $h\nu \gg kT$. For the Gaussian and Lorentzian shapes, respectively we have

$$T_1' = 0.88 \frac{NL}{\rho(\nu)\Delta\nu_s v}\left[\ln\left\{\left(\frac{\ln 2}{\pi}\right)^{1/2}\frac{NL}{\rho(\nu)\Delta\nu_s v T_{10}}\right\}\right]^{1/2} \quad (7')$$

and

$$T_1' = 1.22 T_{10}\left[\frac{NL}{\rho(\nu)\Delta\nu_s v T_{10}}\right]^{1/2}. \quad (9')$$

V. BROADENING OF THE ENERGY DISTRIBUTION IN THE LATTICE

Thus far we have emphasized that the phonon bottleneck can lead to observed relaxation times $T_1' > T_1$ the intrinsic spin-lattice relaxation. In this section we will examine two approaches which enable us to calculate the spectral distribution of lattice energy in the presence of phonon trapping.

Let us first imagine that the paramagnetic sites in a crystalline rod of length L have been uniformly saturated. We then inquire as to the nature of the phonon spectrum which reaches one end. The radiation emitted by a layer of thickness dx is equal to $Ak(\nu)dx$, where $k(\nu)$ is the absorption coefficient characterizing the spin system and A is a constant. It is assumed that $k(\nu)$ is identical with the emission spectrum from a small volume (see Appendix C). The lattice modes suffer some attenuation as the phonons travel to the end of the rod so that the amount emerging is equal to $Ak(\nu)dx \exp[-k(\nu)(L-x)]$. The frequency distribution of phonons from the entire length is then

$$P(\nu) = A[1 - e^{-k(\nu)L}]. \quad (10)$$

If $k(\nu)L \ll 1$, $P(\nu) \propto k(\nu)$. When $k(\nu)L \gg 1$, $P(\nu)$ is independent of frequency until one is sufficiently far from the resonance "core" that $k(\nu)L \approx 1$. Self-reversal in the phonon spectrum has been precluded because of the assumption of a spatially uniform spin temperature. If $k(\nu)$ is symmetric about some frequency ν_0, then the spectral width of phonon excitation, $\Delta\nu_L$, is given by

$$2P(\nu_0 + \Delta\nu_L/2) = P(\nu_0). \quad (11)$$

If, furthermore, $k(\nu_0)L \gg 1$, we find that

$$k(\nu_0 + \Delta\nu_L/2) = \ln 2/L. \quad (12)$$

We may also note that the frequency ν_c which determines the absorption edge, i.e., the frequency at which a phonon can traverse a distance $\sim L$ before absorption by the spin system is given by the equation $I = I_0/e = I_0 \exp[-k(\nu_c)L]$. Thus the condition $k(\nu_c)L \approx 1$ indicates that $\Delta\nu_L/2 \approx |\nu_0 - \nu_c|$.

Using (6) and (8) and the values for k_G and k_L which can be obtained from the expression in Appendix B, we find that for a Gaussian line the spectral width of phonon excitation is

$$\Delta\nu_L = \frac{\Delta\nu_s}{(\ln 2)^{1/2}}\left\{\ln\left[\frac{1}{2(\pi \ln 2)^{1/2}}\left(\frac{h\nu}{kT_B}\right)^2 \times \frac{NL}{\rho(\nu)\Delta\nu_s T_1 v}\right]\right\}^{1/2} \quad (13)$$

and for a Lorentzian line

$$\Delta\nu_L = \Delta\nu_s\left[\frac{1}{2\pi \ln 2}\left(\frac{h\nu}{kT_B}\right)^2 \frac{NL}{\rho(\nu)\Delta\nu_s T_1 v}\right]^{1/2}. \quad (14)$$

For dilute samples the spin resonance line shape is Lorentzian if dipolar coupling is dominant.[28] However in the extreme wings a cutoff will occur since the spin-spin interaction will have some upper limit[28] given roughly by that for two spins in neighboring sites.

Another instructive approach towards examination of the phonon spectral distribution follows from examination of the individual emission and absorption processes. The net rate of change of the lower state spin density N_1 is

$$dN_1/dt = A_{21}N_2 + \langle n\rangle\rho(\nu)h\nu[B_{21}N_2 - B_{12}N_1]. \quad (15)$$

The Einstein coefficients are related by $A_{21} = T_{10}^{-1} = \rho(\nu)h\nu B_{12} = \rho(\nu)h\nu B_{21}$, and hence

$$d\Delta N/dt = 2A_{21}[\langle n+1\rangle N_2 - \langle n\rangle N_1]. \quad (16)$$

The net rate of change of the phonon density per unit frequency interval, $\langle n\rangle\rho(\nu)$, for a rectangular resonance of width $\Delta\nu_s$, is

$$\frac{d}{dt}\langle n\rangle\rho(\nu) = \frac{1}{2\Delta\nu_s}\frac{d\Delta N}{dt} - \frac{\rho(\nu)[\langle n\rangle - \langle n\rangle_B]}{\tau_{LB}}. \quad (17)$$

[27] A. C. G. Mitchell and M. W. Zemansky, *Resonance Radiation and Excited Atoms* (Cambridge University Press, Cambridge, England, 1961), pp. 31–34.

[28] C. Kittel and E. Abrahams, Phys. Rev. **90**, 238 (1953).

For an arbitrary line shape $f(\nu)$ the frequency dependence can be incorporated into either A_{21} or N_i of (16). If we assume that the spins and the modes to which the spins relax come into equilibrium rather rapidly, and that the net rate at which these modes change their populations is much smaller[9] than either the rate at which spin energy is converted into lattice quanta or the rate at which phonons are damped by a frequency-independent loss mechanism, we may write

$$f(\nu)A_{21}[\langle n+1\rangle N_2-\langle n\rangle N_1]=\frac{\rho(\nu)[\langle n\rangle-\langle n\rangle_B]}{\tau_{LB}}. \quad (18)$$

The emission and absorption spectra are assumed identical (Appendix C), and $\int f(\nu)d\nu=1$. One more assumption will be made which greatly simplifies the job of obtaining the distribution of phonon energy. This assumption is that all phonons have the same rate of absorption by the "bath," independent of frequency. If the "bath" is outside the crystal, τ_{LB} will depend upon the resonant scattering of phonons by the spins. We shall discuss this point further below; for our present purposes we will regard τ_{LB} as the lifetime of a phonon against decay to "sinks" which are distributed uniformly throughout the crystal.

If we solve (18) we find

$$\langle n(\nu)\rangle-\langle n\rangle_B=\left\{\frac{N\tau_{LB}f(\nu)}{2T_{10}}\left[1-\frac{T_B}{T_S}\right]\right\}\Bigg/\left[\frac{h\nu}{kT_B}\frac{N\tau_{LB}f(\nu)}{2T_{10}}+\rho(\nu)\right]. \quad (19)$$

We may determine $\Delta\nu_L$ from the equation

$$\langle n(\nu_0)\rangle-\langle n\rangle_B=2\left[\left\langle n\left(\nu_0+\frac{\Delta\nu_L}{2}\right)\right\rangle-\langle n\rangle_B\right].$$

For

$$\langle n\rangle_B\approx\left(\frac{kT_B}{h\nu}\right)$$

and $T_S\approx T_B$ we find for Gaussian and Lorentzian lines, respectively, that

$$\Delta\nu_L=\frac{\Delta\nu_s}{(\ln 2)^{1/2}}\left\{\ln\left[\frac{1}{2}\left(\frac{\ln 2}{\pi}\right)^{1/2}\left(\frac{h\nu}{kT_B}\right)^2\frac{N\tau_{LB}}{\rho(\nu)\Delta\nu_s T_1}\right]\right\}^{1/2} \quad (20)$$

and

$$\Delta\nu_L=\Delta\nu_s\left[\frac{1}{2\pi}\left(\frac{h\nu}{kT_B}\right)^2\frac{N\tau_{LB}}{\rho(\nu)\Delta\nu_s T_1}\right]^{1/2}. \quad (21)$$

Equations (20) and (21) are seen to be in good agreement with Eqs. (13) and (14). It follows that under bottleneck conditions, when the expressions within the square brackets are large compared to one, not only is $T_1'>T_1$, but also $\Delta\nu_L>\Delta\nu_s$.

Before going on to the next section we would like to emphasize that the approach just examined actually precludes the diffusion of phonons. It was pointed out in Sec. III that the spin-bath diffusion time T_1' could be obtained from a solution of $\partial\Delta N/\partial t=D\partial^2\Delta N/\partial^2 x$. This equation can be derived from

$$\frac{\partial}{\partial t}[\langle n\rangle\rho(\nu)\Delta\nu_s]-\frac{1}{2}\frac{\partial\Delta N}{\partial t}=D'\nabla^2[\langle n\rangle\rho(\nu)\Delta\nu_s],$$

which is a diffusion equation for the radiation density with a source term. If one multiplies (17) by $\Delta\nu_s$ and compares it with the above equation one finds that we have in effect assumed that either $\langle n\rangle\rho(\nu)\Delta\nu_s$ or $\nabla[\langle n\rangle\rho(\nu)\Delta\nu_s]$ is spatially uniform.

VI. ENERGY TRANSFER VIA LATTICE MODES

In this section the relaxation process is treated classically and phenomenologically in terms of the individual lattice modes. We obtain the "interruption width" of the modes, the spectral distribution of energy in the lattice, and the apparent relaxation time T_1' for the case of homogeneously broadened Lorentzian and Gaussian lines. The special case for which the interruption width becomes comparable to the linewidth is considered in the following section.

We discuss two extreme cases. In the first, the bath damping arises from a frequency-independent uniformly distributed absorption at the bath temperature T_B. In this case, for which the spin temperature T_S will also be uniform, the modes are the well-known solutions of the wave equation with totally reflecting boundaries, and all the modes extend uniformly throughout the crystal. An example would be the case in which the hot band of modes near ν_0 is damped primarily by phonon-phonon scattering near uniformly distributed anharmonicities (cracks or imperfections), in this way making contact with the continuum of modes at the bath temperature.

In the second and more usual case, the bath damping is localized at the crystal boundary. Following saturation by a uniform rf field the spin temperature is initially spatially uniform. As a result of spatial diffusion during the course of the relaxation, the local spin temperature will become a maximum at the crystal center and approach the bath temperature near the surface. We shall be concerned with the decay of this new distribution. Since the bath damping is localized at the crystal surface, heavily damped modes near ν_0 can no longer be treated as independent and as extending over the whole crystal volume. We make the approximation of considering only modes sufficiently far from ν_0 that the absorption length $\Lambda(\nu)\gtrsim L'$ where L' is a characteristic crystal dimension. This approximation is appropriate since at frequencies for which $\Lambda(\nu)\ll L'$ the self-reversal will cause the lattice temperature, as seen from the bath, to be very close to T_B.

The neglect of energy transfer at frequencies of strong self-reversal is equivalent to the neglect of spatial diffusion. The use of this approximation allows us to confine our attention to modes which extend over the whole crystal and which see the spatial average spin temperature. It will be found that the results for the second case are in close agreement with those of Holstein (Sec. IV).

We make the following assumptions. The spin resonance spectrum consists of a single ($S=\frac{1}{2}$) homogeneously broadened line which can be described by a local spin temperature T_S, and whose spin-lattice relaxation occurs by the "direct" process only. The bath temperature T_B is high compared to $h\nu_0/k$ but sufficiently low that the mean free path for both normal and umklapp[17,18] phonon-phonon scattering processes $\Lambda_S \gtrsim L'$. It follows that the modes are independent and that their response to damping by the bath and spin system can be treated according to the well-known theory[29] of the classical Brownian motion of a harmonic oscillator. It will also be assumed that the spin-density N is such that $N\lambda^3 \gg 1$ where λ is the acoustic wavelength at ν_0. In a typical experiment $N\lambda^3=(10^{20}) \times(5\times10^{-5})^3\approx10^7$. The spin system appears to the lattice modes as a resonance in the macroscopic acoustic dispersion and absorption of the crystal; incoherent scattering by individual spins is unimportant.

Consider modes which are solutions of the wave equation for a homogeneous medium. The damping constant $\gamma(\omega_M)$ of a mode at frequency $\nu_M=\omega_M/2\pi$ is given by

$$\gamma(\omega_M)=\frac{1}{\tau_{LB}}+\frac{1}{\tau_{LS}}\frac{f(\omega_M)}{f(\omega_0)}, \tag{22}$$

where τ_{LB} is the decay time due to the bath damping, τ_{LS} is the decay time of a mode at the spin resonance frequency $\omega_0=2\pi\nu_0$, and $f(\omega)$ is the spin resonance line shape normalized such that $\int f(\omega)d\omega=1$. The damping constant $\gamma(\omega_M)$ represents the "interruption width" of a lattice oscillator at ω_M. The equation of motion of an oscillator having an undamped frequency ω_M is given by Eq. (23) in the presence of the spin system and the bath:

$$\ddot{x}+\gamma(\omega_M)\dot{x}+\omega_M{}^2x=F_B(t)+F_S(t). \tag{23}$$

The oscillator coordinate is x, and $F_B(t)$ and $F_S(t)$ represent the random, incoherent, and rapidly fluctuating noise sources associated with the bath and the spin system. Since only modes which uniformly sample the whole crystal will be of interest here, the temperature of the source $F_S(t)$ will be the spatial average spin temperature T_S. In Eq. (23) we neglect the pulling of the oscillator frequency by the spin system. It will be shown in the following section that this pulling is negligible as long as the interruption width $\gamma(\omega_M)$ is small compared to the spin-resonance linewidth $\Delta\omega_S$.

[29] S. Chandrasekhar, Rev. Mod. Phys. **15**, 1 (1943).

The statistical properties of the noise source $F(t)$ are discussed in Ref. 29. For modes which extend over the whole crystal, the Fourier amplitudes $|F_B(\omega)|$ will have no important frequency dependence in the vicinity of ω_0. Since $|F_S(\omega)|^2$ is proportional to the rate of energy transfer at ω between the spin system and lattice the spectrum of $|F_S(\omega)|^2$ will be proportional to $f(\omega)$. The phases of $F_B(\omega)$ and $F_S(\omega)$ are random functions of frequency. We set

$$|F_B(\omega)|^2\equiv F_B{}^2 \tag{24}$$

$$|F_S(\omega)|^2\equiv F_S{}^2[f(\omega)/f(\omega_0)]. \tag{25}$$

The response of an ω_M mode at the driving frequency ω is given by Eq. (26):

$$x(\omega)=\frac{F_B(\omega)+F_S(\omega)}{\omega_M{}^2-\omega^2-i\omega\gamma(\omega_M)}. \tag{26}$$

The energy stored in an ω_M mode between ω and $\omega+d\omega$ is $W(\omega_M,\omega)d\omega$, where

$$W(\omega_M,\omega)=\tfrac{1}{4}m(|\dot{x}(\omega)|^2+\omega_M{}^2|x(\omega)|^2)$$
$$=\frac{m}{2}\frac{|F_B(\omega)|^2+|F_S(\omega)|^2}{4(\omega_M-\omega)^2+\gamma^2(\omega_M)}, \tag{27}$$

where m is an inertial parameter. We evaluate $m|F_B|^2$ and $m|F_S|^2$ from the requirements of equipartition of energy. The total energy stored in the ω_M mode, $W(\omega_M)=\int d\omega W(\omega_M,\omega)$, must approach the limiting values kT_B and kT_S as $1/\tau_{LS}\to0$ and $1/\tau_{LB}\to0$, respectively. It follows from Eqs. (22), (24), (25), and (27) that

$$\begin{aligned} mF_B{}^2&=4kT_B/\pi\tau_{LB},\\ mF_S{}^2&=4kT_S/\pi\tau_{LS}, \end{aligned} \tag{28}$$

and that the energy stored in the ω_M mode is

$$W(\omega_M)=\left[kT_B\left(\frac{1}{\tau_{LB}}\right)+kT_S\left(\frac{1}{\tau_{LS}}\right)\frac{f(\omega_M)}{f(\omega_0)}\right]\Bigg/ \left[\frac{1}{\tau_{LB}}+\frac{1}{\tau_{LS}}\frac{f(\omega_M)}{f(\omega_0)}\right]. \tag{29}$$

Let ρ be the density of lattice modes in the vicinity of ω_0. From Eq. (29) the energy stored in the lattice between ω and $\omega+d\omega$ is $W(\omega)$ and is given by

$$W(\omega)=\rho\left[kT_B+\frac{(kT_S-kT_B)}{[\tau_{LS}f(\omega_0)/\tau_{LB}f(\omega)]+1}\right] \tag{30}$$

and the total stored energy in excess of the equilibrium

value is

$$\Delta W=\int_0^\infty (W(\omega)-\rho kT_B)d\omega$$

$$=\int_0^\infty d\omega\left[\frac{\rho(kT_S-kT_B)}{[\tau_{LS}f(\omega_0)/\tau_{LB}f(\omega)]+1}\right]. \quad (31)$$

The spectrum of the lattice excitation energy $W(\omega)-\rho kT_B$ is considerably broader than the linewidth $\Delta\omega_S$ of the spin resonance when $\tau_{LB}>\tau_{LS}$. The frequencies at which the spectrum has dropped to half-maximum intensity are the roots of the equation

$$\frac{f(\omega)}{f(\omega_0)}=\frac{1}{2+\tau_{LB}/\tau_{LS}}. \quad (32)$$

The spectral widths of lattice excitation from Eq. (32) for various line shapes are summarized below.

Since all the modes under consideration transfer energy to the bath with a damping constant τ_{LB}, we obtain

$$\frac{\hbar\omega}{2}\frac{d}{dt}(\Delta N_0-\Delta N)=-\frac{\Delta W}{\tau_{LB}}=-\frac{C_S(T_S-T_B)}{T_1'}, \quad (33)$$

where C_S is the heat capacity of the spin system and T_1' is the apparent relaxation time. It has been assumed that $T_S-T_B\ll T_B$ and that the heat capacity of the participating lattice modes is small compared to C_S. For an $S=\frac{1}{2}$ line,

$$C_S=(Nk/4)(\hbar\omega/kT_B)^2.$$

From Eqs. (31) and (33), T_1' is given by

$$\frac{1}{T_1'}=\frac{k\rho}{C_S\tau_{LS}f(\omega_0)}\int\frac{f(\omega)d\omega}{1+[f(\omega)/f(\omega_0)](\tau_{LB}/\tau_{LS})}. \quad (34)$$

In the limit as $\tau_{LB}/\tau_{LS}\to 0$, $T_1'\to T_1$. It follows that

$$T_1=C_S\tau_{LS}f(\omega_0)/k\rho \quad (35)$$

and

$$\frac{1}{T_1'}=\frac{1}{T_1}\int\frac{f(\omega)d\omega}{1+[f(\omega)/f(\omega_0)](\tau_{LB}/\tau_{LS})}. \quad (36)$$

Equation (36) is a general expression for the apparent relaxation time T_1' in terms of the true relaxation time and an integral over the lattice-mode frequencies participating in the relaxation.

Case I: Uniformly distributed losses at temperature T_B damp all the lattice modes at rate $1/\tau_{LB}$. The integral in Eq. (36) extends over all the lattice modes near ω_0. For Lorentzian, Gaussian, and a hypothetical rectangular line shape the results are summarized below. We denote by $\Delta\omega_L$ the frequency width at half-maximum intensity of the excess lattice excitation as determined from Eq. (32). The interruption width of a lattice mode at ω_0 is denoted $\Delta\omega_M=\gamma(\omega_0)$. The spin resonance linewidth at half-maximum intensity is $\Delta\omega_S$.

Lorentzian:

$$f(\omega)=\frac{\Delta\omega_S/2\pi}{(\omega-\omega_0)^2+(\Delta\omega_S/2)^2},$$

$$T_1'=T_1(1+\tau_{LB}/\tau_{LS})^{1/2}$$

$$=T_1\left[1+\left(\frac{\hbar\omega}{kT_B}\right)^2\frac{N\tau_{LB}}{2\pi\rho\Delta\omega_S T_1}\right]^{1/2}, \quad (37)$$

$$\Delta\omega_L=\Delta\omega_S(1+\tau_{LB}/\tau_{LS})^{1/2},$$

$$\Delta\omega_M=1/\tau_{LS}+1/\tau_{LB}, \quad (38)$$

$$\tau_{LS}=\pi k\rho T_1\Delta\omega_S/2C_S.$$

Gaussian:

$$f(\omega)=\frac{2}{\Delta\omega_S}\left(\frac{\ln 2}{\pi}\right)^{1/2}\exp\left\{-\left[\frac{2(\ln 2)^{1/2}(\omega-\omega_0)}{\Delta\omega_S}\right]^2\right\}, \quad (39)$$

$$T_1'=T_1\left[\frac{2}{\sqrt{\pi}}\int_0^\infty\frac{dx}{e^{x^2}+\tau_{LB}/\tau_{LS}}\right]$$

$$\simeq\frac{\sqrt{\pi}}{2}T_1\frac{\tau_{LB}}{\tau_{LS}}\left[\ln\left(\frac{\tau_{LB}}{\tau_{LS}}\right)\right]^{-1/2}, \quad \frac{\tau_{LB}}{\tau_{LS}}\gg 1$$

$$\simeq\frac{(\ln 2)^{1/2}}{4}\left(\frac{\hbar\omega}{kT_B}\right)^2\frac{N\tau_{LB}}{\Delta\omega_S\rho}$$

$$\times\left\{\ln\left[\frac{1}{2}\left(\frac{\ln 2}{\pi}\right)^{1/2}\left(\frac{\hbar\omega}{kT_B}\right)^2\frac{N\tau_{LB}}{\Delta\omega_S\rho T_1}\right]\right\}^{-1/2}, \quad (40)$$

$$\Delta\omega_L=\Delta\omega_S\left[\frac{\ln(2+\tau_{LB}/\tau_{LS})}{\ln 2}\right]^{1/2},$$

$$\Delta\omega_M=1/\tau_{LS}+1/\tau_{LB}, \quad (41)$$

$$\tau_{LS}=\left(\frac{\pi}{\ln 2}\right)^{1/2}\frac{k\rho T_1\Delta\omega_S}{2C_S}.$$

Rectangular:

$$f(\omega)=\frac{1}{\Delta\omega_S}, \quad \omega_0-\frac{\Delta\omega_S}{2}\le\omega\le\omega_0+\frac{\Delta\omega_S}{2}$$

$$=0, \quad \omega>\omega_0+\frac{\Delta\omega_S}{2}, \quad \omega<\omega_0-\frac{\Delta\omega_S}{2},$$

$$T_1'=T_1(1+\tau_{LB}/\tau_{LS})$$

$$=T_1\left[1+\left(\frac{\hbar\omega}{kT_B}\right)^2\frac{N\tau_{LB}}{4\rho\Delta\omega_S T_1}\right], \quad (42)$$

$$\Delta\omega_L=\Delta\omega_S,$$

$$\Delta\omega_M=1/\tau_{LS}+1/\tau_{LB}, \quad (43)$$

$$\tau_{LS}=k\rho T_1\Delta\omega_S/C_S.$$

Case 2: Damping by the bath occurs at the crystal surface only. In the approximation described earlier, we consider only modes having an absorption length $\Lambda \gtrsim L'$ where L' is a characteristic crystal dimension. As a crystal geometry we take an infinite plane parallel slab of thickness L. The rate at which energy leaks to the bath for a wave traveling at an angle θ to the surface normal is $(dW/dt)=fW/(v/L\cos\theta)$, where f is the fractional energy loss per transit and $(v/L\cos\theta)$ is the transit time between surfaces. The average damping constant averaged over solid angle is therefore $1/\tau_{LB}=fv/2L$. We shall consider the case[20] in which the acoustic mismatch at the surface is small and $f\sim 1$.

The apparent relaxation time T_1' is calculated from Eq. (36) by integrating only over frequencies for which the lattice modes are effective in transmitting energy to the surface. An approximate cutoff frequency ω_C is that for which the damping length $v\tau_{LS}(\omega_C)\approx L/1.5$. At ω_C the penetration depth normal to the surface averaged over modes in all directions is $L/3$. One-half of the spins are within this distance of the surface.[21] Notice that although T_S-T_B is spatially nonuniform, the absorption length which is proportional to T_S is essentially uniform when $T_S-T_B\ll T_B$. The results are as follows for the case of a large bottleneck, $\tau_{LB}\gg\tau_{LS}$. In these equations $\tau_{LB}=2L/v$ and the cutoff frequency ω_C is defined by $\tau_{LS}f(\omega_0)/f(\omega_C)=L/1.5v=\tau_{LB}/3$.

Lorentzian:

$$\omega_C=\omega_0\pm(\Delta\omega_S/2)(\tau_{LB}/3\tau_{LS})^{1/2},$$

$$T_1'=1.5T_1(\tau_{LB}/\tau_{LS})^{1/2}$$

$$=0.85T_1\left[\left(\frac{\hbar\omega}{kT_B}\right)^2\frac{N}{\rho\Delta\omega_S}\frac{L}{vT_1}\right]^{1/2}. \tag{44}$$

Gaussian:

$$\omega_C=\omega_0\pm\frac{\Delta\omega_S}{2}\left[\frac{\ln(\tau_{LB}/3\tau_{LS})}{\ln 2}\right]^{1/2},$$

$$T_1'=T_1\left[\frac{2}{\sqrt{\pi}}\int_{[\ln(\tau_{LB}/3\tau_{LS})]^{1/2}}^{\infty}\frac{dx}{e^{x^2}+\tau_{LB}/\tau_{LS}}\right]^{-1} \tag{45}$$

$$\approx 1.6T_1\frac{\tau_{LB}}{\tau_{LS}}\left[\ln\frac{\tau_{LB}}{\tau_{LS}}\right]^{1/2}$$

$$=0.8\left(\frac{\hbar\omega}{kT_B}\right)^2\frac{N}{\rho\Delta\omega_S}\frac{L}{v}$$

$$\times\left\{\ln\left[\frac{1}{2}\left(\frac{\hbar\omega}{kT_B}\right)^2\frac{N}{\rho\Delta\omega_S T_1}\frac{L}{v}\right]\right\}^{1/2}. \tag{46}$$

Rectangular:

$$\omega_C=\omega_0\pm\Delta\omega_S/2,$$

$$1/T_1'=0. \tag{47}$$

The approximations made in the evaluation of the Gaussian integrals of Eqs. (39) and (45) are shown in Appendix D. Comparison of T_1' for the Lorentzian and Gaussian lines [Eqs. (44) and (46)] with the same expressions derived from Holstein's theory, Eqs. (9) and (7), respectively, shows the same functional dependence and numerical agreement to within small factors, 1.4 and 3.6, respectively.[30]

In the complete absence of wings, the present method indicates an infinite relaxation time for the nonphysical rectangular line. The method of Holstein, on the other hand, would lead to the diffusion equation and a solution for T_1' proportional to L^2 for this case. The satisfactory agreement of the present results with Holstein's theory for the Gaussian line, where wings are present but not extensive, suggests that the present method is generally useful for physically important line shapes and gives results equivalent to those of the latter theory. It is interesting to note the agreement between T_1' predicted by the mode theory for the rectangular line shape [Eq. (42), case I] and that predicted by the diffusion theory of Milne for the case of marginal imprisonment [Eq. (5)]. The comparison is made with $\tau_{LB}\approx 2L/v$ in Eq. (42). The good agreement is expected since for the case of marginal imprisonment all the modes of the crystal become effective in carrying energy to the surface.

We conclude that a good approximation to T_1' can be obtained in the case of an extreme bottleneck by neglect of the diffusion energy transport near the line center, and consideration of energy transport by extended lattice modes in the wings.

VII. CASE OF THE LATTICE MODE INTERRUPTION RATE GREATER THAN THE SPIN-RESONANCE LINEWIDTH

Various authors have discussed the possibility of the phonon interruption width $\Delta\omega_M=1/\tau_{LS}$ becoming comparable to or greater than the spin-resonance linewidth $\Delta\omega_S=2/\tau_S$. It was conjectured in an early paper of Van Vleck[1] and more recently by Townes, Alsop, and the present authors,[3] that when $\Delta\omega_M>\Delta\omega_S$ the modes available for transfer of energy to the bath are those within the frequency range $\Delta\omega_M$ rather than within the smaller band $\Delta\omega_S$. This broadening of individual modes $(\Delta\omega_M)$ is not to be confused with the broadening of the lattice mode spectrum $(\Delta\omega_L)$ described in the previous section.

When a substantial phonon bottleneck occurs, say $\tau_{LB}/\tau_{LS}\sim 10^2$, the mode width $\Delta\omega_M$ will often begin to approach $\Delta\omega_S$. For a typical lattice-bath time of

[30] One is not free to choose a damping length $<L/1.5$ in order to make both equations agree exactly since one would then have to contend with the fact that on the average, some modes would have energy removed by resonant interactions with spins and that the energy would very likely be directed back into the interior of the crystal. Our present estimate of $v\tau_{LS}(\omega_C)$ assures that on the average a phonon can reach the surface uninterrupted if the average spin is at a distance of $L/3$ from the bath.

$\tau_{LB}=10^{-6}$ sec, and $\tau_{LB}/\tau_{LS}=10^2$, $\Delta\nu_{LS}\sim 5$ gauss, already comparable with the width of a narrow spin resonance. Since even shorter times τ_{LS} may be found in certain materials, the question of extreme mode widths is important.

According to an argument similar to Anderson's,[4] a mode cannot have an interruption width $\Delta\omega_M>\Delta\omega_S$, since energy conservation would be violated in the reabsorption by the spin system of phonons having energy less well-defined than $\Delta\omega_S$. The course of events as $1/\tau_{LS}$ approaches and exceeds $\Delta\omega_S$ involves an apparent paradox.

It is pointed out in this section that the "paradox" is resolved by taking into account the reactive coupling between the spin system and the lattice modes. It will be shown that when $1/\tau_{LS}$ approaches $\Delta\omega_S$ separate spin and acoustic resonances no longer occur near ω_0. We consder specifically the case of a spin system obeying the Bloch equations, where the bath damping is uniformly distributed over the lattice (case I of the previous section), and for which the lattice excitation can be decomposed into modes extending over the whole crystal. It will again be assumed that phonon-phonon scattering can be ignored and that $kT\gg h\nu$.

For a spin system obeying the Bloch equations, Jacobsen and Stevens[31] have shown that the coupling between ultrasonic waves and the spin system leads to a dispersion relation of the form

$$k^2=\frac{\omega^2}{v^2}\left(1+\frac{2/\tau_S\tau_{LS}}{\omega_0^2-\omega^2-2i\omega/\tau_S}\right). \tag{48}$$

In Eq. (48) the coupling constant and other parameters of Eq. (8) of Ref. 31 have been expressed as τ_S and the parameter τ_{LS}, the latter denoting as usual the energy damping time of a lattice wave at ω_0. The velocity v is the acoustic velocity, τ_S is equal to T_2, and ω_0 is the perturbed spin-resonance frequency. For frequencies close to ω_0, and in the presence of the small lattice bath damping $1/\tau_{LB}$, Eq. (48) becomes

$$k=\frac{\omega}{v}\left[1+\frac{i}{2\omega\tau_{LB}}+\frac{(1/2\tau_{LS})(1/\omega_0\tau_s)}{\omega_0-\omega-i/\tau_S}\right]. \tag{49}$$

The imaginary part of Eq. (49) corresponds to a reciprocal energy damping time of

$$\left[\frac{1}{\tau_{LB}}+\frac{1}{\tau_{LS}}\frac{1}{(\omega-\omega_0)^2\tau_S^2+1}\right]$$

as described for a Lorentzian line in the previous section.

Consider a lattice mode having a frequency $\omega_M=ck$ in the absence of the spin system. The perturbed frequency in the presence of the spin system is obtained from the solution of Eq. (49) with k set equal to ω_M/v

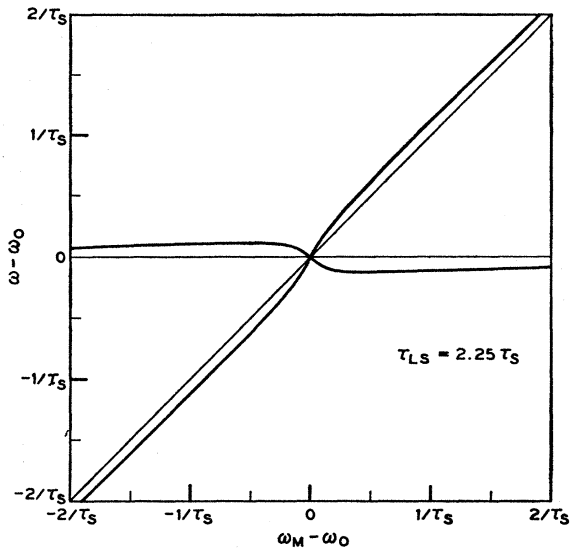

FIG. 1. Real part of ω as a function of ω_M for ω_M near ω_0. Weak-coupling case, $\tau_{LS}>2\tau_S$. The acoustic branch (slope $\sim$1) and the spin-wave branch (slope $\sim$0) are distinct.

since we are interested in the time decay of a mode which extends uniformly over the whole crystal, i.e., real k. Were we interested in the spatial decay of energy, k would be complex. The general solution is

$$\omega=\frac{1}{2}\left(\omega_M-\frac{i}{2\tau_{LB}}\right)+\frac{1}{2}\left(\omega_0-\frac{i}{\tau_S}\right)$$
$$\pm\frac{1}{2}\left\{\left[\left(\omega_0-\frac{i}{\tau_S}\right)-\left(\omega_M-\frac{i}{2\tau_{LB}}\right)\right]^2+\frac{2}{\tau_{LS}\tau_S}\right\}^{1/2}. \tag{50}$$

In the *extreme weak coupling* case the condition for the binomial expansion of (50) is

$$\frac{1}{\tau_{LS}}\ll\frac{1}{2\tau_S}[(\omega_0-\omega_M)^2\tau_S^2+1],$$

assuming that $2\tau_{LB}\gg\tau_S$. The roots of (50) then have the limiting values

$$\omega_{ac}=\omega_M-\frac{i}{2\tau_{LB}}-\frac{i}{2\tau_{LS}}\frac{1}{(\omega_0-\omega_M)^2\tau_S^2+1}$$
$$-\frac{\tau_S}{2\tau_{LS}}\frac{\omega_0-\omega_M}{(\omega_0-\omega_M)^2\tau_S^2+1}, \tag{51}$$

$$\omega_{sp}=\omega_0-\frac{i}{\tau_S}+\frac{i}{2\tau_{LS}}\frac{1}{(\omega_0-\omega_M)^2\tau_S^2+1}$$
$$+\frac{\tau_S}{2\tau_{LS}}\frac{\omega_0-\omega_M}{(\omega_0-\omega_M)^2\tau_S^2+1}. \tag{52}$$

The first solution (51), having a frequency close to the unperturbed mode frequency ω_M, represents an

[31] E. H. Jacobsen and K. W. H. Stevens, Phys. Rev. **129**, 2036 (1963).

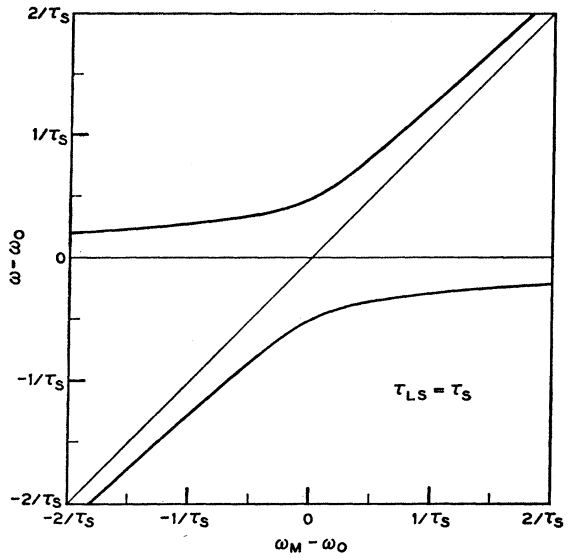

FIG. 2. Strong coupling case $\tau_{LS}<2\tau_S$. Near $\omega=\omega_0$ the branches represent composite spin-acoustic waves.

acoustic branch with a small admixture of spin energy and is illustrated qualitatively by the diagonal branch in Fig. 1. These are the modes considered in the previous section. The contribution to the real part of ω_{ac} represents a maximum pulling of $1/4\tau_{LS}$ at $\omega_M=\omega_0\pm 1/\tau_S$ and was previously neglected (Sec. VI) in the approximation that $1/4\tau_{LS}\ll 1/\tau_S$. This is *a fortiori* justified since the weak-coupling condition, used to derive (51) and (52), was $1/\tau_{LS}\ll 1/2\tau_S$. The imaginary part indicates a mode width of $(1/\tau_{LB}+1/\tau_{LS})$ at $\omega_M=\omega_0$.

The second solution has a frequency close to ω_0 and represents a transverse spin wave branch having a small admixture of acoustic energy. In the weak-coupling case

$$|\partial\omega_{sp}/\partial k|\lesssim(\tau_S/2\tau_{LS})v;$$

these waves will propagate negligible energy in comparison with the acoustic branch. This solution is illustrated qualitatively by the horizontal branch in Fig. 1.

In the *extreme strong coupling* case

$$\frac{1}{\tau_{LS}}\gg\frac{1}{2\tau_S}[1+\tau_S^2(\omega_0-\omega_M)^2]$$

and the roots of Eq. (50) have the limiting values

$$\omega_1=\tfrac{1}{2}(\omega_0+\omega_M)+\left(\frac{1}{2\tau_S\tau_{LS}}\right)^{1/2}+\frac{(2\tau_S\tau_{LS})^{1/2}}{8}\left[(\omega_0-\omega_M)^2-\frac{1}{\tau_S^2}\right]-\frac{i}{2}\frac{1}{\tau_S}-\frac{i}{4}\left(\frac{2\tau_{LS}}{\tau_S}\right)^{1/2}(\omega_0-\omega_M),\quad(53)$$

$$\omega_2=\tfrac{1}{2}(\omega_0+\omega_M)-\left(\frac{1}{2\tau_S\tau_{LS}}\right)^{1/2}-\frac{(2\tau_S\tau_{LS})^{1/2}}{8}\left[(\omega_0-\omega_M)^2-\frac{1}{\tau_S^2}\right]-\frac{i}{2}\frac{1}{\tau_S}+\frac{i}{4}\left(\frac{2\tau_{LS}}{\tau_S}\right)^{1/2}(\omega_0-\omega_M).\quad(54)$$

In Eqs. (53) and (54) the relatively small lattice bath damping has been ignored. Near resonance $\omega_M=\omega_0$ the two solutions are split by $(\Delta\omega_S/2)(2\tau_S/\tau_{LS})^{1/2}$ and represent neither pure acoustic, nor pure spin waves but composite waves in which acoustic and spin energy are interchanged at a rate $\sim(\Delta\omega_S/2)(2\tau_S/\tau_{LS})^{1/2}$. Each component has a damping time of $2\tau_S$ at resonance.

The appearance of the splitting at the transition between weak and strong coupling can be seen exactly from the general solution [Eq. (50)] at the resonance frequency $\omega_M=\omega_0$. For the *weak-coupling* region, defined by $1/\tau_{LS}<1/2\tau_S$

$$\omega_{ac}=\omega_0-\frac{i}{2}\left[\frac{1}{\tau_S}-\left(\frac{1}{\tau_S^2}-\frac{2}{\tau_{LS}\tau_S}\right)^{1/2}\right],\quad(55)$$

$$\omega_{sp}=\omega_0-\frac{i}{2}\left[\frac{1}{\tau_S}+\left(\frac{1}{\tau_S^2}-\frac{2}{\tau_{LS}\tau_S}\right)^{1/2}\right].\quad(56)$$

As $1/\tau_{LS}$ approaches $1/2\tau_S$ the frequencies of the acoustic and spin branches remain degenerate and the damping rates increase and decrease, respectively, toward $1/2\tau_S=\Delta\omega_S/4$. For the *strong-coupling* region, defined by $1/\tau_{LS}\geq 1/2\tau_S$

$$\omega_{1,2}=\omega_0\pm\frac{1}{2}\left[\frac{2}{\tau_{LS}\tau_S}-\frac{1}{\tau_S^2}\right]^{1/2}-\frac{i}{2\tau_S}.\quad(57)$$

As $1/\tau_{LS}$ increases beyond $1/2\tau_S$ the two solutions are split by $(2/\tau_{LS}\tau_S-1/\tau_S^2)^{1/2}$ and each component retains the fixed damping time of $2\tau_S$. Figures 1 and 2 illustrate quantitatively the intermediate coupling region ($\tau_{LS}\approx 2\tau_S$) for the cases $\tau_{LS}=2.25\ \tau_S$ and $\tau_{LS}=\tau_S$, respectively.

The apparent paradox of a pure acoustic mode having an interruption rate $1/\tau_{LS}$ greater than $1/\tau_S$ arises only when the reactive coupling between spins and lattice is neglected. Physically, when a lattice mode can deliver energy to the spin system at a rate $1/\tau_{LS}\gg 1/\tau_S$ the energy can be interchanged many times before the spin wave decays via dipole-dipole interactions, the interchange giving rise to the splitting $(2/\tau_{LS}\tau_S-1/\tau_S^2)^{1/2}$. The interaction of acoustic waves with a spin system is closely analogous to the inter-

action of electromagnetic waves with the optical modes of crystals.[32]

Since a continuous distribution of modes will be excited near ω_0 during the relaxation process, it will be difficult to detect the splitting experimentally during relaxation.

VIII. CONCLUSION

In the preceding sections we have demonstrated that a phonon bottleneck will occur in pmr when the rate of lattice-bath energy transfer *via* lattice modes within the spin resonance linewidth $\Delta\nu_s$ is less than the rate of spin-lattice energy transfer. This condition is given by the inequality $\Delta N/2T_1 > \langle n\rangle\rho(\nu)\Delta\nu_s/(L/v)$.

If the paramagnetic resonance line is inhomogeneously broadened (Sec. III), the wings of the line will cool quickly leaving the bulk of the energy in a hot central region in which phonons *diffuse* to the surface. In the approximation that the central region has a rectangular shape and width $\Delta\nu_s$, the apparent relaxation time T_1' was found to be proportional to $N^2L^2T_1^{-1}\Delta\nu_s^{-2}T_B^{-4}$. We note that $T_1' \propto L^2$ and that the escape of energy is governed completely by diffusion. In many cases T_1' will be much longer than T_1; however the spectral width of lattice excitation will not differ significantly from $\Delta\nu_s$.

If the line is homogeneously broadened (Secs. IV and V) the energy transfer under bottleneck conditions occurs primarily in the wings of the line. For Gaussian and Lorentzian lines the apparent relaxation times are proportional to

$$NL\Delta\nu_s^{-1}T_B^{-2}$$

and

$$N^{1/2}L^{1/2}T_1^{1/2}\Delta\nu_s^{-1/2}T_B^{-1},$$

respectively. These proportionalities are valid as the spin temperature approaches the bath temperature T_B and do not include slowly varying $(\ln)^{1/2}$ dependences discussed in detail above. In many cases T_1' will be much longer than T_1; for homogeneously broadened lines the bandwidth of lattice excitation $\Delta\nu_L$ will then be significantly broader than the spin-resonance linewidth $\Delta\nu_s$, reflecting the important role in energy transfer played by the lattice modes in the wings.

We conclude from Sec. V that energy transfer to the surface in the case of a bottlenecked homogeneously broadened line is accurately described in terms of acoustic modes extending throughout the crystal and having frequencies in the wings of the spin resonance. The neglect of the strongly perturbed modes near the line center where energy transfer occurs by diffusion is justified by the self-reversal effect accompanying a strong bottleneck. Although the width of lattice excitation may greatly exceed the spin-resonance linewidth, no violation of energy conservation of the type described by Anderson occurs, since energy absorbed by the spins undergoes spectral diffusion in a time short compared to T_1.

When the acoustic mode interruption rate is sufficiently high to approach the spin resonance linewidth, the (ω,k) dispersion curves describing the spin resonance and the acoustic waves no longer cross at resonance but split into two unconnected branches, separated in frequency at resonance by $\Delta\omega=(\Delta\omega_S\Delta\omega_M-\Delta\omega_S^2/4)^{1/2}$. Near resonance the two branches represent composite transverse spin wave–acoustic modes. The "paradox" of an acoustic mode broader than the spin resonance does not arise since acoustic modes and a spin resonance can no longer be separately defined under the conditions assumed for the "paradox." Although the acoustic mode width $\Delta\omega_M$ in this sense can never exceed the spin-resonance linewidth $\Delta\omega_S$, it will be apparent that even when $\Delta\omega_M \ll \Delta\omega_S$ the spectral width of lattice mode excitation $\Delta\omega_L$ may be very large, i.e., $\Delta\omega_L \gg \Delta\omega_S$, and represents an important feature of the relaxation process.

Faughnan and Strandberg[9] have solved the coupled differential equations (16) and (17). Their numerical solution and a quasisteady-state approximation (i.e., $\langle\dot{n}\rangle\approx 0$) were in agreement and in our notation they obtained

$$T_1'=T_1+\frac{\Delta N_0}{[2\langle n\rangle_0+1]\rho(\nu)\Delta\nu}\tau_{LB}. \tag{58}$$

Scott and Jeffries[7] linearized the same equations in the limit $\Delta N\approx\Delta N_0$, also obtaining (56) and an equation for the phonon damping time constant τ_{LS}

$$\tau_{LS}=\frac{[2\langle n\rangle_0+1]\rho(\nu)\Delta\nu}{\Delta N_0}T_1. \tag{59}$$

Both groups assumed the effective width of lattice excitation $\Delta\nu$ to be given by $\Delta\nu_s$, and they neglected diffusion. We have demonstrated that in general these assumptions are not simultaneously valid. However, for a homogeneously broadened Gaussian resonance whose wings are not extensive, $\Delta\nu$ may not be very different from $\Delta\nu_s$ and hence Eq. (58) with $\Delta\nu=\Delta\nu_s$ can be expected to give a reasonable estimate[7] of T_1' for this case. Although Scott and Jeffries[7] give no discussion of their second derived time constant, it is clear from (59) that it is the phonon reabsorption time, which has been amply discussed from several points of view in this paper.

The good agreement that we have found between our results and those of Holstein[14,15] and Veklenko[16] suggests that our simpler approach can give some physical insight into the phonon bottleneck. Since we have assumed that phonons are transported to the bath

[32] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, Oxford, England, 1956), pp. 82–100.

in a time $\sim L/v$ over some range of modes which we designate as δ, it is clear from our agreement with Holstein that the bottleneck does not have its origin in the relatively slow diffusion of energy to the surface, and that solution of the spatial transport problem can be avoided. Nor does the bottleneck lie in the spectral redistribution of energy since we have assumed that the homogenization processes which act within the resonance to transfer energy to the "wings," are operative in a time which is much less than any time constant in our treatment. For a bottleneck associated with a homogeneously broadened resonance, $T_1'>T_1$ and can be written in the form

$$T_1'\sim\left[\frac{\Delta N}{2\langle n\rangle\rho(\nu)\delta}\right]\frac{L}{v}.$$

The bracketed portion is the number of quanta to be delivered to the bath divided by the number of available carriers. The paucity of the latter indicates that T_1' may be thought of as the number of traversals of the crystal which a phonon must make multiplied by the traversal time.

Note added in proof. Direct and striking evidence of a phonon bottleneck is found in recent observations of the relaxation of an *inverted* spin system [W. J. Brya and P. E. Wagner, Phys. Rev. Letters **14**, 431 (1965)]. In this experiment a population inversion is suddenly established by a microwave pulse in a spin system suspected of phonon bottleneck relaxation. Following a short delay a "phonon avalanche" occurs in which the spin temperature returns to near its equilibrium value in a time *short* compared to T_1. Brya and Wagner interpret this behavior as (1) an initial slow relaxation with a relaxation time T_1 characteristic of the bath temperature T_B, prior to warm up of the lattice; (2) a rapid increase in the temperature T_P of the lattice modes near resonance, accompanied by a decrease in T_1.

The magnitude of the effect can be inferred from Sec. II above. In the example discussed there, a spin system having $T_1=7$ msec for $T_P=T_B=1.4$°K showed a bottleneck ratio $(T_P-T_B)/(T_S-T_P)\approx 21$. Assuming a T_P^{-1} temperature dependence for T_1 substitution in the expression for $(T_P-T_B)/(T_S-T_P)$ in Sec. II shows that the steady state value of T_P together with $1/T_1$ approach ∞ at a spin temperature of $T_S\approx -29$°K, a relatively small inversion. It follows that any spin system showing a substantial phonon bottleneck should exhibit the avalanche behavior on inversion.

It should be noted that the nonlinear behavior occurring as a result of the variation of T_1 with T_P is avoided throughout this paper since it is assumed that the relaxation measurements are made with $T_S\approx T_P\approx T_B$.

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APPENDIX A

The net time rate of change of ΔN follows from the use of the Einstein coefficients [Eq. (16) in text]. However it is also a common practice to define $d\Delta N/dt$ through

$$d\Delta N/dt=2[W_{21}N_2-W_{12}N_1]. \tag{A1}$$

At equilibrium $W_{12}/W_{21}=N_{20}/N_{10}$ and if we let $W_{21}+W_{12}=W$ then

$$d\Delta N/dt=W[\Delta N_0-\Delta N]=(\Delta N_0-\Delta N)/T_1. \tag{A2}$$

Comparison of (A1) and (16) yields

$$W_{12}+W_{21}\equiv W\equiv\frac{1}{T_1}=A_{21}\langle 2n+1\rangle=\frac{2\langle n\rangle+1}{T_{10}}.$$

APPENDIX B

If a "white" spectrum is incident upon an absorbing medium, the intensity transmitted after passage through a distance x is given by $I(\nu)=I_i\exp[-k(\nu)x]$ where this equation defines the frequency-dependent absorption coefficient, $k(\nu)$. It can be shown[33] that

$$\int_0^\infty k(\nu)d\nu=\frac{h\nu}{4\pi}B_{12}'\Delta N, \tag{B1}$$

where the B_{12}' coefficient (defined according to radiation intensity) is related to the B_{12} (defined according to radiation density) of Sec. V by $B_{12}=(v/4\pi)B_{12}'$; v= radiation propagation velocity.

Equation (B1) may be used to derive a relationship for τ_{LS}. Since $A_{21}^{-1}=T_{10}=T_1(2\langle n\rangle+1)=[B_{12}\rho(\nu)h\nu]^{-1}$ and since $vk(\nu)$ is the rate of absorption of a phonon at frequency ν, then if our absorption is uniform over $\Delta\nu$ and $\int k(\nu)d\nu=k\Delta\nu$, we find that $vk=(1/\tau_{LS})=\Delta N/(2\langle n\rangle\rho(\nu)\Delta\nu T_1)$. This is just the expression that one would get if equilibrium was established between the spins and the modes. Orbach[18] has derived an expression for τ_{LS} which is identical to that above except for a small numerical factor which depends upon the particular line shape.

APPENDIX C

Let us consider the validity of the assumption that the probability for emission of a phonon by an excited spin has the spin resonance shape and is independent of

[33] Reference 27, pp. 92–95.

the manner in which the spin was excited. As is known[34] from resonant scattering, an atom which has absorbed radiation of frequency ν, and which is stationary and undisturbed, emits radiation only at the same frequency. This is a consequence of the conservation of energy. If in our case a spin is excited monochromatically and it emits its full line shape, then there must be some source of interaction which allows the spin to change its energy.

A given spin has a number of neighbors which interact with it through their magnetic fields, or spin-spin interaction. This interaction is frequently the primary source of broadening of the spin resonance and therefore is normally of the order of magnitude of the line breadth. Each spin is radiating or absorbing phonons. Thus during the time of radiation for a single spin, which we shall designate as spin A, one or more of its neighbors would have spin-lattice transitions, varying the local magnetic field and the spectrum of frequencies emitted by spin A. This mechanism for varying the energy of spin A is that pointed out by Anderson[4] as a mechanism for diffusion of energy throughout a spin resonance. A rough approximation would be to consider neighboring spins to have a distribution of configurations during the radiating time of spin A which corresponds to their spectrum of distributions over a long period of time. Then the emission spectrum of the spin is just the line shape due to spin-spin interactions. Actually such a spectrum of emission does not occur during a single emission process, since the transition time for each neighboring spin is the same as the emission time of spin A. However, it represents a coarse approximation, and one which is very nearly correct after two or three emission times. The situation in more concentrated crystals is more favorable for the assumption of homogeneity within a time of T_1. Multiple spin flips whose importance has been emphasized by Bloembergen *et al.*,[35] in connection with "cross-relaxation," represent a more rapid source of disturbance for spin A.

APPENDIX D

The integrals of Eq. (39) and Eq. (45) are approximated as follows, with the aid of expansion derived in Ref. 36. Let $A=\tau_{LB}/\tau_{LS}$.

$$\int_0^\infty \frac{dx}{e^{x^2}+A}=\frac{1}{2A}\int_0^\infty \frac{1}{\sqrt{y}}\frac{dy}{e^{y-\ln A}+1}$$

$$=\frac{1}{2A}\left[\int_0^{\ln A}\frac{dy}{\sqrt{y}}-\frac{\pi^2}{12}\frac{1}{(\ln A)^{3/2}}-\frac{7\pi^4}{192}\frac{1}{(\ln A)^{7/2}}-\cdots\right]$$

$$=\frac{(\ln A)^{1/2}}{A}\left[1-\frac{\pi^2}{24(\ln A)^2}-\frac{7\pi^4}{384(\ln 4)^4}-\cdots\right].$$

For $A=50$, the error involved in retaining only the first term is less than 4%.

$$\int_{(\ln A/3)^{1/2}}^\infty \frac{dx}{e^{x^2}+A}$$

$$=\frac{1}{2A}\int_0^\infty \frac{dz}{[z+\ln(A/3)]^{1/2}(e^{z-\ln 4}+1)}$$

$$=\frac{1}{2A}\left[\int_0^{\ln 3}\frac{dz}{[z+\ln(A/3)]^{1/2}}-\frac{\pi^2}{12}\frac{1}{(\ln A)^{3/2}}-\frac{7\pi^4}{192}\frac{1}{(\ln A)^{7/2}}-\cdots\right]$$

$$=\frac{(\ln A)^{1/2}}{A}\left[1-\left(1-\frac{\ln 3}{\ln A}\right)^{1/2}-\frac{\pi^2}{24}\frac{1}{(\ln A)^2}-\frac{7\pi^4}{384(\ln A)^4}-\cdots\right]$$

$$=\frac{\ln 3}{2A(\ln A)^{1/2}}\left[1-\left(\frac{\pi^2}{12\ln 4}-\frac{\ln 3}{4}\right)\frac{1}{\ln A}+\frac{(\ln 3)^2}{8(\ln A)^2}-\left(\frac{7\pi^4}{192\ln 3}-\frac{5}{64}(\ln 3)^3\right)\frac{1}{(\ln A)^3}+\cdots\right].$$

For $A=50$, the error involved in retaining only the first term is less than 10%.

[34] W. Heitler, *Quantum Theory of Radiation* (Oxford University Press, Oxford, England, 1944), 2nd ed., pp. 138–144.

[35] N. Bloembergen, S. Shapiro, P. S. Pershan, and J. O. Artman, Phys. Rev. **114**, 445 (1959).

[36] J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (John Wiley & Sons, Inc., New York, 1940), p. 383.