inverse width of the echoes is a direct measure of the magnitude of the defects. However, the theory is valid only if the condition (4), $\gamma H_1 \gg a$, is fulfilled; and in an early stage of this work we found the width of the echoes to be strongly dependent upon the magnitude of H_1. This fact can be understood in a somewhat elementary manner by saying that H_1 turns only the iodine spins for which $a < \gamma H_1$, so that the distribution of the spins contributing to the signal has a width γH_1. Therefore, one should expect for small H_1 an inverse echo width proportional to H_1. Figure 4 shows that this is indeed the case. The fact that the inverse echo width becomes independent of H_1 for the larger values ($H_1 > 50$ gauss) makes us believe that we have reached the real distribution. Since the signal is too small to study in detail the distribution of the gradients $f(a)$, we define an average value ΔH expressed in gauss (or $\Delta\nu$ expressed in frequency units) by

$$\Delta H = 1/\gamma T, \quad \Delta\nu = 1/2\pi T, \tag{23}$$

T being the half-width of the echo E_1 at half maximum. ΔH is the quantity plotted on Fig. 4. Sample A is a tube filled with small crystals ($\sim$1 mm^3) of KI of commercial grade and shows a ΔH of 18 gauss ($\Delta\nu = 15.3$ kc/sec). Sample B is a single crystal of KI and shows a ΔH of 35 gauss ($\Delta\nu = 29.8$ kc/sec). After crushing crystals of sample A, we get a ΔH of 25 gauss. By melting and quenching of the same crystals, we get

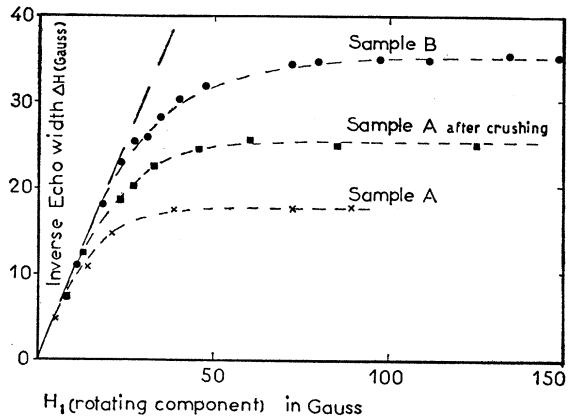

FIG. 4. Inverse echo width ΔH as a function of the rf field H_1. In the limit of large H_1, ΔH is a measure of the average interaction between the quadrupole moment of iodine and the random gradients due to the defects in the KI crystals.

$\Delta H = 36$ gauss. Melting and quenching of sample B did not change, within experimental error, the distribution of the gradients. This method seems to be a powerful tool for the study of strains and defects of cubic crystals.

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Spin-Lattice Relaxation*

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The measurement of electron spin-lattice relaxation times for paramagnetic crystals at low temperatures is complicated by the fact that the spin specific heat can be much larger than the lattice specific heat. At low temperatures direct processes dominate in the spin-lattice relaxation mechanism and evidence exists that indicates that only a narrow portion of the phonon spectrum takes part in the relaxation processes. This situation is not encompassed by usual treatments of the spin-lattice problem and a microscopic treatment is presented which allows for this selective excitation of the phonon spectrum. It is pointed out that phonon relaxation times can be the dominant quantity measured in the usual saturation spin-lattice relaxation measurements. The analysis indicates how pulse measurements may be used to evaluate the actual spin-lattice relaxation time independent of the phonon relaxation time. A discussion of some conditions under which the concept of temperature may be applied to quantum-mechanical systems interacting with electromagnetic fields, such as in solid-state amplifiers or absorbers, is given.

INTRODUCTION

CONVENTIONALLY, in tracing the transfer of energy between interconnecting systems thermodynamic considerations are used for deriving the necessary conditions that must hold between the system parameters. In applying thermodynamic principles to a system such as an electron spin that transfers energy to its surrounding lattice, we imply that the source of energy, the spins, has low heat capacity and that the thermodynamic bath, the lattice, has very large or infinite heat capacity. A more general approach

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considers the transfer of energy from the source to a system that plays the part of a thermal conductor connected to a bath of infinite heat capacity, with properties that can be expressed in terms of temperature gradients and thermal conductivities.[1] Even this system is unnecessarily restrictive because the simple notion of thermal conductivity assumes that there is an interaction that brings about an equilibrium among all of the energy levels contributing to the conductivity of the conductor so that a simple temperature has some meaning or can even be defined.

The attempt to define a temperature for any of the elements of a system, source, conductor, or bath, requires the further assumption that the system can be described in terms of phaseless constants which describe the average behavior of the system. To state it differently, the density matrix described by the eigenrepresentation for the system must have off-diagonal elements whose time average is zero. [*Added in proof.*—That this is a general requirement is supported by W. Kohn and J. M. Luttinger, Phys. Rev. **108**, 590 (1957).] For example, the description of a phase-coherent system, such as a sample of water in a state that gives rise to a free nuclear induction signal, in terms of temperature is unnatural. The radiation rate is far too high and the radiation signal is coherent, a condition not envisioned by the averaging concept of temperature.

A particular system which illustrates this difficulty is an electron spin relaxing through lattice phonon states, especially at low temperatures.[2,3] It is well known that the spin specific heat at sufficiently low temperatures is many times the lattice specific heat; hence the lattice cannot be considered as an infinite bath. This is not the case when the relaxation of nuclear paramagnetic energy states to the lattice is considered. Unfortunately, the elegance and simplicity with which the nuclear spin-lattice relaxation problem has been handled have created an aura of understanding in the field of electron spin-lattice relaxation so that the inherent difficulties in the electron spin-lattice relaxation problem have been overlooked. Since the lattice specific heat is so small at sufficiently low temperature, a conduction problem must be visualized; that is, the electron spins relax with their energy going selectively to lattice modes that are resonant with, or, to use Van Vleck's apt phrase, on "speaking terms" with the spin.[4] The lattice phonons that are in direct contact with the spin then relax to thermal equilibrium by transferring their energy to other phonon states and to the actual bath. The concept of temperature is irrelevant here, since it is not a useful parameter with which to discuss the problem. We propose to discuss this problem without persistent reference to temperature.

In a previous paper, which was a discussion of the inherent noise of quantum-mechanical amplifiers, we chose to abandon the use of temperature as a primary parameter in the discussion of the problem.[5] It turns out, however, that a temperature can be introduced to characterize the thermal emission from the quantum-mechanical amplifier, since the problem is simple enough to be reduced to a suitable description in terms of a temperature parameter. In a very exact sense this problem of thermal emission of quantum-mechanical amplifiers was stated initially in a form which allows the introduction of a temperature parameter. The quantum-state populations were described in terms of phaseless population numbers. This implies that the quantum states are simply describable in terms of the average over all possible phases of the eigenrepresentation for the unperturbed system. It should be noted that this is a powerful, albeit popular, assumption. Many reasons can be presented to justify it. For example, in paramagnetic systems spin-spin dipole coupling provides a convenient mechanism to produce this necessary averaging within the eigenstates of the system. Several writers use the presence of this coupling as an argument for the meaningful application of a temperature to such a system.[6] We would prefer to keep the assumption about the system in sight and to introduce the temperature, if it is indeed useful, at a later point.

The use of the smeared eigenpresentation for the dipole-broadened system, which was introduced by Kronig and Bouwkamp,[7] is of long standing. Its use assumes that the observations on the state will measure the average of the coupled system that the dipole coupling creates, and thus the phaseless, single-spin representation is adequate. This averaging effect of the dipole field is important and, in fact, such a system is describable as an average (which will eventually allow the introduction of a temperature parameter if it is important) only as long as the dipole term in the Hamiltonian is the dominant perturbation. It would be inappropriate to use such an average over all possible state phases in a case in which an electromagnetic field perturbs the system so that the transition probability is greater than the inverse of the transverse relaxation time, τ_2 which is the spin-averaging time. Thus, for, example, for our calculations of the inherent noise in quantum-mechanical amplifiers to be applicable to a system of three or more levels that interact with a strong electromagnetic field, the following inequality must hold:

$$(\pi\tau_2)^{-2} \gg |\boldsymbol{\mu}_{ij}\cdot\mathbf{H}_{\mathrm{rf}}|^2/\hbar^2,$$

[1] J. Eisenstein, Phys. Rev. **84**, 548 (1951).
[2] Strandberg, Davis, and Kyhl, Proceedings of the Fifth International Conference on Low Temperature Physics and Chemistry, Madison, Wisconsin, August 30, 1957 (to be published).
[3] Gorter, van der Marel, and Boljer, Physica **21**, 103 (1955); van der Marel, van den Broek, and Gorter, Physica **23**, 361 (1957).
[4] J. H. Van Vleck, Phys. Rev. **57**, 426 (1940).
[5] M. W. P. Strandberg, Phys. Rev. **106**, 617 (1957).
[6] N. F. Ramsey, Phys. Rev. **103**, 20 (1956); H. B. G. Casimir and F. K. du Pré, Physica **5**, 507 (1938).
[7] R. de Kronig and C. J. Bouwkamp, Physica **5**, 521 (1938).

where the latter expression may be greater or less than $(\pi\tau_1)^{-2}$, with τ_1 the spin-lattice relaxation time. This restriction is also necessary for the discussion of other properties of the system, e.g., its polarization, if the discussion in terms of simple state populations is to be accepted without more extensive proof.

We intend to discuss a system with dipole averaging which is describable in terms of phaseless constants; hence one or several temperatures can be introduced eventually to describe the relevant state populations. We still avoid the apparent attractiveness of such a procedure for the reasons already given; the lattice is far from being an infinite bath and possibly it is not even in thermal equilibrium within itself. Under these conditions, the use of a temperature parameter is not only artificial, but misleading, and tends to cause uneasiness because it allows the ready comparison of a nonequilibrium system with better understood, but essentially different, equilibrium systems.

STATEMENT OF THE PROBLEM

Consider the system of a spin with its characteristic energy states broadened so that it exhibits an equivalence with a system of coupled spins. We follow Van Vleck[4] exactly [starting from his Eq. (18)]. As he delineates clearly, the spin is coupled to the lattice through the mixing in second- and higher-order perturbations of the spin-orbit and orbit-lattice coupling. Such mixing gives rise to spin-lattice matrix elements that depend on the parameters of the spin and electronic state of the ion, and on the phonon excitation expressed in terms of the phonon quantum number, n. The orbit-lattice terms that are linear in the lattice-mode displacement have the familiar $(n|n\pm 1)$ off-diagonal matrix elements for their dependence on phonon excitation. The harmonic oscillator representation that is used makes these elements proportional to $\sqrt{(n+1)}$ and $\sqrt{n}$ for the $+$ and $-$, respectively. The absolute squares of these elements appear in the perturbed Hamiltonian. If we keep sight of these elements explicitly, we can indicate the necessary change in the equilibrium values of the phonon quantum number which is necessary to accommodate the spin energy that is being transferred to the lattice. The power transfer for a pair of levels i and j, with spin populations N_i and N_j, an energy difference $E_i-E_j=h\nu_{ij}$, and a spin transition probability per unit of phonon excitation, A_{ij}, can be given as

$$P_{ij}=h\nu\rho(\nu_{ij})[N_iA_{ij}\langle n_{ij}+1\rangle-N_jA_{ji}\langle n_{ij}\rangle], \tag{1}$$

where $\langle n_i\rangle$ is the mean phonon quantum number for phonons having a characteristic frequency ν_{ij}, and $\rho(\nu_{ij})$ is the density of phonon states,

$$\rho(\nu_{ij})=V\left(\frac{1}{v_l^3}+\frac{2}{v_t^3}\right)4\pi\nu_{ij}^2,$$

where V is the crystal volume, and v_l and v_t are the longitudinal and transverse sound velocities at ν_{ij}. Note that by maintaining the explicit phonon population the spin transition probability has the familiar property $A_{ij}=A_{ji}$. The more obscure form of transition probability, which suppresses the dependence on n, has the property that $w_{ij}=\exp(h\nu/kT)w_{ji}$ only because of the restrictive assumption that thermal equilibrium in the phonon states exists; that is, $\langle n\rangle=[\exp(h\nu/kT_L)-1]^{-1}$, and thus $\langle n+1\rangle/\langle n\rangle=[\exp(h\nu/kT_L)]$.

Equation (1) now simplifies to

$$P_{ij}=h\nu_{ij}A_{ij}N_i\rho(\nu_{ij})\left[1-\langle n_{ij}\rangle\left(\frac{N_j}{N_i}-1\right)\right]. \tag{2}$$

Now, the first important observation to be made is that when $N_j\simeq N_i$, that is, with the spin system truly saturated, the relaxation is independent of the lattice "temperature" or is independent of the degree of phonon excitation. This is drastically different from previous pictures that postulated a conduction process from spin to lattice. This process assumed that the spin temperature is nearly equal to the lattice temperature, and hence has no applicability to the cases of spin saturation usually encountered. In any case, only as long as the phonon excitation is small compared with $N_i/(N_j-N_i)$, will the lattice phonon temperature have a negligible effect on the rate of spin-lattice energy transfer. Finally, we note that the conventional heat-flow equation can be obtained from Eq. (2) for the case of $h\nu\ll kT$, so that the following approximation holds:

$$\langle n_{ij}\rangle\simeq\frac{kT_L}{h\nu_{ij}},\quad \frac{N_j}{N_i}\simeq 1+\frac{h\nu_{ij}}{kT_s},$$
$$P_{ij}=h\nu_{ij}A_{ij}N_i\rho(\nu_{ij})\left[\frac{T_s-T_L}{T_s}\right]. \tag{3}$$

The rate of change of phonon quantum number can be written in terms of the power transferred from the spin to the resonant lattice modes, and of the transfer rates of this phonon energy to other lattice modes and to the actual bath. From a physical point of view, it seems best to express phonon-phonon relaxation in terms of the actual phonon quantum numbers if an umklapp process is used.[8] Such a process arises from vibrational anharmonicity, and thus it will increase with the phonon quantum numbers, since they measure the vibrational energy, and hence the anharmonic contribution. If the phonon-phonon process is so improbable that processes induced by wall effects predominate, then it would seem that this relaxation effect can be lumped with the direct transfer of phonon excitation to the true bath.

It might appear dangerous to even consider the volume umklapp process, since this implies a general increase in lattice phonon excitation, and a possible increase in the higher-order Raman scattering process

[8] R. Berman, in *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1953), Vol. 2, p. 103.

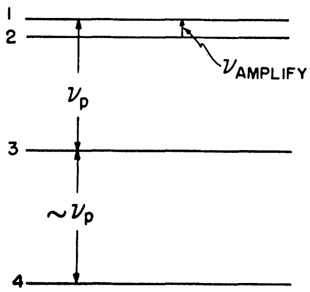

FIG. 1. Energy-level diagram for spin system which allows for indirect saturation of spin levels through the use of anomalous phonon excitation.

in the spin-lattice coupling. This is probably not the the case here, however, for the phonon modes that are on "speaking terms" with the spins form such a small fraction of the total number of modes, i.e., $3\nu^2\Delta\nu/\nu_{\max}^3 \simeq 10^{-12}$, and, even at microwave frequencies, they are at the low-energy end of the distribution. The Raman process is dependent upon having high excitation at more than one frequency region in the phonon distribution, which is apparently not the case here. The other modes could hardly build up sufficient excitation to enter strongly into a Raman process, and thus they act more as an energy sink.

That the high phonon excitation is restricted to one frequency interval is known to be true from the fact that saturation quantum-mechanical amplifiers have been operated with large active-state populations. These amplifiers have spin populations far from thermal equilibrium which are in contact with phonons in states that are not resonant with the saturation field. The states of inverted spin population provide a potent source, and the remaining transition, a potent sink, for phonon excitation. Thus operation of a quantum-mechanical amplifier would be difficult in the presence of high phonon excitation away from the saturating frequency. But, as has been shown, a solid-state quantum-mechanical amplifier has been made to operate with the microwave input power saturating a pair of levels whose frequency difference is nearly degenerate with the frequency difference of the appropriate pumping levels. This physical situation is as indicated on Fig. 1. The device can be made to operate by predominantly saturating levels 3–4 and amplifying between levels 1–2. Or alternatively, the device may be operated more conventionally by saturating directly levels 1–3 with the electromagnetic radiation. In the first mode of operation the electromagnetic radiation saturates the levels 3–4, which, in turn, create an anomalous phonon excitation in the region of the phonon spectrum of frequency ν_p. Levels 1–3 are in contact with these anomalously excited phonons, since the frequency of 1–3 is nearly equal to the frequency of 3–4. Levels 1–3 serve as a sink for this anomalous phonon excitation and are saturated by it. This anomalous phonon excitation substantiates our model of a saturated spin system in contact with, and giving rise to, a selectively-excited lattice phonon spectrum.[9] It is apparent that the anomalous phonon spectral width cannot be great, for if this were so levels 2–3 would also be saturated and the device would have marginal operation. Only by means of a narrow anomalous phonon excitation could the necessary states be saturated and the device be made to operate in the fashion described. This phonon distribution is shown in Fig. 2.

The anharmonic umklapp process is dependent likewise upon the excitation of the interacting modes with the anomalous phonon distribution that we visualize here. The modes outside the spin-relaxation frequencies would interact much less with each other and, within the limitations imposed on the mean free path by lattice imperfection, would provide a high conductivity path to the bath. The possibility of umklapp at microwave frequencies is probably comparatively low in reasonably good crystals.[10] The most probable points for scattering phonons of long wavelengths (several thousand angstroms) which correspond to phonons at microwave frequencies, are lattice imperfections sufficiently large to be "seen" by these long wavelengths.

We may also note that although the phonon modes away from spin-resonance frequency are fairly well uncoupled from each other, those in the region of the spin resonance are strongly coupled to each other because of their interaction with the paramagnetic spin. For this reason, we can justifiably treat these phonons by a simple mean-value parameter.

With these things in mind, we can write the time dependence of the mean phonon quantum number with a lumped umklapp and scattering relaxation time (which will depend upon the phonon excitation) and a direct bath relaxation time as

$$\langle\dot{n}_{ij}\rangle=\frac{P_{ij}}{h\nu_{ij}\rho(\nu_{ij})\Delta\nu}-[\langle n_{ij}\rangle-\langle n_{ij}\rangle_0]\left[\frac{1}{\tau_L}+\frac{1}{\tau_B}\right]. \quad (4)$$

Equation (4) introduces an excitation width, $\Delta\nu$, which characterizes the effective width of the phonons that are on speaking terms with the spins. From the uncertainty relationship, it is apparent that this width will depend not only upon the spin-spin relaxation time τ_2, or the effective width of the spin levels, but also upon the effective phonon relaxation time. Presumably, then, $\Delta\nu$ could be written as

$$\Delta\nu\cong\frac{1}{\pi}\left[\frac{1}{\tau_2}+\frac{1}{\tau_L}+\frac{1}{\tau_B}\right]. \quad (5)$$

Because of the shortness of the usual spin-spin relaxation times, this phonon width will correspond in many cases quite closely to the width of the spin levels themselves. We may write the steady-state form of Eq. (4) as

$$\frac{P_{ij}}{h\nu_{ij}\rho(\nu_{ij})\Delta\nu}=(\langle n_{ij}\rangle-\langle n_{ij}\rangle_0)\left[\frac{1}{\tau_L}+\frac{1}{\tau_B}\right]. \quad (6)$$

[9] Strandberg, Davis, Faughnan, Kyhl, and Wolga, Phys. Rev. **109**, 1988 (1958).

[10] C. Kittel, Phys. Rev. **75**, 972 (1949).

Equation (6) may be used to demonstrate forcefully the need to investigate the phonon-excitation spectrum under the saturation conditions that are possible with microwave excitation. We note that $P_{ij}/h\nu_{ij}$ would normally be given as $(N_i-N_{i0})/\tau_1$. Typical values for (N_i-N_{i0}) would depend upon the degree of saturation, the actual crystal used, and the paramagnetic dilution. This factor is approximately 10^{18} to 10^{21} spins/cm^3. The term $\rho(\nu_{ij})$ at $\nu_{ij}=10^{10}$ cycles/sec is approximately 10^5V sec. We estimate $\Delta\nu$ to be approximately 10^8, and τ_1 to be from 10^{-1} to 10^{-4} sec. The factor for the phonon relaxation time $[\tau_L^{-1}+\tau_B^{-1}]^{-1}=\tau_L'$ must be less than 10^{-5} to 10^{-6} sec, a number dictated by the usual crystal dimensions. These numbers yield a possible range in the deviation of the phonon excitation from equilibrium, $[\langle n_{ij}\rangle-\langle n_{ij}\rangle_0]$, of between $10^6\tau_L'$ and $10^{12}\tau_L'$. This means that the deviation of the phonon excitation from equilibrium with the bath would be given as from $10^6\tau_L'/2T_B{}^\circ$ to $10^{12}\tau_L'/2T_B{}^\circ$, where $T_B{}^\circ$ is the bath temperature. In order for this phonon deviation to be negligible at low bath temperatures, in one extreme τ_L' would have to be less than $2\times10^{-6}T_B{}^\circ$ sec or the phonon mean free path would be of the order of millimeters, and at the other extreme τ_L' must be less than $2\times10^{-12}T_B{}^\circ$ sec and the required phonon mean free path would be the rather ridiculous amount of approximately 1/100 of a wavelength.

If the value of $\langle n_{ij}\rangle$ given by Eq. (6) is used in Eq. (2) and a saturation parameter κ is introduced by defining it as

$$\kappa=(N_j-N_i)/(N_{j0}-N_{i0}),\quad\text{and}\quad N=N_i+N_j, \tag{7}$$

we find that the saturation power is given as

$$P_{ij}=\frac{h\nu_{ij}A_{ij}\rho(\nu_{ij})N(1-\kappa)}{2[1+A_{ij}(N_{j0}-N_{i0})\rho(\nu_{ij})\tau_L'\kappa/\rho(\nu_{ij})\Delta\nu]}. \tag{8}$$

With equilibrium phonons, i.e., $\Delta\nu\rightarrow\infty$, the spin-lattice relaxation time $\tau_{1ij}{}^0$, for the parameter $(1-\kappa)$ would be given from Eq. (8) as $\tau_{1ij}{}^0=2/A_{ij}\rho(\nu_{ij})$. Thus, saturation alters the spin-lattice relaxation time for a similarly defined parameter. Hence

$$[\tau_{1ij}]=\tau_{1ij}{}^0+\frac{2(N_{j0}-N_{i0})\tau_L'\kappa}{\rho(\nu_{ij})\Delta\nu}. \tag{9}$$

A spin-lattice relaxation time inferred from a saturating c-w magnetic field may actually measure the lattice-phonon relaxation rate (which is independent of the properties and quantum state of the paramagnetic ion) along with the spin-lattice rate, except for systems with very large saturation ratios.

Several things should still be mentioned. First, in the case of near degeneracy of energy-level differences, either within one ion or between different impurity ions in a crystal, anomalous relaxation rates can be observed that arise from energy transfer to states that have nearly degenerate frequency differences because they serve as a thermal sink. This effect is really important only because $\tau_2\ll\tau_1'$ so that off-resonant spin exchange is still reasonably probable compared to spin-lattice effects.

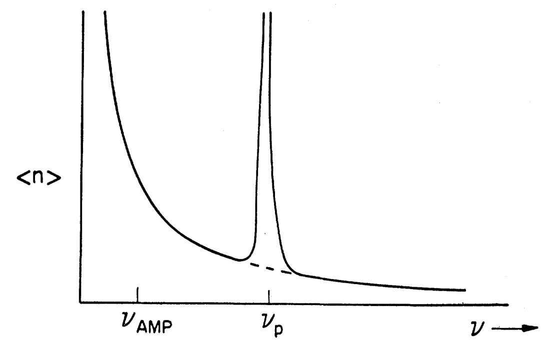

Fig. 2. Anomalous phonon distribution.

The treatment of spin-phonon interactions presented here has been limited to the special case of two-spin levels, mainly for the purpose of expositional clarity. The extension of the model presented here to models of more levels is accomplished by summing over ij in Eq. (1). Extension of these ideas to particular cases with many levels will, no doubt, disclose many interesting situations. The purpose here was mainly that of sketching in a general way the reason for possible discrepancies in the evaluation of spin-lattice relaxation times, as determined from cw and from pulse measurements.

Second, we reiterate that direct radiative relaxation is unimportant in the case we treat, i.e., incoherent operation with

$$1/(\pi\tau_2)^2\gg|\boldsymbol{\mu}_{ij}\cdot\mathbf{H}_{\mathrm{rf}}|^2\hbar^{-2}.$$

Obvious examples in which this is not so are the proton-free induction situation and the ferrite parametric device.

Third, it is apparent that a spin-lattice relaxation time cannot be defined for the model that is discussed above. The general equations, Eqs. (2) and (7), describe the spin system with a nonlinear differential equation, so that a spin-lattice relaxation time can be defined only in equilibrium fashion, or at best in step-wise fashion. Measurement of spin relaxation over a wide range of saturation conditions should allow the separation of the effect of phonon excitation from the effect of direct spin-phonon coupling. This means that the relaxation of a spin system to thermal equilibrium should be observed, if it is observed in the time domain, throughout its observable history. But if the spin-lattice relaxation time is inferred from frequency-domain measurements, e.g., by observation of the cw saturation effect,[11] the saturation parameter must be observed and analyzed for a wide range of saturation conditions in order to separate phonon relaxation effects from these direct spin-lattice relaxation effects.

[11] G. Feher and H. E. D. Scovil, Phys. Rev. **105**, 760 (1957).