

## Localized Modes and Spin-Lattice Interactions

P. G. KLEMENS

*Westinghouse Research Laboratories, Pittsburgh, Pennsylvania*

(Received October 31, 1961)

Localized lattice modes can contribute to the strain at a paramagnetic impurity and thus influence the spin-lattice interaction. Their contribution to the spin relaxation is estimated. It is governed by the rate with which a local mode attains equilibrium with the phonon continuum, estimated in a previous paper. Studies of the spin relaxation of paramagnetic substitutional impurities, lighter than the parent atom, should yield information about the nature of local modes.

### I. INTRODUCTION

IN the theory of spin-lattice relaxation, one considers the effect of a strain in the immediate vicinity of a paramagnetic ion on the spin Hamiltonian, and uses this perturbation Hamiltonian to calculate the spin relaxation by the usual perturbation method.<sup>1</sup> It is also usual to express the thermal strain as a superposition of lattice waves, and in this way one can describe spin-phonon interaction processes. To lowest order, the component linear in strain gives rise to the direct, or one-phonon processes, while the component quadratic in strain gives rise to two-phonon or Raman processes.

In many cases, the paramagnetic ion is at a defect site, and since the lattice vibrations are modified by the defect, one is not justified in using the usual relation between strain and amplitude of a lattice wave, which holds in a perfect crystal. In view of the phenomenological nature of the theory, one would, of course, be very hard put to isolate the error thus introduced from the consequences of an incorrect choice of the strain dependence of the spin Hamiltonian, except when the temperature dependence of the spin-lattice relaxation is modified in some characteristic and unusual manner.

Thus, Castle *et al.*,<sup>2</sup> have considered the effect of the excess mass of the substitutional chromium ion in magnesium oxide on the temperature dependence of the Raman spin lattice relaxation, while the effect of loosely bound interstitial ions is evident in the spin-lattice relaxation of the  $E_1'$  and  $E_2'$  centers in quartz.<sup>3</sup>

Montroll and Potts<sup>4</sup> have pointed out that in some cases, in particular in the case of a substitutional impurity which is lighter than the parent atom, the character of the lattice vibrations is particularly strongly modified, and a new lattice mode arises, which is localized near the impurity, and has a frequency above the acoustic band. Since the energy of the localized mode is concentrated in the immediate vicinity of the defect, one would expect it to modify very substantially the

spin-lattice relaxation of a paramagnetic impurity associated with this defect site.

It is not possible to have a spin-phonon interaction involving a local mode so as to conserve energy. The only conceivable process is one in which a spin-flip is accompanied by the absorption and subsequent re-emission of a localized phonon. If the local mode frequency were sharp, this process would also violate energy conservation. It has been shown, however, that the local mode frequency is broadened by anharmonic interactions with the phonons of the lattice wave continuum<sup>5</sup>; even at zero temperature a localized phonon can split into two ordinary phonons, and this gives a broadening of the local mode frequency of about 1%. The broadening is therefore larger than the spin energy, and energy conservation is relaxed sufficiently to allow this process to occur.

To take account quantitatively of how the anharmonic broadening of the local mode permits the spin-lattice interaction with absorption and emission of a local phonon, we consider their combined effect to the next order of perturbation theory. A local phonon and the spin combine; in the intermediate state we have the same local phonon, but the spin is inverted, and in the final state the spin stays inverted, and the local phonon has split by anharmonic interaction into two phonons of the Debye continuum. Since there is only one intermediate state, there is a one-to-one correspondence between the over-all second order matrix element and the matrix element for the anharmonic interaction between a local phonon and two lattice-wave phonons. Thus the contribution of local phonons to the spin-lattice relaxation is related in magnitude to the anharmonic relaxation time of the local mode.

### II. INTERACTION WITH TRAVELING WAVES

Let the spin-lattice interaction Hamiltonian be

$$H' = Ae + Be^2, \quad (1)$$

where  $e$  is the strain of the unit cell surrounding the paramagnetic ion, and  $H'$  is the change in the energy difference of the two spin states as a function of strain.

A lattice wave of wave-vector  $\mathbf{q}$  and frequency  $\omega$

<sup>1</sup> J. H. Van Vleck, *Phys. Rev.* **57**, 426 (1940); *ibid.* **59**, 724 (1941). R. D. Mattuck and M. W. P. Strandberg, *Phys. Rev.* **119**, 1204 (1960). R. Orbach, *Proc. Phys. Soc. (London)* **77**, 821 (1961).

<sup>2</sup> J. G. Castle, Jr., D. W. Feldman and P. G. Klemens, in *Advances in Quantum Electronics*, edited by J. R. Singer (Columbia University Press, New York, 1961), p. 414.

<sup>3</sup> J. G. Castle, Jr., D. W. Feldman, and R. S. Weeks (private communication).

<sup>4</sup> E. W. Montroll and R. B. Potts, *Phys. Rev.* **100**, 525 (1955).

<sup>5</sup> P. G. Klemens, *Phys. Rev.* **122**, 443 (1961).

causes a displacement at a site  $\mathbf{x}$  of

$$\mathbf{u} = \frac{1}{\sqrt{G}} \boldsymbol{\varepsilon} b e^{i(\omega t + \mathbf{q} \cdot \mathbf{x})}, \quad (2)$$

where  $G$  is the number of unit cells in the crystal,  $\boldsymbol{\varepsilon}$  the polarization direction, and  $b$  the amplitude. The strain, apart from numerical factors of order unity, is given by

$$e = \frac{1}{(3G)^{1/2}} \sum_{\mathbf{q}} a(\mathbf{q}) q e^{i\mathbf{q} \cdot \mathbf{x}}, \quad (3)$$

where  $a(\mathbf{q}) = b e^{i\omega t}$ , and is given in terms of the number of phonons  $N$  as either matrix elements

$$a(\mathbf{q}) = \left( \frac{\hbar}{M\omega} \right)^{1/2} \left[ \begin{matrix} N \\ N+1 \end{matrix} \right], \quad (4)$$

being an annihilation or creation operator respectively. The factor  $1/\sqrt{3}$  was included as a root-mean-square value of the direction cosine between  $\boldsymbol{\varepsilon}$  and  $\mathbf{q}$ .

If  $s$  is the fraction of paramagnetic ions in the upper spin state, then the rate of change of  $s$  due to spin-phonon Raman interactions can be written as

$$\frac{ds}{dt} = \sum_{\mathbf{q}, \mathbf{q}'} A_{\mathbf{q}, \mathbf{q}'} [(1-s)(N+1)N' - sN(1+N')], \quad (5)$$

where the summation is over all pairs of lattice modes,  $N$  and  $N'$  are the number of phonons in modes  $\mathbf{q}$  and  $\mathbf{q}'$ , and the coefficient  $A_{\mathbf{q}, \mathbf{q}'}$  vanishes unless

$$E + \hbar\omega' = \hbar\omega, \quad (6)$$

where  $E$  is the energy difference between the two spin states. In equilibrium, when  $s$  and  $N$  are given by the appropriate distribution functions, the expression in the square bracket of (5) vanishes for each pair  $\mathbf{q}, \mathbf{q}'$  separately. If the phonon distribution is kept at equilibrium but  $s$  deviates from equilibrium by  $\delta s$ ,

$$\frac{ds}{dt} = -\delta s \sum_{\mathbf{q}, \mathbf{q}'} A_{\mathbf{q}, \mathbf{q}'} [N + N' + 2NN']. \quad (7)$$

We define the Raman relaxation time  $\tau_R$  as

$$\frac{1}{\tau_R} = -\frac{1}{\delta s} \frac{ds}{dt}. \quad (8)$$

We use second order perturbation theory to calculate  $A_{\mathbf{q}, \mathbf{q}'}$  in terms of the interaction Hamiltonian  $B e^2$ , where  $e$  in turn is expressed in terms of (3) and (4), and obtain after some reduction

$$\frac{1}{\tau_R} = \frac{2B^2}{G^2} \sum_{\mathbf{q}, \mathbf{q}'} \frac{(qq')^2}{M^2\omega\omega'} \frac{1 - \cos\Delta\omega t}{t\Delta\omega^2} \frac{e^x + e^{x'}}{(e^x - 1)(e^{x'} - 1)}, \quad (9)$$

where  $\Delta\omega = \omega - \omega' - E/\hbar$ ,  $x = \hbar\omega/kT$ , etc., and the summation is over all wave vectors, but no longer over polarizations. If  $E \ll kT$ , so that  $x \simeq x'$  for the important phonons, we obtain after summing over all wave vectors, and taking account of the resonance factor in (9), that

$$\frac{1}{\tau_R} = \frac{1}{\pi^3} \frac{B^2 a^6}{M^2 v^3} \int_0^{q_D} q^6 \frac{e^x}{(e^x - 1)^2} dq, \quad (10)$$

where  $q_D$  is the Debye limiting wave number. Since  $q = x q_D T/\theta$ , and since  $(a q_D)^3 = 3(2\pi)^3/4\pi$ , we can re-write (10) in the form

$$\frac{1}{\tau_R} = 36\pi \left( \frac{B}{Mv^2} \right)^2 \omega_D \left( \frac{T}{\theta} \right)^7 \int_0^{\theta/T} \frac{x^6 e^x}{(e^x - 1)^2} dx, \quad (11)$$

where  $\omega_D = k\theta/\hbar$  is the Debye frequency. The function

$$J_6(X) = \int_0^X \frac{x^6 e^x}{(e^x - 1)^2} dx \quad (12)$$

has been tabulated<sup>6</sup>; for small  $X$  (i.e.,  $T > \theta$ ), it becomes  $X^5/5$ , for large  $X$ , it tends to a limiting value of 732.4. Thus  $1/\tau_R$  varies as  $T^7$  at temperatures below about  $\theta/10$ , and as  $T^2$  above about  $\theta/2$ . This result has, of course, been obtained previously.<sup>1</sup>

Similar considerations apply to the direct processes, which arise from the term  $Ae$  in (1). One obtains

$$\frac{1}{\tau_D} = 32\pi^3 \left( \frac{3}{4\pi} \right)^{1/2} \omega_D \frac{A^2 E^2}{M v^2 (k\theta)^3} \left( \frac{T}{\theta} \right). \quad (13)$$

Comparing the direct and the Raman process, we find that at lowest temperatures the former predominates, at higher temperatures the latter, and that the two are comparable at a temperature

$$T_c \simeq \frac{1}{2} (A/B)^{1/2} \theta^{1/2} (E/k)^{1/2}. \quad (14)$$

One would generally expect  $A$  and  $B$  to be of comparable magnitude, since in (1) the quadratic term should be comparable to the linear term for unit strain. Thus, putting  $(A/B)^{1/2} \simeq 1$ ,  $T_c \simeq \frac{1}{2} \theta^{1/2} (E/k)^{1/2}$ . In most microwave experiments,  $E/k \simeq 0.5^\circ\text{K}$ . In the case of  $\text{Cr}^{3+}$  in  $\text{MgO}$ , Castle *et al.*<sup>2</sup> found  $T_c = 30^\circ\text{K}$ . In this case,  $\theta = 750^\circ\text{K}$ , so that according to (14),  $T_c$  should indeed be around  $30^\circ\text{K}$ . This agreement with the above crude considerations is satisfactory.

### III. INTERACTION WITH LOCALIZED MODES

Consider a two-stage process going from states  $i$  to  $k$  via an intermediate state  $j$ ; let  $\Delta E$  be the energy difference between state  $j$  and states  $i$  and  $k$ , respectively; this is equivalent to going from state  $i$  to  $k$  with an

<sup>6</sup> W. M. Rogers and R. L. Powell, *Tables of Transport Integrals*, National Bureau of Standards Circular No. 595 (U. S. Government Printing Office, Washington, D. C., 1958).

effective perturbation Hamiltonian

$$H_{\text{eff}}' = \sum_j \frac{H_{ij}' H_{jk}'}{\Delta E}, \quad (15)$$

where  $H_{ij}'$ ,  $H_{jk}'$  are the perturbation Hamiltonians linking  $i$  and  $j$ , and  $j$  and  $k$ , respectively.

As initial state, we take the local mode excited with one phonon, and the ion in a given spin state. As intermediate state, we need to consider only one state, i.e., with one phonon in the local mode, and the spin inverted. The interaction Hamiltonian is the Raman term  $H_{ij}' = B e_0^2$ , where  $e_0$  is the strain due to one local phonon (expressed as appropriate matrix elements). The final state is one with the spin as in the intermediate state, but with the local phonon removed and, instead, two traveling lattice modes excited by an additional phonon each. The interaction Hamiltonian for that second step arises from the cubic anharmonicities (involving three phonons at a time), and is the same as was used to describe the relaxation to equilibrium of excess energy in the local mode.<sup>5</sup>

We can write  $H_{jk}'$  in the form

$$H_{jk}' = a \left[ \frac{N_0(N_1+1)(N_2+1)}{(N_0+1)N_1N_2} \right]^{\frac{1}{2}}, \quad (16)$$

depending on whether a local phonon is annihilated or created, and where  $N_0$ ,  $N_1$ , and  $N_2$  are the number of phonons in the local mode and the traveling modes. The relaxation time for the local mode is then inversely proportional to  $\sum_k (H_{jk}')^2$ , i.e.,

$$\frac{1}{\tau_0} \propto a^2 \sum_k (N_1 + N_2 + 1), \quad (17)$$

and at absolute zero, where  $N_1$  and  $N_2$  vanish, one obtains<sup>5</sup>

$$\frac{1}{\tau_0} \simeq \omega_0 \frac{\hbar \omega_0}{M v^2 \omega_D}, \quad (18)$$

where  $\omega_0$  is the circular frequency of the local mode.

There is a one-to-one correspondence between every final state in the sum (17) and the final state in the two-stage process considered here, since the spin energy is negligibly small compared with the phonon energies. The effective matrix element (15) is the matrix element (16) multiplied by  $[B e_0^2 / \Delta E]$ . Since we must consider also inverse processes, the rate of change of  $s$ , the fraction of ions in the upper state, due to each set of final states, is proportional to

$$s N_0(1+N_1)(1+N_2) - N_1 N_2(1+N_0)(1-s). \quad (19)$$

This expression vanishes at equilibrium. If  $s$  deviates from equilibrium by  $\delta s$ , the term in  $\delta s$  is proportional to

$$\delta s [N_0(N_1+N_2+1) + N_1 N_2], \quad (20)$$

and at low temperatures, where  $N_1 \ll 1$ ,  $N_2 \ll 1$  and  $N_1 N_2 = N_0$ , this simply becomes  $2 N_0 \delta s$ . Thus the relaxation time for spins by the two-stage Raman process involving local phonons is

$$\frac{1}{\tau_{R0}} = \frac{2}{\tau_0} \left[ \frac{B e_0^2}{\Delta E} \right]^2 N_0, \quad (21)$$

where  $e_0^2$  is the square of the strain at the paramagnetic ion due to one local phonon, and  $N_0$  is the equilibrium average number of local phonons.

One can estimate  $e_0^2$  from the condition that half the energy of a localized vibration is potential energy, and since the displacement falls off exponentially very rapidly, practically all that energy resides in the volume enclosed by the nearest neighbors of the defect. Thus if  $\kappa$  is the elastic modulus describing the localized vibration,

$$\frac{1}{2} \hbar \omega_0 \simeq \frac{1}{2} \kappa e_0^2 a^3, \quad (22)$$

where  $a^3$  is the volume per atom. Now the velocity of sound is given by  $v = (\kappa a^3 / M)^{\frac{1}{2}}$ , so that  $\kappa a^3 = M v^2$ , and

$$e_0^2 \simeq \frac{\hbar \omega_0}{M v^2}. \quad (23)$$

For most solids  $\hbar \omega_D / M v^2 = 1/100$ , and since  $\omega_0$  and  $\omega_D$  of comparable magnitude,  $e_0 \simeq 0.1$ .

Substituting (23) into (21) we obtain for the contribution of localized modes to the Raman relaxation

$$\frac{1}{\tau_{R0}} \simeq \omega_0 \left( \frac{\hbar \omega_0}{M v} \right)^3 \left( \frac{B}{E} \right)^2 e^{-\theta_0/T}, \quad (24)$$

where  $\theta_0 = \hbar \omega_0 / k$  and  $E = \Delta E$  is the spin energy.

Equation (24) is an approximation which holds only at temperatures well below  $\theta_0/2$ . At sufficiently high temperatures, one can show that  $1/\tau_{R0}$  varies as  $T^2$ , in the same manner as  $1/\tau_R$ , and makes a comparable contribution to  $1/\tau$ .

By comparing (24) and (11) one can estimate that in typical cases (i.e.,  $\theta_0 \simeq \theta$ ,  $E/k\theta_0 \simeq 1/1000$ ) these two Raman processes become comparable at a temperature of about  $\theta/20$ ; the ordinary Raman process predominates below that temperature, the exponentially increasing local mode Raman process above that temperature.

Since the direct process predominates over the Raman process below  $T_c$  given by (14), and since  $T_c$  is typically of order  $\theta/20$  or somewhat lower, we can expect the temperature dependence of  $1/\tau$  to show two or possibly three regions: the direct region at very low temperatures, where  $1/\tau \propto T$ ; the local mode Raman region at higher temperatures, but generally below room temperatures, where  $1/\tau \propto e^{-\theta_0/T}$ , and in some cases, depending on the value of the microwave frequency used, on the values of  $\theta$  and  $\theta_0$ , and on the relative values of  $A$  and  $B$ , there may be a significant range of temperatures where

the ordinary Raman process predominates, and where  $1/\tau \propto T^7$ .

In the latter case, we could intercompare  $1/\tau_R$  and  $1/\tau_{R0}$  and eliminate the common interaction parameter  $B$  from them. In this way, Eq. (24) could be tested. This would not only test the present theory, but also Eq. (18), i.e., the theory of the anharmonic relaxation time of local modes. In other cases, a cruder test is possible by taking  $A \simeq B$  and intercomparing  $\tau_{R0}$  and  $\tau_D$ .

According to the theory of Montroll and Potts,<sup>4</sup> one would expect local vibrational modes to occur at paramagnetic ions which are substitutional impurities and are either of lighter mass than the normal atom at that site, or are bound to the neighboring atoms with forces stronger than the normal forces. If a lighter atom was also more weakly bound, such that the effect of the mass was compensated by weaker bonds, a local mode would not occur. In general, we know little about interatomic forces, but it may be presumed that if the paramagnetic ion is substantially lighter than the parent atom (say half), a local mode will occur, and the present considerations will apply. Unfortunately, none of the paramagnetic ions in various environments, whose spin lattice relaxation has been studied to date, fulfills this

condition of local mode occurrence. Examples of cases to which the present theory may apply are paramagnetic ions from Ti through Cu in environments such as cadmium sulfide, silver halides or in a suitable heavy III-V compound (indium antimonide, grey tin).

The present treatment is valid only if the local mode frequency  $\omega_0$  is well separated from the continuum of lattice modes. As  $\omega_0$  approaches  $\omega_D$ , the mode becomes progressively less localized, and it is wrong to assume that most of the strain energy lies within the unit cell containing the impurity. Thus  $e_0^2$  will be less than given by (23), and Eq. (24) will likewise overestimate  $1/\tau_{R0}$ . In the limit as  $\omega_0$  becomes  $\omega_D$ ,  $e_0^2$  and thus  $1/\tau_{R0}$  vanish, and the spin-lattice relaxation is given by the normal theory. The relationship between  $\omega_0/\omega_D$  and the spatial extent of the local mode is discussed by Montroll and Potts.<sup>4</sup> It is readily shown that (23) remains a good approximation provided  $\omega_0$  is not less than about  $1.1\omega_D$ , that is, provided the mass difference is not less than about 20%.

#### ACKNOWLEDGMENTS

The author is indebted to Dr. J. G. Castle, Jr., and Dr. D. Feldman for many stimulating discussions.

## Systematic Analysis of Many-Body Interactions in Molecular Solids\*

LAURENS JANSEN

*Battelle Memorial Institute, International Division, Geneva, Switzerland*

(Received August 7, 1961)

An analysis is undertaken of the different possible types of simultaneous interactions between more than two atoms or molecules in so-called molecular solids. The analysis is carried out on the basis of a double series expansion: (1) in terms of linked exchange-clusters of increasing numbers of atoms; (2) as a series in increasing orders of perturbation theory. The use of a multipole series for the electrostatic interactions between different atoms is avoided by retaining this interaction in unexpanded form. Instead, an effective-electron model is used with a Gaussian form for the charge distributions. The method is illustrated by computing the exchange quadrupole moment of two argon atoms as a function of their distance. Calculations by Rosen and by Shostak for first-order interactions between three helium atoms are extended to atoms of the heavy rare gases. It is found that the relative magnitude of this many-body effect may amount to 20% of the first-order interaction energy. Possible implications with respect to stability of the cubic structures of heavy rare-gas crystals are briefly discussed.

### INTRODUCTION

THE possible importance of simultaneous interactions between more than two atoms, molecules, or nucleons for the interpretation of properties of compressed gases, liquids, solids, and nuclear matter has from time to time aroused interest in the literature. In molecular physics, this interest arose principally from a possible role of many-body interactions in a solution to the problem concerning the stability of the observed

cubic crystal structures of the heavy rare gases. Calculations based on pair interactions had revealed that a hexagonal structure should be somewhat more favorable, in contradiction with experiment. It seemed, therefore, that the pair assumption (additivity) of interactions between rare-gas atoms could not be reconciled with their crystal structure.

In contrast with nuclear problems, we possess for molecular systems complete knowledge regarding the origin of the forces between the particles, so that, in principle, it should be possible to assess the significance of many-body interactions for the properties of molec-

\* This research has been made possible through the support and sponsorship of the U. S. Department of Army, through its European Research Office.