SPIN-PHONON INTERACTION

IN this chapter we shall be primarily concerned with the mechanisms by which energy is exchanged between the paramagnetic ions (or spin system) and thermal reservoirs such as electromagnetic radiation, the lattice vibrations (or phonon radiation) within the paramagnetic crystal, and the surroundings of the paramagnetic crystal, such as a bath of liquid helium. These mechanisms are fairly well established; they give a good qualitative, and sometimes a reasonably quantitative explanation of the way in which the spin-lattice relaxation time varies, particularly with temperature. Some related effects, such as the phonon bottle-neck and phonon avalanche that result from the comparatively small heat capacity at low temperatures of the phonons resonant with the spins, are outlined in the last section.

The spin-phonon interaction also affects the parameters in the static spin Hamiltonian, giving rise to shifts in the g-value, the fine structure splitting, and the hyperfine interaction. The phonons may also induce a 'spin-spin' interaction between ions, as mentioned in § 9.4. Such effects arise at $0°K$ from the zero-point vibrations of the lattice, and though they increase at finite temperatures, they are often rather small and we shall not discuss them further. In addition we shall be mainly concerned with fairly dilute paramagnetic substances, thus avoiding the complexities that arise in more concentrated compounds from the interplay of spin-spin interaction and spin-lattice relaxation. The excellent review by Stevens (1967) covers similar ground; its different approach strongly recommends it as companion reading.

10.1. The attainment of thermal equilibrium

If we have a system whose temperature is not the same as that of its surroundings, it cannot be in thermal equilibrium with these surroundings, and provided there is thermal contact between the two, their temperatures will approach a common value at a rate determined by the heat capacities of the system and the surroundings together with the rate at which energy can be transferred from one to the other. If the surroundings have a heat capacity that is immensely greater than the heat capacity of the system, the temperature of the latter will approach the temperature of the surroundings at a rate determined only by the heat capacity of the system and the rate of heat transfer.

We start by assuming that the surroundings are essentially infinite in their heat capacity, and that they are in thermal equilibrium with a bath of electromagnetic radiation whose density ρ_{em} is that appropriate to a temperature T_0, which is thereby defined as the temperature of the surroundings.

For an atomic system, energy transfer occurs through transitions between the atomic energy levels, such transitions being accompanied by the emission and absorption of quanta of electromagnetic radiation. For simplicity we consider first a system of just two energy levels a, b in which a is the lower level and b the upper level, for which the difference in energy is

$$W_b - W_a = \hbar\omega. \tag{10.1}$$

A simple example would be a spin system $S = \frac{1}{2}$ which is subjected to an external field that separates the two levels by an energy $\hbar\omega$. Let the populations of the lower and upper levels respectively be n_a and n_b at any instant. Then owing to interaction with the radiation bath, transitions will be taking place between the two levels in either direction, the number leaving the lower state being proportional to n_a and the number leaving the upper state being proportional to n_b. Thus the populations of the two levels obey the differential equation

$$-\frac{dn_a}{dt} = \frac{dn_b}{dt} = w_{\uparrow}n_a - w_{\downarrow}n_b, \tag{10.2}$$

where $w_{\uparrow}$, $w_{\downarrow}$ are the rates at which ions make transitions from the lower to the upper state, and vice versa. If the spin system is in thermal equilibrium with a radiation bath at temperature T_0, the time differentials are zero and the populations of the two states will have their equilibrium values N_a, N_b. Thus

$$0 = w_{\uparrow}N_a - w_{\downarrow}N_b \tag{10.3}$$

and hence

$$N_a/N_b = w_{\downarrow}/w_{\uparrow}. \tag{10.4}$$

The transition rates are given by the Einstein coefficients of absorption and emission

$$w_{\uparrow} = B\rho_{em}, \tag{10.5}$$

$$w_{\downarrow} = A + B\rho_{em} = B\rho_{em}\exp(\hbar\omega/kT_0), \tag{10.6}$$

where ρ_{em} is the radiation density, B the coefficient of stimulated emission or absorption, and A the coefficient of spontaneous emission. Hence we have

$$N_a/N_b = (A + B\rho_{em})/(B\rho_{em}) = \exp(\hbar\omega/kT_0), \tag{10.7}$$

showing that the transition rates must differ just by the factor required to maintain the ratio of the populations in accordance with Boltzmann's law.

We return now to the case where the spin system is not in equilibrium with the radiation bath. By a simple algebraic manipulation we have from (10.2)

$$\frac{\mathrm{d}(n_a-n_b)}{\mathrm{d}t} = -2(w_\uparrow n_a - w_\downarrow n_b)$$
$$= (n_a+n_b)(w_\downarrow - w_\uparrow) - (w_\downarrow + w_\uparrow)(n_a - n_b)$$
$$= (w_\downarrow + w_\uparrow)\{(N_a - N_b) - (n_a - n_b)\}, \qquad (10.8)$$

where we have used the fact that the total number of spins N is constant; i.e.,

$$n_a + n_b = N_a + N_b = N \qquad (10.9)$$

and the relation

$$(w_\downarrow - w_\uparrow)/(w_\downarrow + w_\uparrow) = (N_a - N_b)/(N_a + N_b)$$

from (10.4). The solution of (10.8) is

$$(n_a - n_b) = (N_a - N_b) + \{(n_a - n_b)_0 - (N_a - N_b)\}\exp(-t/\tau_1), \quad (10.10)$$

where $(n_a - n_b)_0$ is the population difference at $t = 0$, and the time constant τ_1 is given by the relation

$$\frac{1}{\tau_1} = (w_\downarrow + w_\uparrow). \qquad (10.11)$$

On substituting from (10.5), (10.6) this becomes

$$\frac{1}{\tau_1} = A + 2B\rho_{\mathrm{em}} = B\rho_{\mathrm{em}}\{\exp(\hbar\omega/kT_0) + 1\}. \qquad (10.12)$$

If now we insert the electromagnetic (photon) radiation density

$$\rho_{\mathrm{em}}\,\mathrm{d}\omega = \frac{\hbar\omega^3}{\pi^2 c^3}\frac{\mathrm{d}\omega}{\exp(\hbar\omega/kT_0) - 1} \qquad (10.13)$$

we have, using the well known relation between the coefficients A, B

$$\frac{1}{\tau_1} = \frac{\hbar\omega^3}{\pi^2 c^3} B \coth\left(\frac{\hbar\omega}{2kT_0}\right) = A \coth\left(\frac{\hbar\omega}{2kT_0}\right). \qquad (10.14)$$

Equation (10.11) gives a quite general relation for the relaxation time for a two-level system. If $\hbar\omega \ll kT_0$, so that the difference between $w_\downarrow$ and $w_\uparrow$ can be neglected, we have simply $1/\tau_1 = 2w$. Further, since the coefficient B is not temperature-dependent, we find from (10.14)

that in this region τ_1^{-1} varies as T_0, corresponding to the classical limit where stimulated emission and absorption predominate, and the rate at which transitions occur at a given frequency is just proportional to the radiation energy density at this frequency, which varies as kT_0. In the opposite extreme where $\hbar\omega \gg kT_0$, τ_1 becomes independent of temperature, being determined entirely by A, the rate of spontaneous emission from the upper state, since in this limit $\coth(\hbar\omega/2kT_0)$ tends to 1, and $A \gg B\rho_{\text{em}}$ in eqn (10.12).

In ordinary laboratory optical spectroscopy we have generally $\hbar\omega \gg kT_0$, though this may be far from true in high temperature plasmas. In the radio-frequency region, we have generally $\hbar\omega \ll kT_0$. In centimetre/millimetre wave-spectroscopy at liquid-helium temperatures, we are just in the transition region, since $(\hbar\omega/kT_0) = 1$ at $T_0 = 1\cdot438°\text{K}$ for a frequency $(\omega/2\pi) = 30\,\text{GHz}$ corresponding to a wavelength of 1 cm. Hence in electron paramagnetic resonance we shall frequently need the more general expression for the dependence on temperature of the relaxation time.

We now identify our two-level system with an assembly of magnetic ions for each of which $S = \frac{1}{2}$, subjected to a field H that splits the levels by an amount $\hbar\omega = g\beta H$. Then the magnetization is given by

$$M = \tfrac{1}{2}g\beta(n_a - n_b), \qquad M_0 = \tfrac{1}{2}g\beta(N_a - N_b), \qquad (10.15)$$

where M_0 is the thermal equilibrium value corresponding to temperature T_0. Substituting in (10.8) and using (10.11) we obtain

$$\frac{\mathrm{d}M}{\mathrm{d}t} = \frac{1}{\tau_1}(M_0 - M), \qquad (10.16)$$

which is identical with eqn (2.31) if H is along the z-axis. On this basis we recognize τ_1 as the 'spin-lattice relaxation time' introduced into the classical equations of motion to describe the way in which the magnetization returns from a non-equilibrium value to the thermal equilibrium value. Our treatment indicates that it is a special case of a general process involving the flow of energy between an assembly of atoms and ions with discrete energy levels and a thermal reservoir (the radiation field). In magnetic terms the flow of energy arises as follows. If the magnetization M in a constant field H changes by an amount $\mathrm{d}M$, the magnetic energy of the system changes by $-H\,\mathrm{d}M$; this magnetic energy is associated with the spin system, which we regard as possessing internal energy that may change through a transfer to or from another thermal reservoir.

The concept of thermal equilibrium involves that of temperature. For our system of ions with two levels separated in energy by $\hbar\omega$, we can define a temperature for the spin system known for brevity as the 'spin temperature' T_s by means of the relation

$$n_a/n_b = \exp(\hbar\omega/kT_s), \qquad (10.17)$$

which is analogous to eqn (10.7). Since the magnetization of such an assembly of N magnetic ions of spin $S = \frac{1}{2}$ is

$$M = \tfrac{1}{2}Ng\beta \tanh(\hbar\omega/2kT_s)$$

we can write eqn (10.16) in the form

$$\frac{d}{dt}\{\tanh(\hbar\omega/2kT_s)\} = \frac{1}{\tau_1}\{\tanh(\hbar\omega/2kT_0) - \tanh(\hbar\omega/2kT_s)\}. \qquad (10.18a)$$

Using eqn (10.14) this becomes

$$\frac{d}{dt}\{\tanh(\hbar\omega/2kT_s)\} = A\left\{1 - \frac{\tanh(\hbar\omega/2kT_s)}{\tanh(\hbar\omega/2kT_0)}\right\}. \qquad (10.18b)$$

In the high-temperature region where $(\hbar\omega/kT) \ll 1$, Curie's law holds, so that M, M_0 vary as T_s^{-1}, T_0^{-1} respectively. Using the nomenclature $\beta_s = (1/kT_s)$, $\beta_0 = (1/kT_0)$, we can write (10.18a) in the approximate form

$$\frac{d\beta_s}{dt} = \frac{1}{\tau_1}(\beta_0 - \beta_s). \qquad (10.19)$$

In the classical thermodynamical approach to spin-lattice relaxation, a specific heat C_H is associated with the spin system at constant field, and it is assumed that the rate of energy transfer between spin system and lattice is proportional to the difference in their temperatures. Then $-C_H(dT_s/dt) = \alpha(T_s - T_0)$, where α is a 'coefficient of thermal contact', or

$$dT_s/dt = (\alpha/C_H)(T_0 - T_s).$$

We can relate this to the magnetization using Curie's law and then, using eqn (10.16), we obtain

$$\frac{dT_s}{dt} = \left(\frac{dM}{dt}\right)\bigg/\left(\frac{dM}{dT_s}\right) = \frac{1}{\tau_1}\left(\frac{T_s}{T_0}\right)(T_0 - T_s).$$

Comparison of the two equations for (dT_s/dt) shows that we can write

$$\tau_1 = C_H/\alpha \quad \text{(cf. Gorter 1947, Cooke 1950)}$$

only if $|T_0 - T_s| \ll T_0$; this is a more stringent condition than the approximation that leads to eqn (10.19), and reflects the fact that both C_H and α are temperature-dependent.

For a system of more than two levels, a spin temperature can be defined provided that the ratio of the populations of *any* two levels is given by (10.17), and the condition for this is that the spin system must be in internal equilibrium. Such internal equilibrium is reached through the spin-spin interaction in a time τ_2, and if $\tau_2 \ll \tau_1$ (as is frequently the case for a magnetically concentrated system) the concept of a spin temperature is valid in dealing with the relatively slow process of spin-lattice relaxation. In a magnetically dilute system, on the other hand, there will be $(2S+1)$ rate equations describing the way in which the populations of the $(2S+1)$ levels change with time, whose solutions are not necessarily describable in terms of a single spin-lattice relaxation time.

We now return to the simple two-level system to obtain an estimate of the relaxation time τ_1 associated with transitions induced by the electromagnetic radiation field. In eqn (10.14) we need the value of B, to obtain which we make use of the standard formula for the induced transition probability rate

$$w_{ij} = \frac{2\pi}{\hbar^2} |\langle i| \mathscr{H}'_0 |j\rangle|^2 f(\omega), \tag{10.20}$$

where $\langle i| \mathscr{H}'_0 |j\rangle$ is the matrix element of the perturbing Hamiltonian $\mathscr{H}' = \mathscr{H}'_0 \exp(\pm i\omega t)$, and $f(\omega)$ is the line shape function introduced in § 2.9. For a linearly polarized electromagnetic field of amplitude H_1, we have from eqns (2.56), (2.57), for the transition $M \leftrightarrow M-1$,

$$|\mathscr{H}'_0|^2 = (\tfrac{1}{4}H_1)^2(l_1^2 + m_1^2)\langle M-1| \mu_- |M\rangle^2$$

and since the mean values of l_1^2, m_1^2 for random polarization are each $(\tfrac{1}{3})$, and $(H_1^2/8\pi) = \rho_{em}\, d\omega$, while for a transition between the two states of a doublet $\langle M-1| \mu_- |M\rangle = \gamma\hbar$, we find

$$w = \left(\frac{\pi}{12}\right)\gamma^2 H_1^2 f(\omega) = (2\pi^2/3)\gamma^2 \rho_{em} f(\omega)\, d\omega. \tag{10.21}$$

If we assume that the line width is so small that we can neglect the variation in the energy density ρ_{em} over the width of the line, then by integrating over the line shape and using the relation $\int f(\omega)\, d\omega = 1$ we have

$$B = (2\pi^2/3)\gamma^2 \tag{10.22}$$

and hence

$$\frac{1}{\tau_1} = \left(\frac{2\gamma^2}{3}\right)\left(\frac{\hbar\omega^3}{c^3}\right)\coth\left(\frac{\hbar\omega}{2kT_0}\right) \tag{10.23}$$

for interaction with the electromagnetic radiation field. For single electron spins ($J = \frac{1}{2}$, $g = 2$) the value of B is $(2\pi^2/3)(e/mc)^2$, and at a frequency of 3×10^{10} Hz and a temperature of $1°$K the value of τ_1 given by eqn (10.23) is about 10^{10} s. In a solid paramagnetic substance, however, equilibrium is established not through interaction with the thermal electromagnetic radiation field but through interaction with the lattice vibrations. These may be regarded as giving a 'phonon radiation field' in the solid whose energy density, apart from the complication arising from the presence of longitudinal and transverse phonons, is higher at a given frequency than that given by eqn (10.13) by a factor of order $(c/v)^3 \sim 10^{15}$, where v is the velocity of sound. Thus unless the coefficient B for stimulated emission and absorption of phonons by the magnetic ions is less than 10^{-15} of that for photons, the former process will dominate the latter.

The very long value of τ_1 obtained above is due to the small radiation density at the resonant frequency. The latter means also that the electromagnetic radiation field has a very small heat capacity compared with the spin system, so that we ought to take into account the rate at which heat flows from the surroundings of high heat capacity into the electromagnetic radiation bath. There is no point in pursuing this here, but in the next section we shall see that even for the phonon radiation bath, with its enormously higher energy density, its heat capacity may still be small compared with that of the spin system. The consequences of this are discussed in § 10.6.

10.2. The phonon radiation bath

The energy density in the phonon radiation bath can be written down quite simply by analogy with that in the photon radiation bath, remembering that as well as two transverse polarizations we have in addition a longitudinal wave motion. If the transverse and longitudinal wave velocities are v_t, v_l we have

$$\rho_{\mathrm{ph}}\, d\omega = \frac{\hbar\omega^3}{2\pi^2}\left\{\frac{2}{v_t^3} + \frac{1}{v_l^3}\right\}\frac{d\omega}{\exp(\hbar\omega/kT_{\mathrm{ph}})-1}\ . \tag{10.24}$$

Since we shall only be making order of magnitude calculations we shall ignore the difference between v_t and v_l (as well as any dispersion in

the wave velocity), obtaining

$$\rho_{\text{ph}} \, \mathrm{d}\omega = \frac{3\hbar\omega^3}{2\pi^2v^3} \frac{\mathrm{d}\omega}{\exp(\hbar\omega/kT_{\text{ph}})-1} \tag{10.25}$$

for the phonon energy density in the frequency range ω to $\omega+\mathrm{d}\omega$. It is readily seen that this is the product of the quantity

$$\Sigma = \frac{3\omega^2}{2\pi^2v^3} \, \mathrm{d}\omega, \tag{10.26}$$

which is the number of phonon modes per unit volume in the frequency range just quoted, and $\bar{p}$, the phonon 'occupation number' given by

$$\bar{p} = \frac{1}{\exp(\hbar\omega/kT_{\text{ph}})-1}, \tag{10.27}$$

multiplied by the energy quantum $(\hbar\omega)$, since the quantity $\bar{p}\,(\hbar\omega)$ is just the average energy per mode. In these equations we have introduced a 'phonon temperature' T_{ph} (see § 10.6), which for a given phonon frequency is essentially defined by eqn (10.27).

The processes by which transitions can be induced in the spin system require the presence of oscillatory electromagnetic fields at the resonance frequency of the spins. The phonons can give rise to such oscillatory electromagnetic fields through the motion with respect to the paramagnetic ion of other ions carrying either electric charges (or electric dipole moments) or magnetic dipole moments. This relative motion is caused by the lattice vibrations, and is determined by the lattice strain ϵ, which we must therefore relate to the phonon energy density. For a vibrational mode with wave-vector $q = \omega/v$, the matrix elements for phonon absorption and emission can be related to a strain ϵ_q, where for a crystal of unit volume and density ρ,

$$\epsilon_q = q\left(\frac{\hbar}{2\rho\omega}\right)^{\frac{1}{2}}p^{\frac{1}{2}}$$

for absorption of a lattice quantum that reduces the vibrational quantum number from p to $(p-1)$, and

$$\epsilon'_q = q\left(\frac{\hbar}{2\rho\omega}\right)^{\frac{1}{2}}(p+1)^{\frac{1}{2}}$$

for emission of a quantum raising the vibrational quantum number from p to $p+1$. On averaging over all values of p, and summing over

all vibrational modes in unit volume in the appropriate frequency range, we have, since $q = \omega/v$,

$$\epsilon^2 = \left(\frac{\omega}{v}\right)^2 \left(\frac{\hbar}{2\rho\omega}\right)\bar{p}\,\Sigma \tag{10.28}$$

for phonon absorption, while the corresponding value for phonon emission is greater by a factor (see eqn (10.27))

$$(\bar{p}+1)/\bar{p} = \exp(\hbar\omega/kT_{\mathrm{ph}}), \tag{10.29}$$

which is just the ratio of emission to absorption rates given in eqn (10.7). Hence from (10.28)

$$2\rho v^2\epsilon^2 = (\hbar\omega)\bar{p}\,\sum = \rho_{\mathrm{ph}}\,d\omega \tag{10.30}$$

where ρ is the crystal density.

The phonon radiation bath differs from the electromagnetic radiation bath in that it is limited by the crystal boundaries, and for an isolated crystal *in vacuo* phonon radiation energy cannot readily flow into or out of the crystal, unlike electromagnetic radiation. This makes it easy to compare the heat capacities of the two systems, the assembly of spins and the phonon radiation. Retaining for simplicity a simple two-level system, such as a spin $S = \frac{1}{2}$, whose two levels have energy difference $(\hbar\omega)$, we find that the specific heat per spin is, at constant field H (since $\hbar\omega = g\beta H$), and at temperature T,

$$C_H/k = \left(\frac{\hbar\omega}{2kT}\right)^2 \mathrm{sech}^2\left(\frac{\hbar\omega}{2kT}\right), \tag{10.31a}$$

while the specific heat per vibrational mode at the same frequency is

$$C_{\mathrm{ph}}/k = \left(\frac{\hbar\omega}{2kT}\right)^2 \mathrm{cosech}^2\left(\frac{\hbar\omega}{2kT}\right). \tag{10.31b}$$

The two functions are plotted in Fig. 10.1 as a function of the reduced parameter $(1/x)$, where $x = (\hbar\omega/kT)$. For high values of $(1/x)$, or high temperatures, C_{ph}/k approaches unity while C_H/k falls as T^{-2}. For low values of $(1/x)$, or low temperatures, the two specific heats become identical since we can neglect the population of all but the lowest two vibrational levels, and both vanish exponentially as $T \to 0$. Hence, except when $(\hbar\omega/kT) \ll 1$, there is no great difference between the specific heat per spin and per vibrational mode.

The situation is very different when we include the relative numbers of spins and of vibrational modes. For an undiluted tutton salt, whose molar volume is about 200 cm³, the number of paramagnetic ions per
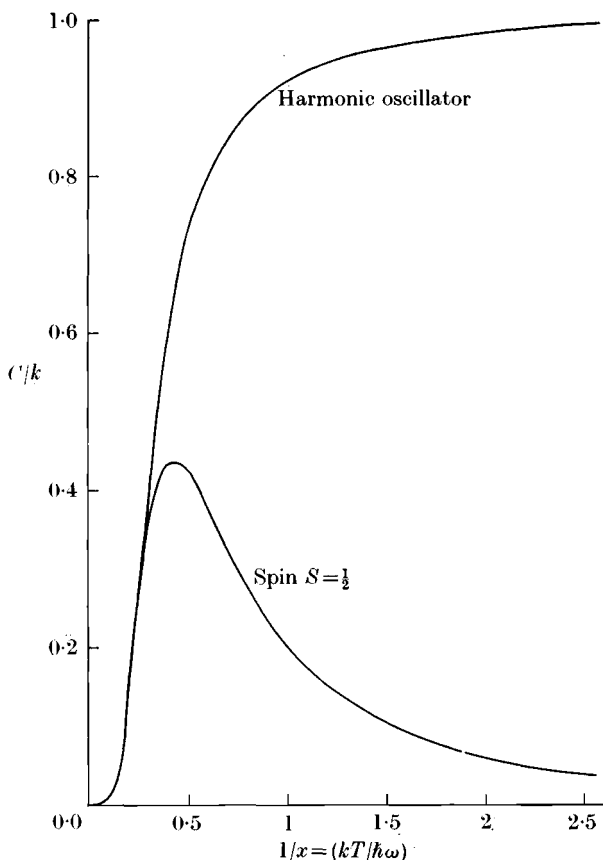
FIG. 10.1. Specific heats of a spin $S = \frac{1}{2}$ with splitting $\hbar\omega$ and of a harmonic oscillator of the same frequency.

cm^3 is about 3×10^{21} per cm^3. For the number of vibrational modes given by eqn (10.26) which are in resonance with the spins, we need to know the value of $d\omega$, which is roughly equal to the width of the resonance line. If we take a line width $\Delta\nu = 0\cdot1$ cm^{-1}, corresponding to a spread in field ≈ 1 kG in the resonance line, we have $d\omega = 2\pi(3 \times 10^9)$, and for a resonance frequency of 1 cm^{-1} we find $\sum = 4 \times 10^{15}$ per cm^3. Even if we take a well-diluted salt such as a tutton salt in which only 1 in 10^4 of the dipositive ions are paramagnetic, we still have 3×10^{17} spins per cm^3, while with a line width of say 10 G (due to the nuclear moments of the protons), we have some 4×10^{13} vibrational modes per cm^3. Hence at temperatures in the region of a few °K the heat capacity of the spin system will far outweigh that of the vibrational modes in resonance with the spins, a point we shall return to in § 10.6. In the immediately

following sections we shall ignore this point, and calculate the spin-lattice relaxation time on the assumption of a constant phonon temperature T_0. Clearly this assumption is only realistic if the resonant phonons are in close thermal contact with a third system of high thermal capacity at the temperature T_0 which we shall refer to as the 'bath temperature'.

In the estimate of $\sum$ given above we have used the convenient value of 3×10^3 ms^{-1} for the phonon velocity v. Few measurements of v exist for crystals of the type normally used in paramagnetic resonance experiments: for LaCl$_3$ an estimate of 2×10^3 ms^{-1} has been obtained by Mikkelson and Stapleton (1963), while Shiren (1962) has measured a velocity of $9 \cdot 25 \times 10^3$ ms^{-1} for longitudinal waves of frequency 10 GHz along the $\langle 100 \rangle$ axis of MgO. (The velocity for transverse waves is only $6 \cdot 5 \times 10^3$ ms^{-1}.) For simplicity we shall continue to use the value 3×10^3 ms^{-1} for later calculations in this chapter. For acoustic waves of frequency 30 GHz (which corresponds to an electromagnetic wavelength of 1 cm), the phonon wavelength is $\lambda \approx 10^{-5}$ cm $= 10^2$ nm, which is large compared with inter-ionic distances in a crystal. This justifies the approximation that ϵ_q is proportional to $(2\pi/\lambda) = q = (\omega/v)$ which appears as the first factor in equations for the strain such as (10.28). At liquid-helium temperatures phonons of wavelengths near the inter-ionic distance (i.e. phonons near the upper frequency limit corresponding to the Debye temperature) are no longer excited, and this simplifies a number of integrals over all phonon modes and frequencies that we shall encounter later. These are commonly of the form

$$I_n = \int\limits_0^\infty \frac{x^n e^x}{(e^x - 1)^2}\, dx \approx I_n' = \int\limits_0^\infty x^n e^{-x}\, dx = n!\,. \qquad (10.32)$$

For example the exact value of $I_4 = 4\pi^4/15 = 26 \cdot 0$ while $I_4' = 4! = 24$. The fractional error is smaller for larger values of n.

10.3. Spin-lattice relaxation by phonons—Waller processes

The relaxation process involves the emission or absorption of a quantum by the spin system, and we consider now how this quantum can be absorbed or emitted by the lattice vibrations (the phonon field). A transition between two levels of the spin system can only be induced by an oscillatory electromagnetic field of the right frequency, and it follows that some mechanism is required whereby the mechanical vibrations of the lattice can produce such an oscillatory electromagnetic

field. In the earliest theory, that of Waller (1932), the mechanism involved was modulation of the spin-spin interaction by the lattice waves; that is, the local magnetic field, which exists at one ion because of the magnetic dipole on a neighbouring ion, fluctuates because the distance between the two ions fluctuates under the action of the lattice vibrations.

It might be thought that modulation of the exchange interaction, which is strongly dependent on distance, would provide a mechanism for spin-lattice relaxation. This is not so for isotropic exchange, since a change in its size merely alters the singlet-triplet splitting in Fig. 9.2 and does not introduce any new matrix elements (in quantum-mechanical language, the isotropic exchange operator and the Zeeman operators commute). Anisotropic exchange, whose operator is formally similar to that for magnetic dipole interaction, does provide such a mechanism (for a discussion, see Harris and Yngvesson (1968)).

The magnetic field of one dipole μ at a neighbouring ion, distance r, is of order μ/r^3. As a result of a lattice strain fluctuating at angular frequency ω, we have $r = r_0(1 + \epsilon \cos \omega t)$ and

$$r^{-3} = r_0^{-3}(1 - 3\epsilon \cos \omega t + \ldots). \tag{10.33}$$

An oscillating magnetic field of frequency ω is thus set up whose mean square value is

$$H_1^2 = (3\epsilon)^2 H_i^2 \tag{10.34}$$

where H_i^2 is the mean square value of the static local field, given by

$$H_i^2 = 2\mu^2 \sum r_0^{-6} = \alpha n^2 \mu^2 \tag{10.35}$$

where α is a constant somewhat greater than unity and n is the number of magnetic ions of moment μ per unit volume. Using eqn (10.30) we have

$$H_1^2 = \frac{9H_i^2}{2\rho v^2} \rho_{\text{ph}} \, d\omega, \tag{10.36}$$

whereas the equivalent value for electromagnetic radiation would be $H_1^2 = 8\pi \rho_{\text{em}} \, d\omega$. The Waller mechanism is therefore faster by a factor

$$\left(\frac{9H_i^2}{16\pi\rho v^2} \right) \left(\frac{3c^3}{2v^3} \right)$$

so that instead of eqn (10.23) we have

$$\frac{1}{\tau_1} = \frac{9H_i^2\gamma^2\hbar\omega^3}{16\pi\rho v^5}\coth\left(\frac{\hbar\omega}{2kT_0}\right) \tag{10.37}$$

$$= \left(\frac{9\alpha}{16\pi}\right)\left(\frac{\gamma^2 n^2\mu^2\hbar}{\rho v^5}\right)\omega^3\coth\left(\frac{\hbar\omega}{2kT_0}\right). \tag{10.38}$$

To obtain an order of magnitude estimate we take the numerical factor $(9\alpha/16\pi)$ as unity, $\rho = 2$ g-cm^{-3} and $n = 3\times 10^{21}$ cm^{-3} (which is typical of an undiluted double sulphate of the iron group). Then with $\mu = 1$ Bohr magneton, the value of τ_1 due to this mechanism at a frequency of 30 GHz and a temperature of 1°K would be about 10^3 s. This value, though much less than that found in § 10.1, is still too high; it would take about 20 min for the heat of magnetization to be transferred to the lattice in a field of 10 kG at 1°K. In highly dilute salts the value of τ_1 would be much longer because of the smaller values of H_i^2, which decrease linearly with the concentration for random dilution; in practice no concentration dependence of τ_1 of this order is found.

The processes considered so far are all 'direct' processes, in which a single quantum is exchanged between the spin system and the radiation field. They result in long relaxation times because the energy density in the radiation field at the resonance frequency is very small. In the electromagnetic case the scattering of a non-resonant photon, combined with a transition in the spin system, is a higher-order process that can be neglected. It was pointed out by Waller that the analogous process for phonons, in which we consider one phonon to be absorbed and another emitted, can be very important. This mechanism can be discussed in very simple terms by considering the modulation of the internal field. Suppose that two strains are present of different frequencies, which we write as $\epsilon_1\cos\omega_1 t$ and $\epsilon_2\cos\omega_2 t$. Then in the expansion of r^{-3} we have

$$\begin{aligned}r^{-3} &= r_0^{-3}(1+\epsilon_1\cos\omega_1 t+\epsilon_2\cos\omega_2 t)^{-3}\\&= r_0^{-3}[1-3\epsilon_1\cos\omega_1 t-3\epsilon_2\cos\omega_2 t\\&\quad +3\epsilon_1\epsilon_2\{\cos(\omega_1-\omega_2)t+\cos(\omega_1+\omega_2)t\}\ldots],\end{aligned} \tag{10.39}$$

from which it is apparent that in second order there will be fluctuations at the frequencies $(\omega_1-\omega_2)$ and $(\omega_1+\omega_2)$. This means that a fluctuating magnetic field at the frequency ω which is required to cause transitions within the spin system will be set up by the combined effect of the

strains at frequencies ω_1 and ω_2 provided that $\omega = \omega_1 \pm \omega_2$. In practice (see below) we shall be concerned with the difference frequency, and we can regard the process as consisting of the absorption of a phonon of energy $\hbar\omega_1$ by the spin system combined with the emission of a phonon of energy $\hbar\omega_2$, the difference in energy $\hbar\omega$ being supplied by the spin system, so that in the final state energy is conserved (see Fig. 10.2). This process is analogous to the Raman effect in optical
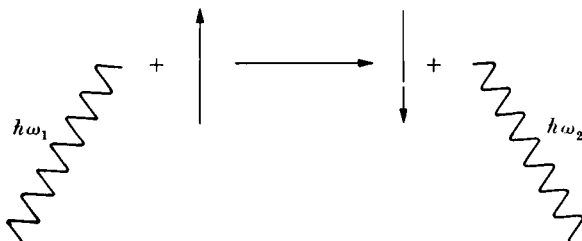

FIG. 10.2. Schematic representation of a 'Raman process', in which a 'spin-flip' occurs through the scattering of a phonon with a change in the phonon frequency. It may be regarded as the virtual absorption of a phonon of energy $\hbar\omega_1$ and the emission of a phonon of energy $\hbar\omega_2$, energy being conserved provided that $\hbar\omega_2 - \hbar\omega_1 = \hbar\omega$, where $\hbar\omega$ is the change in the energy of the spin. Obviously, if the latter is positive, $\hbar\omega_2 < \hbar\omega_1$, and vice versa.

spectroscopy, and is often referred to as a 'Raman process'. Its importance as a mechanism for spin-lattice relaxation can be seen from a plot of the energy density in the phonon system, Fig. 10.3. In the direct process only phonons of frequency ω can take part, and these are very few in number. In the Raman process any two phonons can take part provided that their frequency difference is equal to the resonance frequency of the spin system, so that the much more abundant phonons near the peak of the energy distribution are also available. At high temperatures this more than compensates for the fact that a second-order process involves a much weaker coupling mechanism than a first-order process.

It is obvious from Fig. 10.3 that the number of phonons for which $\omega_1 + \omega_2 = \omega$ is negligible compared with those for which $\omega_1 - \omega_2 = \omega$, and this is the reason why we disregard contributions from the former.

From the expansion of r^{-3} we find that the mean square magnetic field fluctuating at the frequency $\omega = \omega_1 - \omega_2$ is

$$H_1^2 = (3\epsilon_1\epsilon_2)^2 H_i^2 = 9\alpha n^2 \mu^2 \epsilon_1^2 \epsilon_2^2, \tag{10.40}$$
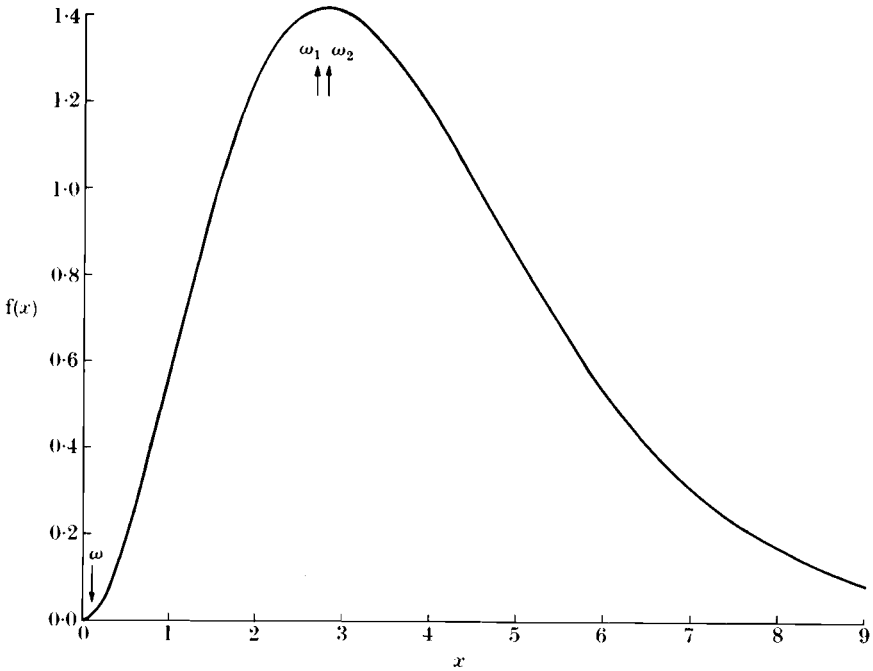
FIG. 10.3. Plot of $f(x) = x^3/(e^x - 1)$ showing the energy density of phonons as a function of $x = \hbar\omega/kT_0$. The arrows indicate the energy density of phonons available for direct processes (ω), at $(\hbar\omega/kT_0) = 0.1$, compared with the densities at (ω_1, ω_2) available for Raman processes, which may be anywhere in the spectrum.

and from eqn (10.21) the rate at which transitions occur in the spin system is

$$w = \frac{\pi}{12}\gamma^2 H_1^2 f(\omega).$$

In relating ϵ_1^2, ϵ_2^2 to the energy density in the phonon field we must remember that ϵ_2 refers to a quantum being emitted by the spin system into the phonon field, and ϵ_1 to a quantum absorbed by the spin system from the phonon field so that (cf. eqn (10.30))

$$\left.\begin{aligned}
\rho v^2 \epsilon_1^2 &= \tfrac{1}{2}\rho_1 \, \mathrm{d}\omega_1 \\
\rho v^2 \epsilon_2^2 &= \tfrac{1}{2}\rho_2 \, \mathrm{d}\omega_2 \exp(\hbar\omega_2/kT_0)
\end{aligned}\right\} \tag{10.41}$$

so that

$$w = \frac{3\pi\alpha n^2\mu^2\gamma^2}{16\rho^2 v^4}\iint f(\omega)\rho_1\rho_2\exp(\hbar\omega_2/kT_0) \, \mathrm{d}\omega_1 \, \mathrm{d}\omega_2. \tag{10.42}$$

In evaluating the double integral we must remember that the two integrations are not independent because $|\omega_1 - \omega_2| = \omega$; and since in

general $\omega \ll \omega_1$, ω_2, we can replace the double integral above by

$$\int \rho_{ph}^2 \exp(\hbar\omega_l/kT_0)\,\mathrm{d}\omega_l \int f(\omega)\,\mathrm{d}\omega$$

$$= \int \frac{9\hbar^2\omega_l^6 \exp(\hbar\omega_l/kT_0)\,\mathrm{d}\omega_l}{4\pi^4 v^6\{\exp(\hbar\omega_l/kT_0)-1\}^2}$$

$$= \frac{9\hbar^2}{4\pi^4 v^6}\left(\frac{kT_0}{\hbar}\right)^7 \int_0^{x_m} \frac{x^6 e^x\,\mathrm{d}x}{(e^x-1)^2} = \frac{9\hbar^2}{4\pi^4 v^6}\left(\frac{kT_0}{\hbar}\right)^7 I_6, \quad (10.43)$$

where ω_l denotes a phonon frequency and we have used the fact that $\int f(\omega)\,\mathrm{d}\omega = 1$. The integral over the lattice frequencies is carried from 0 to the Debye frequency but at low temperatures where such frequencies are not excited there is no significant error in replacing the upper limit by infinity. Then the integral I_6 is approximately (see eqn (10.32))

$$\int_0^\infty x^6 e^{-x}\,\mathrm{d}x = 6!$$

and we have

$$\frac{1}{\tau_1} = 2w = 6!\left(\frac{27\alpha}{32\pi^3}\right)\frac{\gamma^2\hbar^2 n^2\mu^2}{\rho^2 v^{10}}\left(\frac{kT_0}{\hbar}\right)^7. \quad (10.44)$$

Using the same parameters as before this gives

$$1/\tau_1 \sim 10^{-13}T_0^7,$$

which is insignificant at 1°K but is more important than the Waller direct process above 50°K.

The integral I_6 can also be evaluated in the high temperature limit where kT_0 is large compared with the maximum phonon energy $(\hbar\omega_m)$, though this is a situation usually of less practical interest. Then since $x \ll 1$,

$$I_6 = \int_0^{x_m} \frac{x^6 e^x\,\mathrm{d}x}{(e^x-1)^2} \sim \int_0^{x_m} x^4\,\mathrm{d}x = \tfrac{1}{5}x_m^5 = \tfrac{1}{5}\left(\frac{\hbar\omega_m}{kT_0}\right)^5$$

and hence

$$\frac{1}{\tau_1} = \left(\frac{27\alpha}{160\pi^3}\right)\frac{\gamma^2 n^2\mu^2}{\rho^2 v^{10}}\omega_m^5 k^2 T_0^2, \quad (10.45)$$

where ω_m is the maximum phonon frequency. Taking the Debye temperature to be about 100°K, which is typical of many paramagnetic

salts, ω_m is about 10^{13}, and using the same parameters as before we find

$$\frac{1}{\tau_1} \sim 10^{-6} T_0^2,$$

so that τ_1 would still be about 10 s at 300°K. This is in violent contrast with experimental results, which show that τ_1 varies from 10^{-6} s to less than 10^{-12} s at room temperature.

10.4. Spin-lattice relaxation by modulation of the ligand field

The relaxation processes considered in the previous section, involving modulation of the internal dipolar field, are clearly insufficiently rapid to explain the experimental results, at any rate in magnetically dilute salts. A more potent mechanism was suggested by Heitler and Teller (1936); the theory was elaborated by Kronig (1939) and Van Vleck (1940), who in a long and detailed paper obtained relaxation times of the right order of magnitude. This mechanism consists of modulation of the crystal electric field or ligand field through motion of the electrically charged ions under the action of the lattice vibrations. Obviously this produces a fluctuating *electric* field that is essentially a dynamic orbit-lattice interaction, with no direct interaction with the electron spin. However, just as a static ligand field splits the orbital states of a magnetic ion and indirectly influences the spin levels through the spin-orbit coupling, so a fluctuating ligand field can cause transitions between these levels. In considering such processes we must of course take account of restrictions on the way in which electric fields can interact with magnetic ions, the most important of these being that the matrix elements of an electric perturbation vanish between a pair of Kramers conjugate states.

A numerical calculation of the effects of lattice vibrations in distorting the crystalline electric field is faced with the same computational difficulties (or more) that arise in calculating the static crystal field (or ligand field). This problem has been side-stepped by Orbach (1961a) by expanding the crystalline electric potential V in powers of the strain:

$$V = V^{(0)} + \epsilon V^{(1)} + \epsilon^2 V^{(2)} + \ldots, \tag{10.46}$$

where the first term on the right is just the static term. The second and third terms represent the additional electric potential generated by the strain in first- and second-order respectively. To find their

effect on the magnetic ion, we must include also the spin-orbit coupling, and use the weak, intermediate, or strong crystal field representation appropriate to the static interaction. On this basis we may regard (10.46) as the 'magnetic ion-lattice interaction'.

If ϵ is a fluctuating strain caused by the lattice vibrations, the second and later terms give the dynamic part of the magnetic ion-lattice interaction. A reasonable assumption (which is considered in more detail by Scott and Jeffries (1962)) is that each of the terms $V^{(n)}$ is of the same order as $V^{(0)}$, though they will of course contain terms of lower symmetry than $V^{(0)}$ because the strain reduces the local symmetry. This assumption makes it possible to obtain some order of magnitude estimates of the spin-lattice relaxation time, and once more we consider first the so-called 'direct process', in which one phonon is emitted or absorbed in a given relaxation transition.

The direct process

From eqns (10.20), (10.46) we obtain

$$w_{ij} = (2\pi/\hbar^2)\epsilon^2 \, |\langle i| \, V^{(1)} \, |j\rangle|^2 f(\omega) \tag{10.47}$$

and on using (10.30) to relate ϵ^2 to the energy density of phonons, and integrating over the line shape, we find

$$B = \frac{\pi}{\hbar^2 \rho v^2} \, |V^{(1)}|^2 \tag{10.48}$$

for the Einstein coefficient of induced emission or absorption of phonons. Hence, using (10.25) for the phonon energy density, we obtain

$$\frac{1}{\tau_1} = \frac{3}{2\pi\hbar\rho v^5} \, |V^{(1)}|^2 \, \omega^3 \coth\!\left(\frac{\hbar\omega}{2kT_0}\right). \tag{10.49}$$

In the case of a non-Kramers ion the ground states generated by the static crystal potential may have different orbital states between which the matrix elements of $V^{(1)}$ are finite and independent of frequency, in which case (10.49) has the same frequency and temperature dependence as for photons (10.23). If the levels are degenerate in zero magnetic field we have $\hbar\omega = g\beta H$, so that

$$1/\tau_1 \text{ varies as } H^3 \coth(g\beta H/2kT_0) \tag{10.50}$$

$$\text{or as } H^2 T_0 \text{ when } (g\beta H/kT_0) \ll 1. \tag{10.51}$$

In the case of a Kramers doublet, because of time reversal, the matrix elements of an electric potential such as $V^{(1)}$ vanish in zero magnetic

field. However the presence of an external magnetic field produces admixtures of excited states of order $(g\beta H/\Delta)$ or $(\hbar\omega/\Delta)$, where Δ is a crystal field splitting. To this order the two states of the doublet are no longer exactly time-reversed states, and we must replace $V^{(1)}$ by roughly

$$(\hbar\omega/\Delta)V^{(1)}.$$

Hence

$$\frac{1}{\tau_1} = \frac{3\hbar}{2\pi\rho v^5} \frac{1}{\Delta^2} |V^{(1)}|^2 \, \omega^5 \coth\left(\frac{\hbar\omega}{2kT_0}\right). \tag{10.52}$$

For the field and temperature dependence this gives

$$1/\tau_1 \text{ varies as } H^5 \coth(g\beta H/2kT_0) \tag{10.53}$$

$$\text{or as } H^4 T_0 \text{ when } (g\beta H/kT_0) \ll 1. \tag{10.54}$$

In the rare-earth group $|V^{(1)}|^2$ for non-Kramers ions is of order 10 to 100 $(\text{cm}^{-1})^2$; thus taking $3V = \Delta = 30 \text{ cm}^{-1}$ makes τ_1 about 10^{-3} s if the levels are split by 1 cm^{-1} at 1°K, while for Kramers doublets $(\hbar\omega/\Delta)^2$ produces an extra factor $\sim 10^{-3}$ in τ_1^{-1} and $\tau_1 \sim 1$ s. In the iron group the matrix elements are rather greater and the relaxation times correspondingly shorter.

The need to break the time-reversal symmetry of a Kramers doublet in order to produce relaxation by the process discussed above was pointed out by Van Vleck (1940). The factor that it introduces is closely related to the temperature-independent (or Van Vleck) term in the magnetic susceptibility, and like it can be quite anisotropic. It follows that for a given crystal orientation we get an ω^5 or H^5 dependence, but if measurements are made at constant frequency, and H is varied as the crystal is rotated, we cannot expect a variation in $(1/\tau_1)$ that follows a simple $H^2\omega^3$ dependence.

A magnetic hyperfine field will also be effective in breaking the time-reversal symmetry of a Kramers doublet, producing admixtures of excited electronic states that are of two kinds. First, the diagonal part of the magnetic hyperfine interaction can be combined with the Zeeman term to give $\hbar\omega = g\beta(H+H_n)$, where H_n is proportional to the nuclear magnetic quantum number m (cf. eqn (1.30) or § 1.6); thus if measurements are made at constant frequency eqn (10.52) still holds, though at low fields $(H < H_n)$ the effect of H_n will be more important than that of H. Second, the off-diagonal terms in the magnetic hyperfine interaction involving $I_\pm$ produce admixtures of excited states of order (A'/Δ') which are independent of ω, so that we get a frequency dependence of τ_1^{-1} that is similar to (10.49) rather than

(10.52), but that is numerically smaller than (10.49) by a factor $\sim (A'/\Delta')^2$. Here A' is the matrix element of the magnetic hyperfine interaction between the ground doublet and an excited state at Δ' (which may not be the same as Δ). This provides a relaxation path through the forbidden transitions $\Delta m = \pm 1$, whose rate in strong fields is slower by a factor $\sim (A'/\hbar\omega)^2$, if we neglect the difference between Δ and Δ', than that for the allowed transitions $\Delta m = 0$ given by eqn (10.52). The importance of these extra relaxation paths has been demonstrated, for example, by Baker and Ford (1964), and more extensively by Larson and Jeffries (1966b).

The two-phonon Orbach process

In 1961 an important two-phonon process suggested by Orbach was verified experimentally by Finn, Orbach, and Wolf (1961) (see also Manenkov and Prokhorov (1962)). Suppose the magnetic ion has a set of energy levels such as that shown in Fig. 10.4(i), where there are two
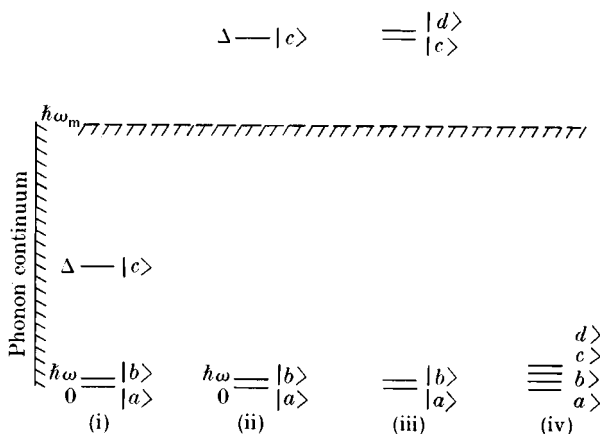

FIG. 10.4. Level schemes for spin-lattice relaxation theory. (i) Orbach process, (ii) Raman process (non-Kramers), (iii) Raman process (Kramers ion), (iv) Orbach–Blume process (ground multiplet).

low-lying states (such as a Kramers doublet) and an excited state $|c\rangle$ whose energy is less than the maximum phonon energy. It is then possible for an ion in, say, state $|b\rangle$ to absorb a phonon of the appropriate frequency by a direct process, and be excited to the state $|c\rangle$. In this state it emits a second phonon by spontaneous or induced emission and falls down to state $|a\rangle$. This gives an indirect transfer of ions from state $|b\rangle$ to state $|a\rangle$, and constitutes a relaxation process that may be faster than the direct transfer from state $|b\rangle$ to $|a\rangle$ because

of the much higher density of phonons of energy Δ. If the direct process between states $|a\rangle$ and $|b\rangle$ is negligible, the rate equations become

$$dn_a/dt = -w_{ac}n_a + w_{ca}n_c,$$
$$dn_b/dt = -w_{bc}n_b + w_{cb}n_c,$$

where the transition rates now refer to transfers from the lower states to the excited state $|c\rangle$. In general, we are concerned with effects that primarily disturb the population of the states $|a\rangle$, $|b\rangle$, such as saturation of the transition $|a\rangle \leftrightarrow |b\rangle$, but which do not in first order change n_c. Hence if we neglect the difference between w_{ac} and w_{bc}, writing them simply as $w_\uparrow$, we have

$$d(n_a - n_b)/dt = -w_\uparrow(n_a - n_b)$$

from which

$$\frac{1}{\tau_1} = w_\uparrow = \frac{3}{2\pi\hbar^4 \rho v^5} \, |V^{(1)}|^2 \, \Delta^3 \frac{1}{\exp(\Delta/kT_0) - 1} \qquad (10.55)$$

where $V^{(1)}$ is a product of matrix elements between the states $|a\rangle$, $|b\rangle$ and the state $|c\rangle$. This gives a relaxation process that is extremely temperature-dependent since, in the limit where $\Delta \gg kT_0$,

$$1/\tau_1 \text{ varies as } \Delta^3 \exp(-\Delta/kT_0) \qquad (10.56)$$

independent of an applied magnetic field except in so far as this may alter the value of Δ.

Using the same parameters as before for the rare-earth group, one finds

$$1/\tau_1 \sim 10^4 \, \Delta^3 \exp(-\Delta/T_0)$$

if Δ is measured in °K; the experimental results lie roughly in the range $(10^3 \text{ to } 10^5) \, \Delta^3 \exp(-\Delta/T_0)$.

In any such two-stage process we may expect to find more than one relaxation rate, but if the rates are materially different the controlling factor is the slower rate. In the discussion above, if $\Delta \gg kT_0$, the slower rate is that for induced phonon absorption raising the ion to state $|c\rangle$, the return to the ground state being primarily due to spontaneous phonon emission that is faster under this condition. Thus the controlling rate is $w_\uparrow$, and this is the rate that appears in (10.55).

If w_{ca}, w_{cb} are not equal we may not get a simple one-exponential relaxation rate. A more general discussion (including the case when the states $|a\rangle$, $|b\rangle$ lie higher in energy than $|c\rangle$) is given by Harris and Yngvesson (1968).

The two-phonon Raman process

We consider now processes involving two phonons which are Raman-type processes similar to those introduced by Waller, but in which the interaction mechanism is provided by the ligand field rather than the magnetic spin-spin interaction. As before, the magnetic ion makes a transition from state $|b\rangle$ to state $|a\rangle$, or vice versa, accompanied by the virtual absorption of a phonon of angular frequency ω_1 and the emission of a phonon of frequency ω_2. The condition for conservation of energy in the final state is again $\omega_2 - \omega_1 = \pm\omega$. Physically this requires that lattice distortions oscillating at frequencies ω_1, ω_2 can combine to generate a crystal potential fluctuating at frequency $\omega = |\omega_2 - \omega_1|$. Like the magnetic spin-spin interaction mechanism discussed in § 10.3, the crystal potential depends on inverse powers of the ligand distance, so that non-linear terms in ϵ^2 (and higher powers) are to be expected, as indicated in eqn (10.46).

We distinguish between two types of Raman process, which we call 'first order' and 'second order' according to the nature of the perturbation involved:

(i) a first-order Raman process arises when the crystal potential $V^{(2)}$ in (10.46) has matrix elements between the two states $|a\rangle$, $|b\rangle$ of the magnetic ion. The corresponding transition probability is then

$$w = (2\pi/\hbar^2)\, |\epsilon_1\epsilon_2 V^{(2)}|^2 f(\omega); \qquad (10.57\text{a})$$

(ii) a second-order Raman process in which one phonon causes a virtual transition from one of the ground states to an excited state $|c\rangle$, followed by another virtual transition induced by the second phonon in which the magnetic ion returns from $|c\rangle$ to the other ground state. In this case the transition probability is

$$w = (2\pi/\hbar^2) \left| \frac{\epsilon_1 V_1^{(1)} \epsilon_2 V_2^{(1)}}{\Delta} \right|^2 f(\omega), \qquad (10.57\text{b})$$

where $V_1^{(1)}$, $V_2^{(1)}$ are matrix elements of $V^{(1)}$ between the states $|a\rangle$, $|b\rangle$ and the excited state $|c\rangle$. The reason why only 'virtual' transitions are involved (unlike the Orbach process) is that the state $|c\rangle$ has an energy Δ that lies outside the continuum of allowed phonon frequencies, as indicated in Fig. 10.4(ii).

As before, each of these mechanisms gives transition rates that depend on the product $\epsilon_1^2\epsilon_2^2$, where the squares of the strains can be related to the energy densities at the phonon frequencies ω_1, ω_2 by eqns (10.28)–(10.30). The calculation proceeds as in § 10.3 and, on

integrating over all phonon frequencies ω_l, we obtain

$$\frac{1}{\tau_1} = 2w = \frac{9}{4\pi^3\rho^2 v^{10}}\left\{(V^{(2)})^2 + \frac{(V^{(1)})^4}{\Delta^2}\right\} \times$$

$$\int_0^{\omega_m} \frac{\omega_l^6 \exp(\hbar\omega_l/kT_0)}{\{\exp(\hbar\omega_l/kT_0)-1\}^2}\, d\omega_l$$

$$= \frac{9}{4\pi^3\rho^2 v^{10}}\left\{(V^{(2)})^2 + \frac{(V^{(1)})^4}{\Delta^2}\right\}\left(\frac{kT_0}{\hbar}\right)^7 I_6. \quad (10.58)$$

At low temperatures the integral can, as before, be carried to infinity and approximated by $I'_6 = 6!$, giving

$$\frac{1}{\tau_1} = \frac{9(6!)}{4\pi^3\rho^2 v^{10}}\left\{(V^{(2)})^2 + \frac{(V^{(1)})^4}{\Delta^2}\right\}\left(\frac{kT_0}{\hbar}\right)^7. \quad (10.59)$$

In an approximation where $V^{(1)} \sim V^{(2)} \sim \Delta$, the two contributions from the first- and second-order processes are clearly comparable, and it is difficult to separate them experimentally. A rough estimate suggests that the Raman processes will be more rapid than the direct process (eqn (10.49)) by a factor of order $(10^{-7}$ to $10^{-6})T_0^6$, so that it may become the more important process above about $10°$K. Equations (10.58), (10.59) are valid, however, only for non-Kramers ions, and we must consider the case of ions with Kramers degeneracy separately.

We have seen that in the direct process the matrix elements of $V^{(1)}$ vanish between two time-conjugate states of a Kramers ion, and the same is true for $V^{(2)}$. However the application of a magnetic field destroys the time-conjugate nature of the doublet to order $(g\beta H/\Delta')$ or $(\hbar\omega/\Delta')$; the first-order Raman process is therefore allowed at a reduced rate which, by a straightforward modification of (10.59), is

$$\frac{1}{\tau_1} = \frac{9(6!)}{4\pi^3\rho^2 v^{10}}\left(\frac{\hbar\omega}{\Delta'}\right)^2(V^{(2)})^2\left(\frac{kT_0}{\hbar}\right)^7. \quad (10.60)$$

Here we have written Δ' rather than Δ because the Zeeman interaction has a matrix element with an excited state (of energy Δ') that is not necessarily the same state as that to which the crystal field $V^{(1)}$ has a matrix element from the ground state.

In the second-order Raman process for a Kramers ion a similar difficulty arises, but in a less direct way. The energy levels of such an ion generated by the static crystal field are always degenerate in pairs, so that the excited state $|c\rangle$ is accompanied by its time-conjugate state $|d\rangle$, as in Fig. 10.4(iii). The matrix elements that occur in eqn

(10.57b) must be summed over both states $|c\rangle$ and $|d\rangle$, and are of the form

$$\frac{\langle a|\ V_2^{(1)}\ |c\rangle\langle c|\ V_1^{(1)}\ |b\rangle}{\hbar\omega_1-\Delta}+\frac{\langle a|\ V_1^{(1)}\ |d\rangle\langle d|\ V_2^{(1)}\ |b\rangle}{-\hbar\omega_2-\Delta}. \qquad (10.61)$$

The products of the matrix elements in the two numerators are equal but of opposite sign, a result often referred to as the 'Van Vleck (1940)' cancellation, and which can be shown to follow generally from time-reversal symmetry (see § 15.4). It follows that the sum of the two terms in (10.61) vanishes except for the difference in the denominators, which arises from the presence of the phonon energy $\hbar\omega_l$ with opposite signs, corresponding respectively to absorption and emission. The net result is a residuum of order

$$\frac{2\hbar\omega_l}{\Delta}\frac{V^2}{\Delta}$$

where ω_l is a lattice frequency, if $\Delta\gg(\hbar\omega_l)$.

Using this matrix element for the transition probability in the second-order Raman process we find

$$\frac{1}{\tau_1} = \frac{9\hbar^2}{\pi^3\rho^2 v^{10}}\left(\frac{V^4}{\Delta^4}\right)\int_0^{\omega_m}\frac{\omega_l^8\exp(\hbar\omega_l/kT_0)}{\{\exp(\hbar\omega_l/kT_0)-1\}^2}\,d\omega_l$$

$$= \frac{9\hbar^2}{\pi^3\rho^2 v^{10}}\left(\frac{V^4}{\Delta^4}\right)\left(\frac{kT_0}{\hbar}\right)^9 I_8, \qquad (10.62)$$

where

$$I_8 = \int_0^{x_m}\frac{x^8 e^x}{(e^x-1)^2}\,dx.$$

At low temperatures this integral can be approximated by $I_8' = 8!$, giving

$$\frac{1}{\tau_1} = \frac{(9!)\hbar^2}{\pi^3\rho^2 v^{10}}\left(\frac{V^4}{\Delta^4}\right)\left(\frac{kT_0}{\hbar}\right)^9. \qquad (10.63)$$

With the same parameters as before, a rough estimate gives

$$(1/\tau_1)\sim 10^{-5}T_0^9,$$

so that this process would predominate over the direct process for a Kramers doublet already above about 5°K. At still higher temperatures the approximations inherent in our treatment of the phonon spectrum

mean that we cannot necessarily expect a simple T_0^9 law to hold (see Kiel and Mims (1967)).

The process just considered allows relaxation to take place within a Kramers doublet at a rate independent of the applied magnetic field, in contrast with the process described by (10.60) which depends on the application of a magnetic field to destroy the time-conjugate nature of the doublet states. If we set $V^{(1)} = V^{(2)} = \Delta = \Delta'$, a very rough estimate shows that (10.60) is slower than (10.63) by a factor $\sim 10^{-2}(\hbar\omega/kT_0)^2$, making it usually unimportant except at extremely low temperatures where, unlike other Raman processes, it gives an H^2 dependence of $1/\tau_1$ for a doublet whose splitting is $\hbar\omega = g\beta H$. At such temperatures the direct process will probably predominate.

Multiplet ground state

Another important case, considered by Blume and Orbach (1962), is that of a multiplet ground state; that is, the case (see Fig. 10.4(iv)) where the states $|c\rangle$, $|d\rangle$ have virtually the same energy as the states $|a\rangle$, $|b\rangle$. Then, in eqn (10.61), Δ is very small and can be neglected in comparison with the phonon energy $\hbar\omega_1$, $\hbar\omega_2$. Since the two numerators are of opposite sign, the two terms now reinforce each other instead of cancelling, giving a matrix element of order $(V^2/\hbar\omega_l)$. Instead of eqn (10.58) we have

$$\frac{1}{\tau_1} = \frac{9}{4\pi^3\rho^2v^{10}}\left(\frac{V^4}{\hbar^2}\right)\int_0^{\omega_m} \frac{\omega_l^4 \exp(\hbar\omega_l/kT_0)}{\{\exp(\hbar\omega_l/kT_0)-1\}^2} \, d\omega_l$$

$$= \frac{9}{4\pi^3\rho^2v^{10}}\left(\frac{V^4}{\hbar^2}\right)\left(\frac{kT_0}{\hbar}\right)^5 I_4. \qquad (10.64)$$

At low temperatures the integral can be taken to infinity, when $I_4 \approx I_4' = 4!$, and

$$\frac{1}{\tau_1} = \frac{9(3!)}{\pi^3\rho^2v^{10}}\left(\frac{V^4}{\hbar^2}\right)\left(\frac{kT_0}{\hbar}\right)^5. \qquad (10.65)$$

For non-Kramers doublets Walker (1968) has described a mechanism that also gives a T_0^5 dependence and can operate between states of a multiplet that are not time-conjugate.

10.5. Summary and comparison with experiment

We now present a summary of the formulae for the spin-lattice relaxation time derived in the previous section, together with a

comparison with some experimental results. We confine ourselves to situations in which the results do not appear to be affected by any phonon bottle-neck, reserving discussion of the latter to § 10.6. We consider first non-Kramers ions, then Kramers ions, followed by ions with $S > \frac{1}{2}$, all in the low-temperature region; finally the high-temperature region will be briefly discussed.

The principal experimental techniques for the measurement of τ_1 may be classified into two main types: steady-state methods and transient methods. The former includes (a) the classical low-frequency method (Gorter 1947, Cooke 1950) and (b) a resonance method in which the degree of saturation is observed as a function of oscillatory power level, but this requires knowledge of the transition probability, the line width and the oscillatory signal strength (cf. §§ 2.8, 2.9). Transient methods include (c) observation of the recovery of the paramagnetic resonance signal at low incident power level following the application of a saturating pulse, a method that has the advantages that each resolved resonance line can be studied separately, and that the presence of more than one relaxation time can be detected; (d) spin-echo methods, which have the further advantage over (c) of better sensitivity because observation of the transient recovery is not restricted to low power level; and (e) observation of the recovery of the steady-state magnetization following a saturating pulse, either by direct measurement or observation of some quantity (e.g. Faraday rotation) that is proportional to the magnetization. Methods (a) and (e) measure an average over all magnetic sub-states, while (b) is determined by the combined action of all relaxation paths. In general, (c) or (d) is the most accurate method, and can readily be used over a wide range of relaxation times. (d) is particularly sensitive and (like (b)) can be applied to very dilute samples.

Non-Kramers ions

For a resonance frequency $(\omega/2\pi)$ our formulae for the relaxation time can be summarized as

$$\left.\begin{aligned}
\frac{1}{\tau_1} = {}& R_{\mathrm{d}}(\hbar\omega)^3 \coth(\hbar\omega/2kT_0) \text{ (direct process, (10.49))} + \\
& + R_{\mathrm{or}}\,\Delta^3\{\exp(\Delta/kT_0)-1\}^{-1} \text{ (Orbach process, (10.55))} + \\
& + R_{\mathrm{r}}T_0^7 \text{ (Raman process, (10.59))},
\end{aligned}\right\} \quad (10.66)$$

where R_{d}, R_{or}, R_{r} are parameters in an obvious notation, and Δ is the

energy of an excited electronic state lying within the phonon energy band.

An experimental determination of the direct and Raman terms is shown in Fig. 10.5 for Tb^{3+} in yttrium ethylsulphate. This non-Kramers ion (see § 5.6) has a doublet ground state, slightly split by a crystal-field effect; the measurements shown are in zero external field, when there are two allowed electronic transitions for the hyperfine states $|m| = \frac{3}{2}$ and $\frac{1}{2}$ respectively. In these measurements $\hbar\omega \ll kT_0$, so that the first term in (10.66) can be approximated by $R_d(\hbar\omega)^2(2kT_0)$, giving the term linear in T_0. When the initial splitting of a non-Kramers
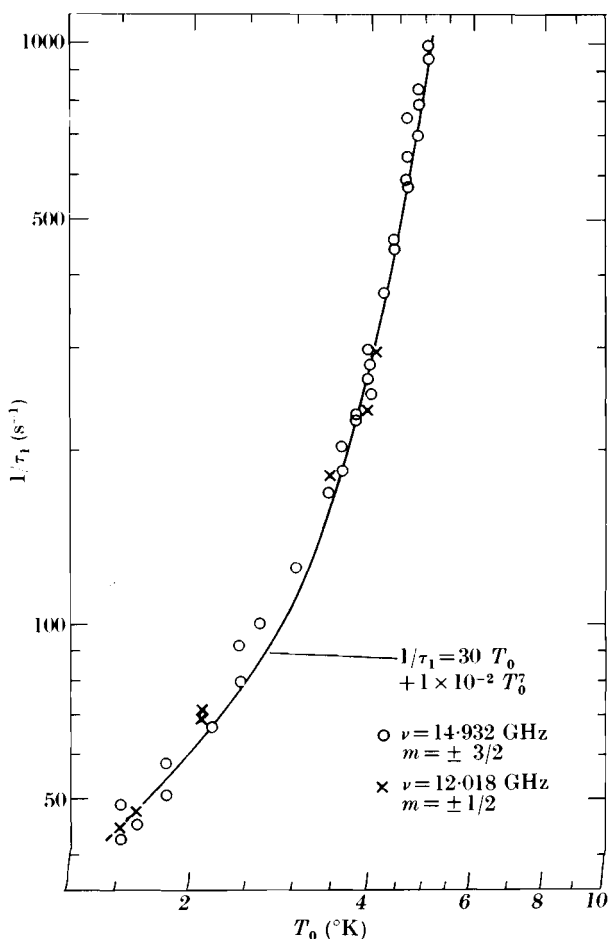
FIG. 10.5. Spin lattice relaxation rate $1/\tau_1$ as a function of temperature T_0 for 1 per cent Tb^{3+} in yttrium ethylsulphate at zero magnetic field. (After Larson and Jeffries 1966a.)

doublet is small compared with the Zeeman splitting the direct process gives $(1/\tau_1)$ varying as H^2T_0.

As a very rough order of magnitude, in the rare-earth group when $\hbar\omega = g\beta H \equiv 1$ cm^{-1}, we may expect

$$1/\tau_1 = 10^3 T_0 + (10^3 \text{ to } 10^5)\,\Delta^3 \exp(-\Delta/T_0) + (10^{-2} \text{ to } 10^2)T_0^7, \quad (10.67)$$

where τ_1 is in seconds and Δ in °K, assuming that $(T_0/\Delta) \ll 1$.

Kramers doublets

The formulae we have obtained can be summarized as follows.

$$\left.\begin{aligned}
\frac{1}{\tau_1} &= R_d(\hbar\omega)^5 \coth(\hbar\omega/2kT_0) \text{ (direct process, (10.52))} + \\
&+ R_{\text{or}}\,\Delta^3\{\exp(\Delta/kT_0)-1\}^{-1} \text{ (Orbach process, (10.55))} + \\
&+ R_r T_0^9 + R_r'(\hbar\omega/k)^2 T_0^7 \text{ (Raman processes, (10.63)} \\
&\qquad\qquad\qquad\qquad \text{and (10.60)).}
\end{aligned}\right\} \quad (10.68)$$

In the region where $g\beta H = \hbar\omega \ll kT_0 \ll \Delta$, this approximates to

$$\frac{1}{\tau_1} = R_d' H^4 T_0 + R_{\text{or}}\,\Delta^3 \exp(-\Delta/kT_0) + R_r T_0^9 + R_r'(g\beta H/k)^2 T_0^7. \quad (10.69)$$

In the direct process it must be remembered that one factor $(\hbar\omega)^2$ or H^2 arises from the need to break the time-conjugate nature of the states, and that R_d, R_d' are dependent on the orientation of the magnetic field. Similar considerations would apply to R_r' (see Kiel and Mims (1967)). As a very rough order of magnitude in the rare-earth group, we have, when $g\beta H = \hbar\omega \equiv 1$ cm^{-1},

$$\frac{1}{\tau_1} = T_0 + (10^3 \text{ to } 10^5)\,\Delta^3 \exp(-\Delta/T_0) + (10^{-5} \text{ to } 10^{-1})\,T_0^9 + (10^{-5} \text{ to } 10^{-1})\,T_0^7, \quad (10.70)$$

where τ_1 is in seconds and Δ is in °K.

Experimental results confirming the terms in T_0 and T_0^9 have already been presented in Fig. 1.24 for Nd^{3+} in yttrium ethylsulphate. Measurements on the same ion in lanthanum magnesium nitrate are shown in Fig. 10.6; in this case the predominant term is an Orbach term together with a direct process $\coth(\hbar\omega/2kT_0)$ measured into the region where $(\hbar\omega/2kT_0)$ is roughly 0·6. No differences are observed for samples containing 1 and 5 per cent Nd^{3+}, confirming that the relaxation times are independent of concentration in this range.
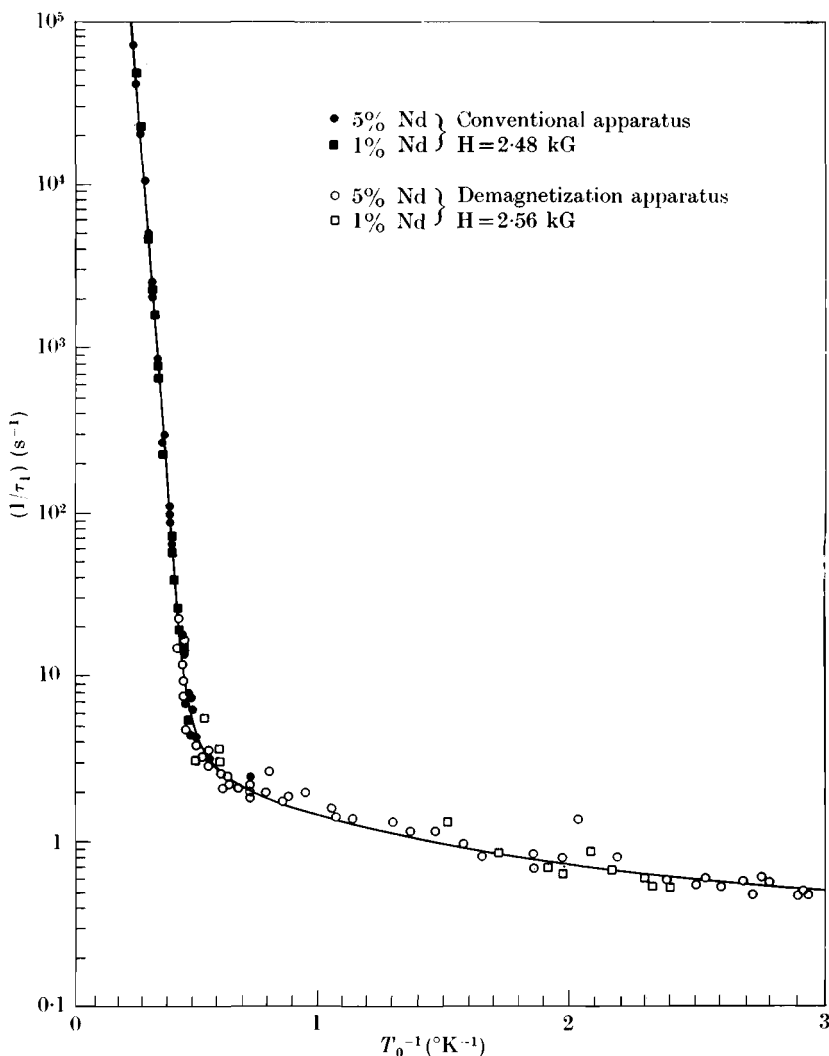
FIG. 10.6. Experimental results for the spin-lattice relaxation rate $1/\tau_1$ for Nd^{3+} in $La_2Mg_3(NO_3)_{12}, 24H_2O$ with H perpendicular to the c-axis in the temperature range from $0.3°K$ to $4.3°K$. The data show no concentration dependence, and are fitted accurately by the formula

$$1/\tau_1 = 6.3 \times 10^9 \exp(-47.6/T_0) + 0.3 \coth(\hbar\omega/2kT_0) \ (s^{-1}),$$

showing that at higher temperatures relaxation is dominated by an Orbach process and at lower temperatures by the direct process. At the lowest temperatures the relaxation rate is chiefly due to the spontaneous emission of phonons. (After Ruby, Benoit, and Jeffries 1962.)
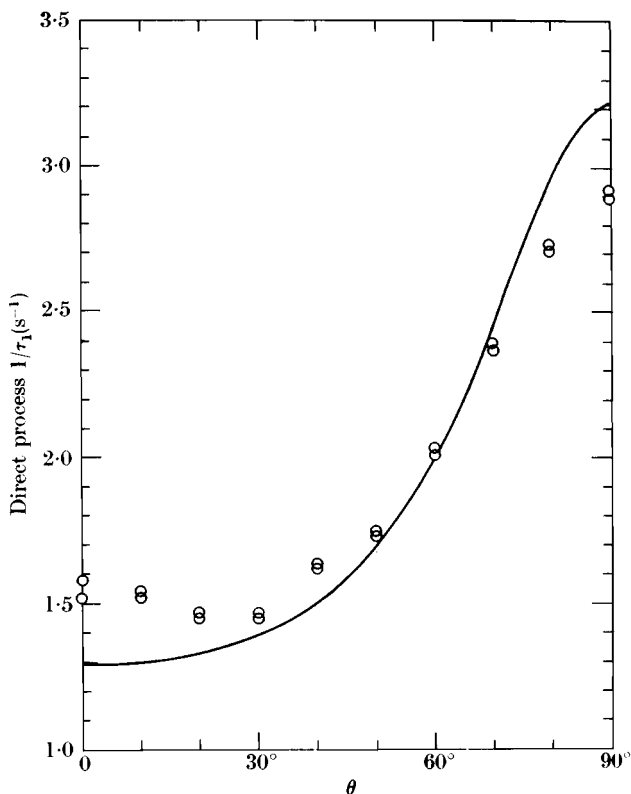
FIG. 10.7. Variation of $(1/\tau_1)$ at 9·41 GHz with the angle θ made by the external magnetic field H with the symmetry axis for 0·1% Nd^{3+} in yttrium ethylsulphate at a temperature $T_0 = 1·52°K$ where the direct process predominates. The full line represents the variation predicted by an approximate theoretical calculation. (Larson and Jeffries 1966b.)

The Nd^{3+} ion in these two substances also illustrates a number of other features of the relaxation process. Figure 10.7 shows how $(1/\tau_1)$ varies with the angle θ which the external field H makes with the crystallographic axis of symmetry at a temperature of 1·52°K where the direct process is dominant, while at 4·21°K where the Raman process is much the more important, the contribution to $(1/\tau_1)$ from the Raman process is independent of angle (Fig. 10.8). Measurements on a sample of 0·5 per cent Nd^{3+} in lanthanum magnesium nitrate, enriched to 91·3 per cent in the isotope ^{143}Nd $(I = \frac{7}{2})$, shown in Fig. 10.9, demonstrate the importance of extra paths involving the magnetic hyperfine interaction. These give an additional direct process

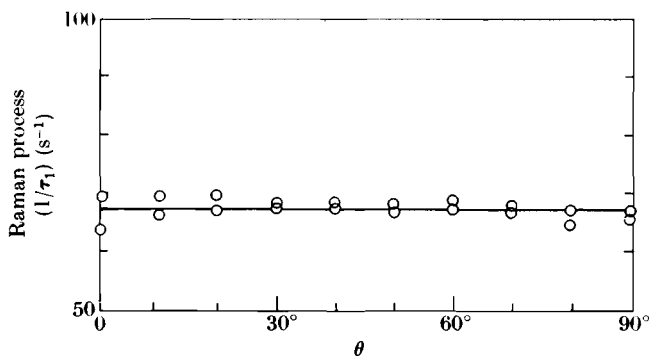$$\frac{1}{\tau_1} = R_d^{hfs}(\hbar\omega)^3 \coth(\hbar\omega/2kT_0) \qquad (10.71)$$

FIG. 10.8. Measurements on the same sample as in Fig. 10.7 but at a higher temperature $T = 4 \cdot 21°K$. The contribution to $(1/\tau_1)$ from the Raman process is found to be isotropic. This agrees with eqn (10.63); the Raman rate is found to vary as T_0^9 (see Fig. 1.24). (Larson and Jeffries 1966b.)
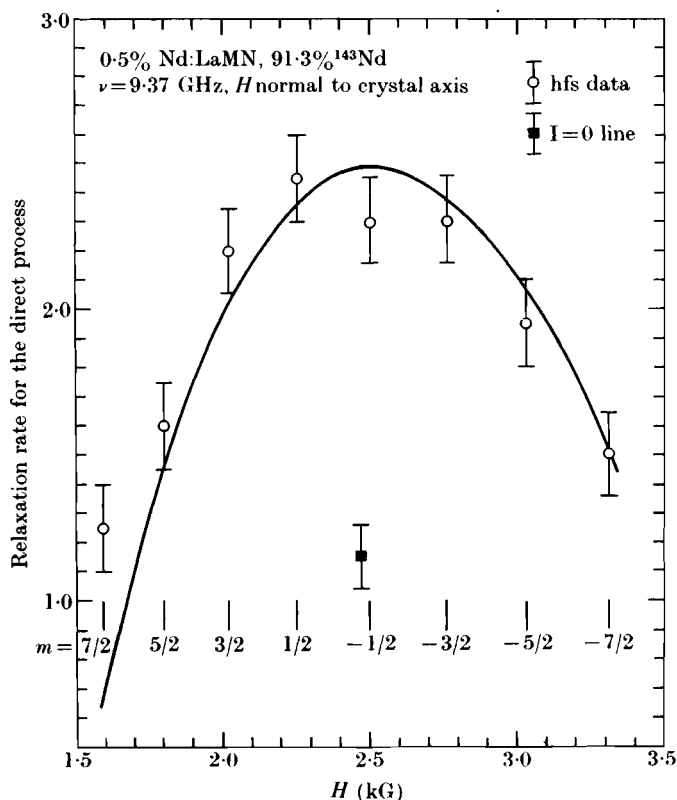

FIG. 10.9. The effect of extra paths involving the hyperfine interaction in $0 \cdot 5 \%$ Nd^{3+} in lanthanum magnesium nitrate. The full line represents the empirical relation $(\tau_1 T_0)^{-1} = 0 \cdot 12 \{I(I+1)-m^2\}+1 \times 10^{-7}H^2$ for the direct process, where the first term arises from the effect of the hyperfine interaction and the second from the external field in breaking the time-conjugate nature of the doublet states. (Larson and Jeffries 1966b.)

where in this case the coefficient

$$R_d^{hfs} \text{ is proportional to } \{I(I+1)-m^2\} \tag{10.72}$$

where m is the nuclear magnetic quantum number.

Multiplets $(S > \frac{1}{2})$

In a system with more than two electronic levels the situation is complicated because of the possibility of a number of transitions within a given ion, not all at the same frequency. The coth formula is not appropriate, but when $(\hbar\omega/2kT_0) \ll 1$ the direct process should give $(1/\tau_1)$ varying as T_0. We have then

$$\left.\begin{array}{l} \dfrac{1}{\tau_1} = R_d T_0 \qquad \text{(direct process)} \\[2mm] \qquad + R_r T_0^5 \quad \text{(Raman process, eqn (10.65))} \end{array}\right\} \tag{10.73}$$

and there may also be an Orbach process if other low-lying levels are present. Equation (10.65) gives a value of order $10^{-3}\,\text{s}^{-1}\,°\text{K}^{-5}$ for R_r, and Chao-Yuan Huang (1965) finds for the $+\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transitions of $Eu^{2+}(4f^7, {}^8S_{\frac{7}{2}})$ in CaF_2

$$1/\tau_1 = 12T_0 + 5\cdot3 \times 10^{-4}T_0^5 \text{ (s)}^{-1}. \tag{10.74}$$

The fit to the experimental results is shown in Fig. 10.10. A T_0^5 term with a coefficient of the same order of magnitude has been found for the iso-electronic ion Gd^{3+} in CaF_2 by Bierig, Weber, and Warshaw (1964). A considerably faster T_0^5 process has been observed for Mn^{2+} in BaF_2 and SrF_2 by Horak and Nolle (1967).

Raman processes in the high-temperature limit

In the high temperature limit where $(kT_0) \gg \hbar\omega_m$, in which $\hbar\omega_m = k\theta_D$ and θ_D is the Debye temperature, all the Raman processes approximate in their temperature dependence to

$$\begin{aligned} \frac{1}{\tau_1} &= R_r(kT_0/\hbar)^{n+1}I_n = R_r(kT_0/\hbar)^{n+1}\int_0^{x_m} x^{n-2}\,dx \\ &= R_r(kT_0/\hbar)^{n+1}\{x_m^{n-1}/(n-1)\} \\ &= R_r' T_0^2 \end{aligned} \tag{10.75}$$

since $x_m = (\hbar\omega_m/kT_0) = (\theta_D/T_0) \ll 1$. Such a dependence on temperature just reflects the fact that two phonons are involved, each with average energy (kT_0) in the classical limit. In some exceptional cases where the vibrations of a defect are involved rather than a second phonon, a
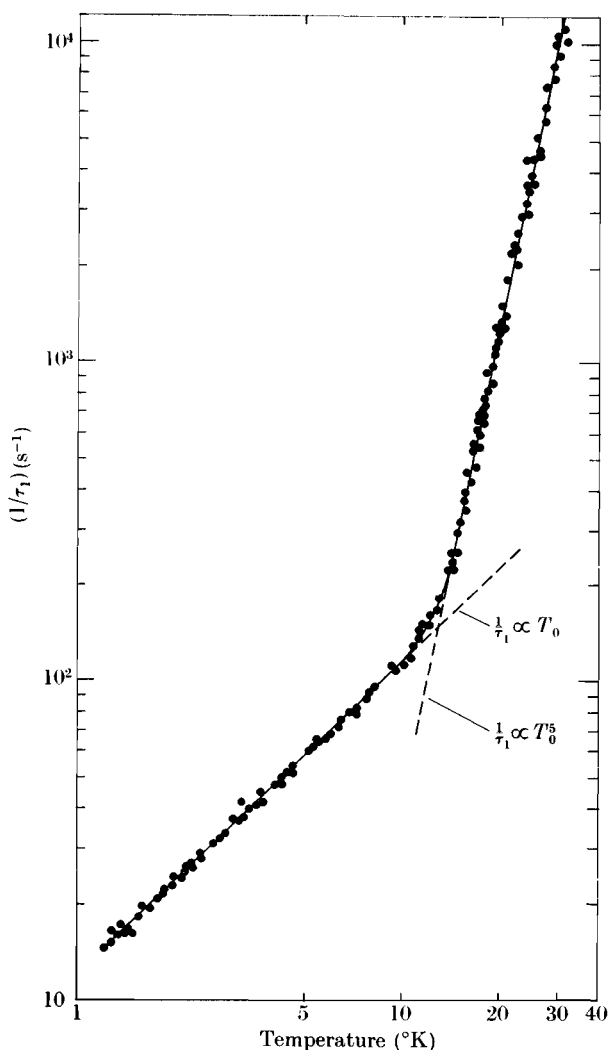
FIG. 10.10. Experimental results for $(1/\tau_1)$ as a function of temperature for Eu^{2+} in CaF_2 at $0\cdot0047\%$ concentration. The measurements are on the $M = +\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transition of the $^8S_{\frac{7}{2}}$ ground state, which has a small initial splitting, at a field of $3\cdot27$ kG along a $\langle100\rangle$ axis and a frequency of about 10 GHz. The data for this concentration, and also for concentrations of $0\cdot0074\%$ and $0\cdot18\%$, are well fitted by eqn (10.74).

(After Chao-Yuan Huang 1965.)

different temperature-dependence is observed (see, for example, Murphy (1966), Feldman, Castle, and Wagner (1966)).

For a few ions (such as S-state ions) where the orbital momentum is rather fully 'quenched', values of τ_1 of order 10^{-6} s at room temperature have been measured by paramagnetic relaxation experiments (Gorter

1947). For other ions τ_1 is very much shorter, and spin-lattice relaxation frequently becomes the dominant process in broadening an electron resonance line at temperatures above $100°K$ (or even less). Values of τ_1 can then be estimated from the line width, the shape being Lorentzian (eqn (2.65)) with $\Delta\omega = 1/\tau_1$. Šroubek and Zdansky (1966) report that a T_0^2 variation of τ_1^{-1} for Cu^{2+} in $CdWO_4$ has been verified in this way between 95 and $300°K$.

10.6. The phonon 'bottle-neck' and phonon 'avalanche'

So far we have assumed that the spins relax to the phonons, and that the latter correspond to a radiation field whose temperature T_0 remains constant and equal to that of the 'bath' (for example, the bath of liquid helium in which the paramagnetic sample is immersed). This implies either that the heat capacity of the phonons is very much larger than that of the spins, so that the energy transferred from the spins to the phonons is insufficient to raise the temperature of the phonons appreciably, or that the phonons are in such intimate thermal contact with the bath that heat received from the spins is transferred instantaneously (or at any rate in a time very much less than τ_1) to the bath. We shall consider this last point first, remembering that in any steady-state experiment the temperature of the spin system will ultimately depend on the rate at which heat is transferred from it to the bath.

In a reasonably perfect crystal at liquid helium temperatures it is known from thermal conductivity data that the mean free path of the phonons is mainly determined by the crystallite size, showing that scattering of the phonons occurs principally through collisions with the boundaries. The latter gives a mean lifetime τ_{ph} for the phonons of order $L/2v$, where L is the linear dimension of the crystallites. For $L = 6$ mm, this gives a value τ_{ph} of order 10^{-6} seconds from boundary wall scattering. However there is usually a large acoustic impedance mis-match at the boundary, so that we cannot assume that every wall collision is efficient in transferring energy to the bath and restoring thermal equilibrium in the phonon system, and the time of 10^{-6} s must be regarded very much as a lower limit.

In a 'direct' process, energy is transferred from the spins only to those modes which (within the resonance line width) have the same frequency as the resonance frequency of the spins. We have seen in § 10.2 that the number of such lattice modes is very much smaller than the number of spins. For an undiluted tutton salt with some

3×10^{21} spins per cm³, the number of resonant lattice modes (even for a splitting ~ 1 cm⁻¹) is smaller by a factor of roughly 10^6. If we regard the spin-phonon relaxation (with characteristic time τ_1) as due to 'collisions' between spins and phonons, then for every collision experienced by a spin there must be some 10^6 collisions experienced by a phonon, so that the mean life time for a phonon between spin collisions is only $10^{-6}\tau_1$. This will lie in the range 10^{-6}–10^{-9} s at helium temperatures, corresponding to mean free paths for the phonons which may be much smaller than the crystallite size. This phenomenon is similar to the optical 'imprisonment of resonance radiation', and the phonons can only 'diffuse' to the walls, greatly increasing the effective phonon-bath relaxation time. If the rate at which phonons collide with spins is greater than $\Delta\omega = 1/\tau_2$, the line width assumed for the spin resonance, the phonon line width would appear to be greater than $1/\tau_2$, and it is not obvious which value we should take in estimating Σ, the number of phonons on 'speaking terms' with the spins. In fact under these circumstances the spins and phonons constitute strongly coupled systems, and we cannot correctly speak of either 'spins' or 'phonons' nor discuss their properties separately. The properties of the coupled spin-phonon system have been considered by Jacobsen and Stevens (1963), and the implications for paramagnetic relaxation discussed by Giordmaine and Nash (1965).

We now consider the transfer of energy from the spin system to the bath via the phonons as a simple classical problem in heat transfer. We represent the situation schematically in Fig. 10.11, where C_H is the heat capacity of the spin system given for $S = \frac{1}{2}$ by eqn (10.31a) multiplied by the number of spins N, and C_{ph} is the heat capacity of the resonant phonons given by (10.31b) multiplied by Σ, the number of phonons on speaking terms with the spins. The rates of heat transfer are characterized by time constants τ_1 for transfer from spins to
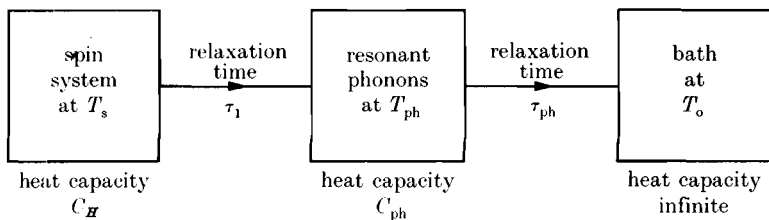

FIG. 10.11. Schematic representation of the flow of energy from the spin system through the resonant phonons to the bath.

phonons, and τ_{ph} from phonons to bath. We assume that we can speak of a spin temperature T_{s} and a phonon temperature T_{ph}. Then writing $T'_{\mathrm{s}} = (T_{\mathrm{s}} - T_0)$, $T'_{\mathrm{ph}} = (T_{\mathrm{ph}} - T_0)$, where T_0 is the bath temperature, we have the differential equations

$$\frac{\mathrm{d}T'_{\mathrm{s}}}{\mathrm{d}t} = -\frac{1}{\tau_1}(T'_{\mathrm{s}} - T'_{\mathrm{ph}}), \tag{10.76}$$

$$C_{\mathrm{ph}}\frac{\mathrm{d}T'_{\mathrm{ph}}}{\mathrm{d}t} = +\frac{C_H}{\tau_1}(T'_{\mathrm{s}} - T'_{\mathrm{ph}}) - \frac{C_{\mathrm{ph}}}{\tau_{\mathrm{ph}}}T'_{\mathrm{ph}}. \tag{10.77}$$

These two equations give differential equations for T'_{s}, T'_{ph} which are each of the form

$$\frac{\mathrm{d}^2T'}{\mathrm{d}t^2} + \frac{\mathrm{d}T'}{\mathrm{d}t}\left\{\frac{1}{\tau_{\mathrm{ph}}} + \frac{1}{\tau_1}\left(1 + \frac{C_H}{C_{\mathrm{ph}}}\right)\right\} + T'\left\{\frac{1}{\tau_1\tau_{\mathrm{ph}}}\right\} = 0. \tag{10.78}$$

The solutions of this equation are of the form

$$T' = a_1\exp\left(-\frac{t}{\tau'_1}\right) + a_2\exp\left(-\frac{t}{\tau_{\mathrm{b}}}\right), \tag{10.79}$$

and in the approximation where $C_H \gg C_{\mathrm{ph}}$ we have

$$\tau'_1 = \frac{C_{\mathrm{ph}}}{C_{\mathrm{ph}} + C_H}\tau_1, \tag{10.80}$$

$$\tau_{\mathrm{b}} = \tau_1 + \tau_{\mathrm{ph}}\left(\frac{C_{\mathrm{ph}} + C_H}{C_{\mathrm{ph}}}\right). \tag{10.81}$$

The first of these time constants is very short, $\tau'_1 \approx \tau_1(C_{\mathrm{ph}}/C_H)$, and corresponds to an initial rapid transfer of energy from the spins to the phonons, heating the latter quickly to the same temperature as the former because of their relatively small heat capacity. The second time constant τ_{b} corresponds to the much slower rate at which the combined systems (spins+phonons) relax to the bath, a time constant that is greater than τ_{ph} in the ratio $(C_H + C_{\mathrm{ph}})/C_{\mathrm{ph}}$, which is the ratio of the combined heat capacities to that of the phonons alone. For a spin system with $S = \frac{1}{2}$, we have, using eqns (10.31a, b),

$$\frac{C_H}{C_{\mathrm{ph}}} = \frac{N}{\Sigma}\tanh^2\left(\frac{\hbar\omega}{2kT_0}\right), \tag{10.82}$$

where we have written T_0 on the assumption that the spin and phonon temperatures do not differ greatly from the bath temperature. This assumption is clearly essential for the validity of (10.76), (10.77).

A similar result is obtained from a microscopic approach on the same

lines as that used in § 10.1 for the spin system alone. The temperature T_{ph} of the phonon system is related to the phonon occupation number $\bar{p}$ by (10.27); for the bath temperature T_0

$$\bar{p}_0 = \frac{1}{\exp(\hbar\omega/kT_0)-1} \tag{10.83}$$

and for a two-level spin system as in § 10.1 we have in thermal equilibrium at temperature T_0

$$\frac{N_a}{N_b} = \frac{\bar{p}_0+1}{\bar{p}_0} = \exp\left(\frac{\hbar\omega}{kT_0}\right). \tag{10.84}$$

The microscopic differential equations are

$$-\frac{\mathrm{d}n_a}{\mathrm{d}t} = +\frac{\mathrm{d}n_b}{\mathrm{d}t} = B' \sum \{n_a(\bar{p})-n_b(\bar{p}+1)\}, \tag{10.85}$$

$$\frac{\mathrm{d}\bar{p}}{\mathrm{d}t} = \frac{1}{\tau_{\text{ph}}}(\bar{p}_0-\bar{p})-B'\{n_a(\bar{p})-n_b(\bar{p}+1)\}, \tag{10.86}$$

where the ratio $(\bar{p}+1)/\bar{p}$ represents the ratio of the probability of emission of a phonon to that of absorption by the spin system. The constant B' is related to $(1/\tau_1)$ by

$$B' \sum (2\bar{p}_0+1) = \frac{1}{\tau_1}, \tag{10.87}$$

as can be verified by comparison with eqns (10.2) and (10.11). In terms of the parameters

$$x = \frac{n_a-n_b}{N_a-N_b}, \qquad y = \frac{\bar{p}-\bar{p}_0}{\bar{p}_0+\frac{1}{2}} \tag{10.88}$$

the differential equations can be written

$$\left.\begin{aligned}
\frac{\mathrm{d}x}{\mathrm{d}t} &= \frac{1}{\tau_1}(1-x-xy), \\
\frac{\mathrm{d}y}{\mathrm{d}t} &= -\frac{1}{\tau_{\text{ph}}}y+b\frac{\mathrm{d}x}{\mathrm{d}t}
\end{aligned}\right\} \tag{10.89}$$

where, with $N = N_a+N_b = n_a+n_b$,

$$b = \frac{N}{\sum (2\bar{p}_0+1)^2} = \frac{N}{\sum} \tanh^2\left(\frac{\hbar\omega}{2kT_0}\right) = \frac{C_H}{C_{\text{ph}}} \tag{10.90}$$

from eqn (10.82). The solutions of these equations are discussed by Faughnan and Strandberg (1961), who plot curves for various ranges

38

of b and τ_{ph}. When recovery is nearly complete ($x \to 1$, $y \to 0$) a simple exponential is obtained with time constant

$$\tau_b = \tau_1 + (1+b)\tau_{ph}$$

in agreement with eqn (10.81).

When $b\tau_{ph}$ is the largest term in this equation for τ_b we expect quite a different temperature and frequency dependence from the ordinary direct process. We have then to a good approximation

$$\frac{1}{\tau_b} = \frac{1}{\tau_{ph}} \left(\frac{3\omega^2 \, d\omega}{2\pi^2 v^3 N} \right) \coth^2 \left(\frac{\hbar\omega}{2kT_0} \right). \tag{10.91}$$

An experimental result of this type is shown in Fig. 10.12. The results fit very well to a $\coth^2(\hbar\omega/2kT_0)$ dependence, corresponding to a temperature-independent value of τ_{ph} which would be expected if a relation such as $\tau_{ph} = L/2v$ is valid. Figure 10.12 shows also a concentration dependence, but R_b is not simply proportional to N^{-1}, presumably because $d\omega$ (and perhaps also τ_{ph}) in eqn (10.91) are concentration (or sample) dependent.

At temperatures where $(\hbar\omega/2kT_0) \ll 1$, $\coth^2(\hbar\omega/2kT_0)$ is approximately $(2kT_0/\hbar\omega)^2$, and $1/\tau_b$ is found to vary as T_0^2. This corresponds to a region where C_H varies as T_0^{-2}, while C_{ph} is independent of temperature, so that $(1/b)$ varies as T_0^2. Thus instead of a spin relaxation rate $(1/\tau_1)$ varying as T_0 in the direct process, we have a variation of $(1/\tau_b)$ as T_0^2, indicating that the temperature dependence is determined just by the heat capacity of the spin system.

The difficulty in transferring energy from the spins to the bath which arises from the presence of relatively few phonons on speaking terms with the spins is known as the 'phonon bottle-neck' and was first recognized by Van Vleck (1941a,b). If instead of just heating the spin system by a saturating pulse, we go further and invert the populations of the spin levels by means of adiabatic rapid passage or a 180° high-power pulse (cf. §§ 2.5–2.7), we have an interesting situation because the phonons, unlike the spins, cannot attain a 'negative' temperature because their energy levels are not finite in number and continue to infinity. This is reflected in the different way in which the parameter y is defined in eqns (10.88); its value is zero in thermal equilibrium, and can rise to large positive values, bounded by $+\infty$; (negative values of y correspond to the phonons being *colder* than the bath). On the other hand, for a two-level spin system, $x = +1$ at thermal equilibrium, falls to zero when the populations of the two levels are equal (corresponding to $T_s = \infty$), and becomes negative when the level populations
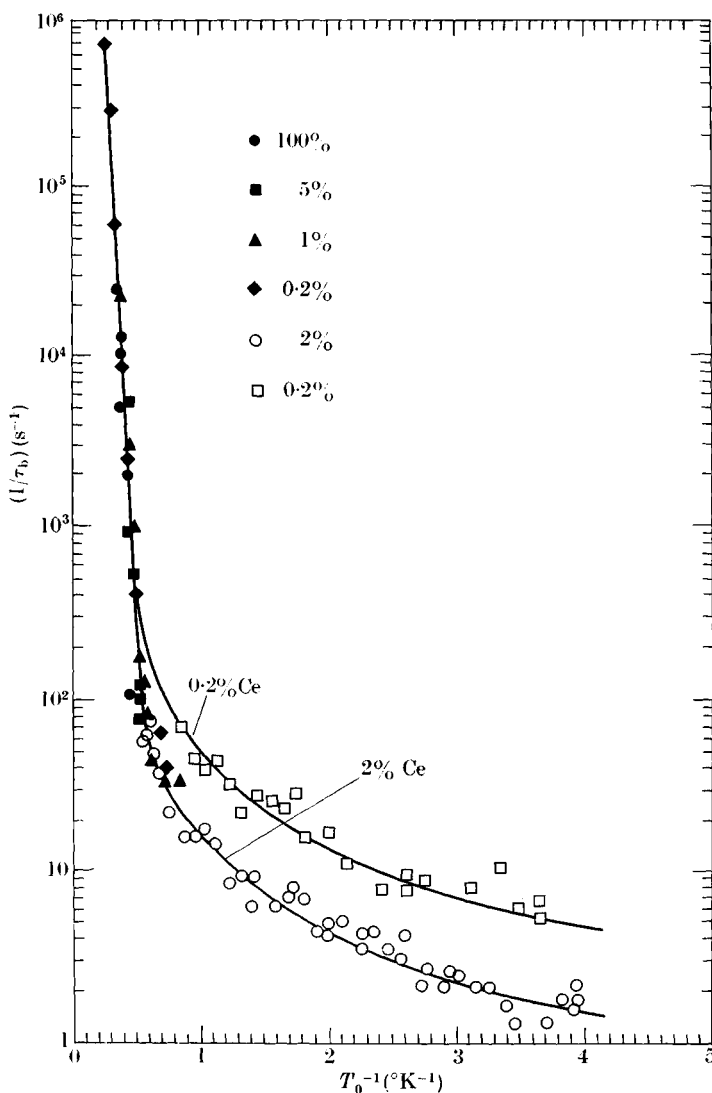
Fig. 10.12. Experimental data for the spin-bath relaxation rate $1/\tau_b$ for Ce^{3+} in $La_2Mg_3(NO_3)_{12}$, $24H_2O$. The data are fitted accurately by the formula

$$1/\tau_b = 2\cdot7\times10^9 \exp(-34/T_0) + R_b \coth^2(\hbar\omega/2kT_0) \ (s^{-1}),$$

where the value of R_b is concentration dependent, being $2\cdot4$ for $0\cdot2$ percent Ce and $0\cdot8$ for 2 per cent Ce. Thus the relaxation rate to the bath is dominated by an Orbach process at the higher temperatures and by the phonon bottleneck (see eqn (10.91)) at lower temperatures. (After Ruby, Benoit, and Jeffries 1962.)

are inverted. If we write $u = -x$, then exact population inversion corresponds to u changing from -1 to $+1$, which will be followed first by a fall in u back to 0 (equal populations), and then by a return through negative values to -1. In this second region the spin temperature is high but positive, so that the position is similar to that analyzed above, and we discuss now just the region where u is positive.

In terms of the parameter $u = -x$, eqns (10.89) become

$$\left.\begin{aligned}
\frac{\mathrm{d}u}{\mathrm{d}t} &= -\frac{1}{\tau_1}(1+u+uy), \\
\frac{\mathrm{d}y}{\mathrm{d}t} &= -\frac{1}{\tau_{\mathrm{ph}}}y - b\frac{\mathrm{d}u}{\mathrm{d}t}.
\end{aligned}\right\} \tag{10.92}$$

These rate equations are non-linear and have been solved by Brya and Wagner (1967) for particular conditions using numerical techniques, representative curves being reproduced in Fig. 10.13. Initially u changes rather slowly, because we start with $y = 0$, and from the first equation in (10.92) the initial rate of change of u is just characterized by the normal spin-phonon relaxation time τ_1. For large values of b, which from eqn (10.90) and the earlier discussion may easily be in the region of 10^4, the second equation in (10.92) shows that y will rise very much faster than u falls, because of the relatively small heat capacity of the phonons. In turn, the rapid increase in the phonon energy density stimulates the emission of further phonons by the spin system, the deluge rapidly becoming catastrophic and resulting in a 'phonon avalanche'. This region is represented by the rapid fall in u and large rise in y shown in Fig. 10.13, the effective relaxation time in this region becoming τ_f where approximately

$$\frac{1}{\tau_f} = (bu_i)\frac{1}{\tau_1}, \tag{10.93}$$

u_i being the initial value of u. Equation (10.92) shows also that at $u = 0$, $(\mathrm{d}u/\mathrm{d}t) = -(1+u)/\tau_1$, so that at this point again u changes at a rate given by τ_1, since there is no net stimulated emission (or absorption) of phonons from the spin system when the populations of the two spin levels are just equal. Thus the value of u changes rather slowly both initially and as u approaches 0, with a very rapid change in the 'avalanche' region. Similarly y rises slowly from zero initially, then very fast to a high value in the avalanche region, followed by a rather swift drop at a rate primarily determined by $1/\tau_{\mathrm{ph}}$ to comparatively small values. It can be seen from Fig. 10.13 that the maximum
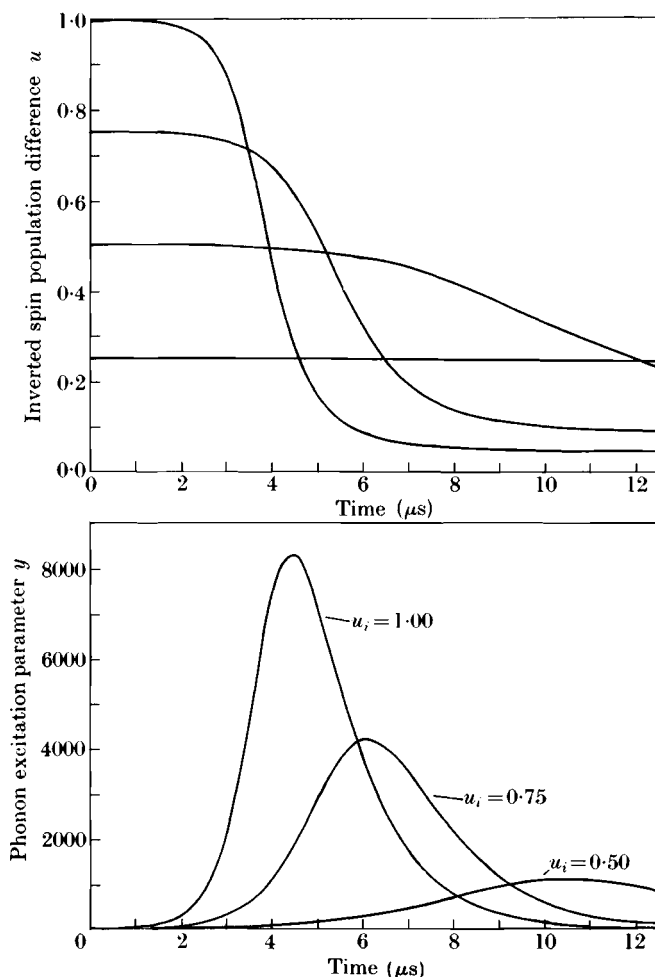
FIG. 10.13. Numerically computed solutions to eqns (10.92) for various initial values of the inverted spin population parameter u, assuming the numerical values $b = 2.5 \times 10^4$, $\tau_{ph} = 10^{-6}$ s, $\tau_1 = 10^{-2}$ s, where b is the ratio of the specific heat of the spin system to that of the resonant phonons at temperature T_0 (the bath temperature). u_i is the value of u at $t = 0$; note that the scale for y is larger than that for u by a factor of 10^4. (After Brya and Wagner 1967.)

value of y attained depends rather sharply on the value of u_i, the initial degree of inversion, and it is clear that much higher values of phonon temperature are generated in the avalanche than can be produced by saturation of the spin system, for which u_i is negative, and at most zero. The experiments of Brya and Wagner using dilute cerium magnesium nitrate give general confirmation of the theory. Similar

results have been obtained for Ni^{2+} and Fe^{2+} in MgO by Shiren (1967), who has succeeded in detecting the phonons generated in an avalanche at one end of an MgO rod doped with Fe^{2+} by their effect on the spin resonance of Fe^{2+} ions (with uninverted level populations) at the other end. In this case the characteristic time constant for the avalanche was 4×10^{-8} s, in contrast with the normal spin-phonon relaxation time τ_1 of 4×10^{-4} s. The phonons generated were predominantly transverse, because the transition probability varies as v^{-5} and in MgO (§ 10.2)

$$(v_t/v_1) \sim 0\cdot7.$$

In this section so far we have obviously been concerned just with the 'direct process', and the phenomena of the phonon bottle-neck and avalanche depend on the very high ratio of the heat capacity of the spin system to that of the resonant phonon modes. It is possible that analogous effects might occur by means of an Orbach process, which also involves a narrow band of phonons, in this case of energy Δ, though the number of such modes will be higher by a factor $(\Delta/\hbar\omega)^2$. In the Raman process all lattice modes are involved so that the specific heat ratio will be much lower than for the direct process; however it should be noticed that a spin system $S = \frac{1}{2}$ in an undiluted tutton salt, with a splitting equal to 1 cm^{-1}, will have a magnetic specific
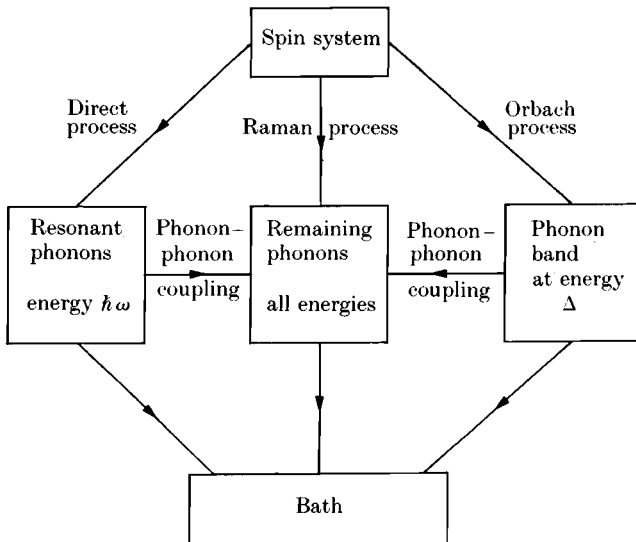

FIG. 10.14. Schematic representation of the various paths for spin-phonon relaxation, phonon-phonon coupling and phonon-bath relaxation. The arrows indicate the direction of energy flow assuming that the spin system is 'hot' and the bath 'cold'.

heat that is larger than the Debye specific heat (i.e. the specific heat of all lattice modes) even up to 4°K, if we assume the Debye θ_D to be about 100°K.

In considering the direct process we have neglected coupling between lattice modes, though this seems a reasonable approximation in a good crystal at helium temperatures if the mean free path of the phonons (in the absence of spins) is limited by crystallite size rather than by scattering through collisions with other phonons. A block diagram that includes all the above relaxation paths, and phonon-phonon coupling, is given in Fig. 10.14. An analysis of a less general system, involving just three 'thermal reservoirs', has been given by Petersen (1965, 1967); this uses rate equations for the quantity $\beta_i = (kT_i)^{-1}$, (cf. eqn (10.19)) which are valid provided that each reservoir i is in internal thermal equilibrium so that it can be characterized by a temperature T_i. This is basically similar to the analysis of Fig. 10.11 given at the beginning of this section; however it is valid over a wide temperature range because population differences (e.g., $n_a - n_b$) are proportional to $(1/T)$ and not to T, and it thus avoids the approximation of small temperature changes which is frequently inherent in the use of classical thermal analysis (cf. eqns (10.76), (10.77)).