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Spectral Diffusion, Phonons, and Paramagnetic Spin-Lattice Relaxation

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The question of paramagnetic relaxation at low temperatures and the "phonon bottleneck" is discussed in terms of the analogy with Holstein's theory of trapping of resonance radiation in gases. It is observed that the diffusion of phonon energy to the wings of the line is the limiting process, and a new mechanism for this in dilute cases is proposed. Since this mechanism involves the spin-spin interactions as well as phonons, it provides a reason for the observed increase of relaxation rate with concentration.

IT is clear that the difficulty of equilibration of the phonons with the temperature bath may be an important and often dominant feature in paramagnetic spin-lattice relaxation at low temperatures, especially for those paramagnetic salts which have a fairly fast intrinsic relaxation rate between spins and phonons. Townes *et al.*[1] have called attention to this fact and have performed a number of experiments which suggest that some salts do have their relaxation limited in this manner. They have also presented a theory of the process.

The purposes of this note are threefold:

(1) to point out that there is a close analogy even as to orders of magnitude of constants between this process and the trapping of resonance radiation in gases[2];

(2) to observe that the theory of Holstein[3] for resonance radiation trapping uses an approach quite different from the Townes[1] way of calculating the spin-lattice relaxation, and that on this question the Holstein scheme is correct;

(3) to add to the Holstein scheme a new concept, diffusion of energy through the spectrum by a specific new process involving the combined effects of spin-lattice relaxation and spin-spin interaction, which leads to better qualitative agreement with experiment than the Townes theory or the Holstein scheme transferred bodily to the spin case.

First let us make the analogy quite clear. In the spin-lattice problem the situation described in reference 1 is the following:

A crystal contains a number $n\sim 10^{19-20}$/cc of paramagnetic ions, which have a paramagnetic resonance line of center frequency ω_0 and width $\Delta\omega\sim 10^8$ sec^{-1} typically. An individual ion absorbs and re-emits phonons of frequency near ω_0 at a rate τ^{-1} which may be $\sim 10^5$/sec. These phonons are reabsorbed at a considerably faster rate because the number of ions is larger than the total number of phonons in the band of width $\Delta\omega$, which is

$$n_{\mathrm{ph}}=\frac{dn_{\mathrm{ph}}}{dE}(h\Delta\omega)=4\pi\omega_0{}^2\Delta\omega c^{-3}\sim 10^{15}\text{-}10^{17}. \tag{1}$$

(We assume kT so low that $kT/\hbar\omega$ is not large enough to affect orders of magnitude.) Thus the phonons are absorbed in a time

$$\tau_{\mathrm{ph}}=\tau(n_{\mathrm{ph}}/n)\sim 10^{-4}\tau\sim 10^{-9}\ \mathrm{sec}. \tag{2}$$

and a distance $\sim 10^{-3}$ cm. If they are to leave the crystal and equilibrate with the bath, it can only be by a kind of diffusion through successive re-emissions and absorptions, which may take a time T_1 of many (perhaps 10^2) τ; this is the observed spin-lattice time.

The resonance radiation trapping situation is in principle exactly the same except that certain numbers are scaled and we must think in terms of photons, not phonons, and of excited atoms, not reversed spins. The gas contains a number $n\sim 10^{16}$ of atoms, a few of which are excited in a resonance state of frequency $\omega_0\sim 10^{16}$ and width $\Delta\omega\sim 10^{11}$. These will radiate spontaneously at a natural rate τ of the order of 10^{-9}/sec (several orders slower than $\Delta\omega$, as in the spin-lattice case). However, these photons can travel only a short time and distance before being reabsorbed, the time again being determined by the number of photon states in the band $\Delta\omega$

$$n_{\mathrm{ph}}=4\pi\omega_0{}^2\Delta\omega c^{-3}\sim 10^{13}, \tag{3}$$

and thus the photon is reabsorbed in

$$\tau_{\mathrm{ph}}=\tau(n_{\mathrm{ph}}/n)\sim 10^{-12}\ \mathrm{sec}, \tag{4}$$

and goes only $\sim 10^{-2}$ cm. Again the process of de-excitation can only go on through successive re-emissions and reabsorptions. The nearly exact analogy is obvious.

On point (2): Recently Townes *et al.*[1] have proposed a theory of the spin-lattice system discussed above in which the phonons are assumed to have an energy width given approximately by $\hbar/\tau_{\mathrm{ph}}\gg\hbar/\tau$. If this is so, their widths may often extend beyond the wings of the resonance line, which leads to their actually being less absorbed on the average; the diffusion rate is then a compromise involving this effect and the dimensions of the sample, etc. A major consequence is the transfer of

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[1] Giordmaine, Alsop, Nash, and Townes, Phys. Rev. **109**, 302 (1958). See also earlier suggestions of Gorter, Van der Marel, and Bölger, Physica **21**, 103 (1955); J. H. Van Vleck, Phys. Rev. **59**, 724 (1959).

[2] Alpert, McCoubrey, and Holstein, Phys. Rev. **76**, 1257 (1949); **85**, 985 (1952).

[3] T. Holstein, Phys. Rev. **72**, 1212 (1947); **83**, 1159 (1951).

excitation between lines, an observed effect which is claimed as experimental proof.

The Holstein resonance trapping theory, on the other hand, proceeds throughout with photons of perfectly sharp frequencies. It is assumed (justifiably in the gas problem, as Holstein proves in his Appendix) that on each re-emission the photon appears with a distribution of frequency given by the actual line shape (that which would be observed in an infinitesimal sample). Then the kinetics are controlled by the fact that the wings of the line are far more transparent than the center, so that excitation persists essentially until by chance the photon is emitted on the wing, where its free path is larger than the sample size, and can fly out through the transparent gas. Correspondingly the phenomenon of self-reversal typically accompanies trapping. Holstein's theory has had detailed experimental confirmation.[2]

Except for slowly varying factors, in fact, the Holstein results can be simply computed in the following way. Choose a ν_c such that $k(\nu_c)L\simeq 1$ (where k is the absorption coefficient, L the sample size). The trapping time T_1 in units of emission time τ will then be the ratio of the whole line intensity to the intensity beyond ν_c, i.e., of the probabilities of being emitted in the center and on the wing. For Gaussian lines, $T_1 \sim k_0 L\tau \propto nLT^0$ where k_0 is the absorption coefficient in the center. For Lorentzian lines, $T_1 \sim (k_0L)^{\frac{1}{2}}\tau \propto n^0T^{-\frac{1}{2}}L^{\frac{1}{2}}$, more nearly the Townes result.

A simple uncertainty principle argument will show why the phonons have a sharp frequency and not a breadth $\hbar/\tau_{\text{ph}}$, aside from whatever external broadening influences act on the spins independently of the phonons. Consider a single reversed spin in the absence of other interactions. It emits a phonon only after a time τ, and thus its energy can be defined at least as well as $\hbar/\tau$. This phonon is immediately absorbed after τ_{ph}. If Townes is right, it had an energy breadth $\hbar\tau_{\text{ph}}^{-1}$ and so it may be reabsorbed at any energy in a band of this width. The reabsorbing spin holds the energy, however, for a time τ and so has an energy again defined to $\hbar/\tau \ll \hbar/\tau_{\text{ph}}$; energy conservation requires that this be the same as the original spin's energy, which limits the phonon breadth also to the natural breadth $\hbar/\tau$. The interactions have the effect of limiting the spatial extension of the phonon without necessarily broadening it. A phonon artifically constrained to exist throughout a large volume, that is to have a sharp momentum distribution, would have a broad frequency spectrum, but that is not the question here.[4]

Now we come to point (3). In the Holstein type of theory a vital part is played by the spectrum of the re-emitted radiation: How rapidly can the energy diffuse to the wings of the line, where it can radiate out of the system directly? In the case of truly homogeneous lines the answer would be immediate. In a time short compared to τ spin-spin or other interactions would homogenize the frequency of a reversed spin, the reradiated spectrum would be the full line shape, and the whole Holstein theory would be valid. This predicts a rather weak temperature dependence, and a concentration dependence from n^0-n^1. Concentrated salts, for which we expect homogeneous lines, show neither; there is observed a rather strong temperature dependence, and a concentration dependence of the wrong sign. This may indicate either that our ideas about spectral diffusion are valid in concentrated salts too or that this case requires still more examination.

Dilution of the paramagnetic salt (or increasing inhomogeneous sources of line broadening) may lead to a phenomenon new to the Holstein theory. The re-emitted phonon is not homogenized, but must have a frequency more or less near to the frequency which was absorbed. This is because under inhomogeneous conditions the spectral diffusion caused by spin-spin interactions alone slows down severely or comes to a complete stop.[5] Qualitatively we expect that now the phonons experience much greater difficulty in getting out to transparent regions of the spectrum, so that there will be a very pronounced slowing of the relaxation process, which is exactly what is observed.[6]

To understand what is happening we have to find the mechanism which does change the frequency of the excitations. This cannot be spin-spin interactions alone (except at an extremely slow rate)[5] and as we have seen phonon interactions are not a good candidate either.[4] Therefore, we look at the simplest combination of these two, which is the following: Surrounding any spin there is a group of neighbors having various interaction energies $I(r_{ij})$ with it. If this spin has just absorbed a phonon, during the course of the time this spin is up one or more of the neighbors will almost certainly themselves absorb or emit phonons. Thus the phonon will effectively change frequency by various combinations of $I(r_{ij})$'s. (One should note that all of these considerations change when the frequencies become much larger than kT, since then the general flip rate is much slower than the absorption and emission time.) A simple way of expressing it is the following: At each re-emission the phonon has a frequency distribution which is very nearly that of the emitting spin caused by its spin-spin interactions alone. The breadth of this distribution is roughly (for dipolar interactions) μ^2/r^3 in energy, so that every τ seconds the phonon may change by this frequency. Then we may very qualitatively expect that

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[4] C. Kittel, *Proceedings of the Kamerlingh-Onnes Memorial Conference on Low-Temperature Physics, Leyden, June, 1958* [Suppl. Physica **24**, 588 (1958)], has pointed out that actually the re-emitted frequency does not even have the natural breadth $1/\tau$, just as in resonance fluorescence [W. Heitler, *Quantum Theory of Radiation* (Oxford University Press, Oxford, 1944)]. Thus the excitation transfer effects cannot even be ascribed to the extreme Lorentzian wings of the natural line. I am indebted to C. H. Townes for telling me of this result.

[5] P. W. Anderson, Phys. Rev. **109**, 1492 (1958).

[6] See for instance Gorter, Van der Marel, and Bölger, Physica **21**, 103 (1955) and references therein.

since $N \cong \hbar\Delta\omega r^3\mu^{-2}$ is the number of steps of this size to the transparent regions at the sides of the line, the time taken and thus the observed T_1 will go as $N^2 \propto n^{-2}$, not inconsistent with the observations in some cases. Note that there is approximate independence of sample size in this region.

In the Appendix we discuss these processes in detail, and also show how phonons may, with a reduced probability, even exchange energies considerably greater than the individual spin-spin interactions, thus explaining transfer of excitation over fairly large gaps in the spectrum.[1]

At great dilutions the extreme, Lorentzian wings of the dipolar interaction line may take over, in which case one can argue that the density dependence may be slower, even as slow as n. We should emphasize that here as in the Holstein theory the extreme wings of the lines, and thus close pairs or triplets of spins, play an important role; they alone may often be enough to transfer excitation from one apparently distinct hyperfine line to another.

At great dilutions or large inhomogeneities various new mechanisms will appear. Ideally, eventually the diffusion time to the extreme wing will become longer than the time to go directly without change of frequency to the surface, which goes as $(L/\text{m.f.p.})^2 \propto n^2$, and there will be a region $T_1 \propto n^2$ decreasing to the true spin-lattice time τ. More likely in many cases is that some paramagnetic impurity of short relaxation time (and thus of large phonon capture cross section), will capture the phonons before they diffuse out of the line and transform their frequency very quickly to a transparent region. The likelihood of this increases as $1/n$ so the relaxation time may slowly curve over and enter a size-independent $T_1 \propto n$ region.[7] Even in such density regions, however, there may be observed a relatively rapid transfer of excitation by the spin-spin mechanism from one region of the line to another with a time constant $\propto n^{-2}$ or less, as is seen in the Ni fluosilicate experiments of Mims and Bowers.[8]

One final comment, related to the explanation of still another experiment: One may expect many rather complex phenomena, like the "quenching" phenomena of gas problems, related to the effects of impurities, especially when these have fast intrinsic relaxation times. As an example, one might interpret the experiments of Feher and Scovil[9] on the Gd-Ce ethyl sulfate system as follows: Suppose that both the Gd and Ce lines are hindered in their relaxations by phonon diffusion effects, this hindrance being slight for the Gd but rather larger for Ce. At the higher temperature, however, Ce relaxes freely because of an extremely fast intrinsic relaxation rate or a Raman process, so that the rate of the Gd is controlled simply (when the lines coincide) by the time τ_{Gd} required to emit a phonon. The Ce absorbs phonons so readily that its full effect is felt far out on the wing where only a few Ce are available to absorb.

At the lower temperature, the Ce relaxation rate is much slower, but still sufficiently faster than Gd that the Gd relaxation rate increases practically to τ_{Gd}^{-1}. The reason why the relaxation time decreases to less than that of Ce may be that under normal circumstances the Gd represents a purely inhomogeneous broadening mechanism as far as Ce is concerned. When the lines coincide, however, coupling between the two allows the Gd spins to flip faster thus also increasing the rate of spectral diffusion for Ce; alternatively, the Ce may be in the $T_1 \propto n^2$ region, and an effective broadening then makes the medium more transparent.

The above is an attempt not at a general explanation of all low-temperature spin-lattice relaxation phenomena but of some fraction of them, those which are limited by the "spin-resonance trapping of phonons." The concepts here presented, if not the whole story, must play an important role in such phenomena. On the other hand, undoubtedly there are cases, especially those with long spin-lattice times, which do not involve trapping; perhaps also there are cases of direct spin-spin interaction effects.

ACKNOWLEDGMENTS

I am indebted for conversations with W. B. Mims, G. Feher, and especially T. Holstein and C. H. Townes, on these subjects.

APPENDIX. DETAILED DISCUSSION OF THE SPECTRAL DIFFUSION PROCESS

One can think of the processes by which the spin interactions change the phonons' energies as inelastic scatterings of pairs of phonons against each other through the spin interactions. The requirement of the phonon pair as well as of the spin interaction may most easily be seen by considering a two-spin system for which we choose a Hamiltonian with a specially simple interaction

$$H=\omega_1 s_{1z}+\omega_2 s_{2z}+V_{12}s_{1z}s_{2z}. \qquad (5)$$

The energy-level diagram is shown in Fig. 1. Suppose

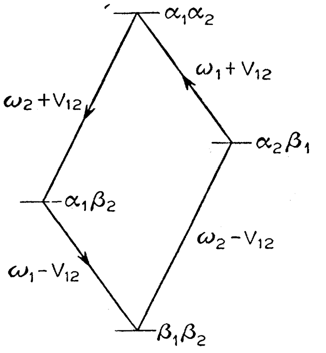

FIG. 1. Energy levels of a simple two-spin system. Arrows show scheme discussed in text.

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[7] G. Feher suggests that indirect, Raman phonon processes may take over in the low concentration region, leading to a concentration-independent, highly temperature-dependent region.

[8] W. B. Mims and K. D. Bowers (private communication).

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

we start in the state $\beta(1)\alpha(2)$. Then spin 1 can absorb a phonon of energy ω_1+V_{12}, and after a time τ this may be re-emitted by spin 2 at ω_2+V_{12}: Apparently our phonon has changed by $\omega_1-\omega_2$. This is, however, fallacious because the system is in the state $\alpha_1\beta_2$ now and still can re-emit ω_1-V_{12} with unchanged probability; i.e., it still contains the first phonon. Clearly the only safe way to consider the system is in terms of a cyclic process by which we start (say) in $\beta_1\beta_2$, absorb ω_1-V_{12} and ω_2+V_{12}, then re-emit ω_1+V_{12} and ω_2-V_{12} to return, thereby effectively scattering these two phonons against each other and interchanging the interaction energy V_{12}. It is only because such a collision will probably occur during a phonon's stay on a spin that the process appears to involve simply the spin interactions and a single phonon.

An anomalous situation where only single phonons are involved has been noted by Mims[7]: Inhomogeneous broadening when single spins have two randomly placed possible final states. This three-level system is much more complex. However, experimentally it will act quite differently from spin interactions. Suppose we saturate it with a frequency ω_1. There will be a series of ω_2's at which the spins excited by ω_1 can also emit. After the initial pulse these ω_2's have decreased susceptibility also: They are partly saturated and represent a breadth of the initially saturated packet. Emission of phonons at either ω_1 or ω_2 leads at first to recovery of the line. That is, this three-level width acts like a true homogeneous width of the initial spin packets, which does not seem to explain Mims' observations.

In the three-interacting-spin case comes our first encounter with a new phenomenon: True shifts in frequency by much more than the spin interaction (at correspondingly reduced rates). A typical system in which this might occur involves three spins of equally spaced frequencies $\omega_0-\Delta\omega$, ω_0, $\omega_0+\Delta\omega$, with the following interactions:

$$H=(\omega_0-\Delta\omega)s_{1z}+\omega_0 s_{2z}+(\omega_0+\Delta\omega)s_{3z} +V_{12}(s_{1+}s_{2-}+s_{1-}s_{2+})+V_{23}s_{2z}s_{3z}. \quad (6)$$

An example of the kind of process which might occur is the following: If V_{12} is small compared to $\Delta\omega$ we can approximately label the states according to the separate spins, and we start with the state labeled "$\beta_1\alpha_2\beta_3$." We absorb phonons at $\omega_0+\Delta\omega$ and $\omega_0-\Delta\omega$ by the usual process, arriving at $\alpha_1\alpha_2\alpha_3$. Again by the usual process we emit ω_0, arriving at "$\alpha_1\beta_2\alpha_3$."

Because of the interaction V_{12}, this state is not pure

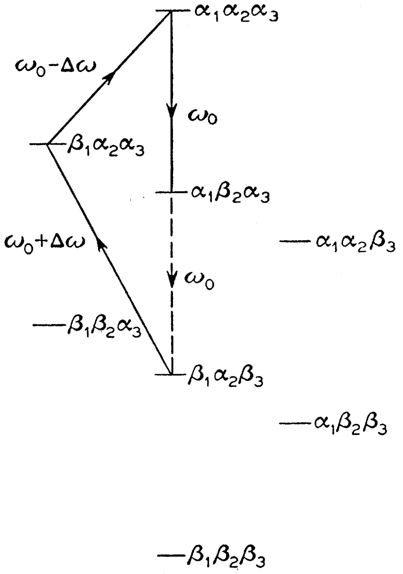

FIG. 2. Energy levels of a three-spin system and a possible transition scheme. Dotted line is forbidden in the absence of interaction.

but is approximately

$$\text{“}\alpha_1\beta_2\alpha_3\text{”}\cong(\alpha_1\beta_2-\epsilon\beta_1\alpha_2)\alpha_3, \quad (7)$$

$$\epsilon=V_{12}/\Delta\omega. \quad (8)$$

Unfortunately, this is nearly orthogonal to the 1-2 combination occurring in "$\beta_1\alpha_2\beta_3$", which will be

$$\text{“}\beta_1\alpha_2\beta_3\text{”}=(\beta_1\alpha_2+\epsilon'\alpha_1\beta_2)\beta_3. \quad (9)$$

But in the presence of the V_{23} interaction, ϵ' differs from ϵ by an amount $V_{23}/\Delta\omega$ because of the different energy denominator. Thus there is a matrix element for returning to "$\beta_1\alpha_2\beta_3$" of order $V_{12}V_{23}/(\Delta\omega)^2$, and a probability

$$P(\omega_0+\Delta\omega,\omega_0-\Delta\omega\rightarrow\omega_0,\omega_0)\simeq V_{12}^2V_{23}^2\Delta\omega^{-4}. \quad (10)$$

Figure 2 shows an energy-level diagram and the cycle we describe. Since in many physical cases V_{12} or V_{23} or both may be quite large relative to $\Delta\omega$, this may be a perfectly valid way of explaining transfer of excitation over fairly large energy ranges. For instance, in the Cu salt reported by Townes *et al.*,[1] his estimate of $\tau\simeq10^{-4}$ sec means that in the one second before observation, excitation could be transferred to the order of several times the nearest neighbor V_{12} or $\sim$10 gauss, or easily over the observed distances, especially considering that it need go only by successive jumps from one line to its neighbor.