

Spin-Lattice Relaxation Due to Local Vibrations with Temperature-Independent Amplitudes

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In the usual treatment of the temperature dependence of spin-lattice relaxation of impurity ions, the vibrational properties of the paramagnetic ion are assumed to be those of a normal host ion. For impurities that do not affect the vibrational properties of the lattice, this is expected to be a reasonable approximation. However, if a paramagnetic impurity is associated with a gross defect in a crystal, it should be expected that the temperature dependence of the spin-lattice relaxation time will be dominated by the vibrational properties of the defect. An ion could be trapped at a site about which the potential is highly anharmonic and such that the vibrational amplitude is very large and effectively independent of the state of excitation. Under these circumstances lattice vibrations whose amplitudes have the usual temperature dependence could beat with the vibrations of the defect, producing a difference frequency resulting in a spin transition. In the high-temperature limit one would expect a spin transition rate that is proportional to T rather than to T^2 because only the lattice-vibration part of the interaction is temperature-dependent and at high temperatures this dependence is linear. In this paper two simple defect models are discussed. In the first, a paramagnetic ion tunnels between two stable positions, and in the second, the ion is trapped in a one-dimensional square well. In the tunneling model, the form of the temperature dependence is independent of the details of the spin-lattice interaction, whereas the square-well results are sensitive to these details. In the latter case, the effect of electric and magnetic interactions is discussed. Recent measurements by Feldman, Castle, and Wagner of the spin-lattice relaxation time of hydrogen centers in fused quartz exhibit the behavior described by either of these models, but their data can be fitted better by the square-well model.

INTRODUCTION

RECENT measurements of Feldman, Castle, and Wagner¹ on the spin-lattice relaxation rate of atomic hydrogen centers in fused quartz display a linear temperature dependence at high temperatures. This result is at first surprising since one generally associates a linear temperature dependence of the reciprocal of the relaxation time with low-temperature processes involving the real absorption or emission of single phonons. The temperature dependence they observed is suggestively close to that given by the function $[\exp(13.5/T) - 1]^{-1}$ which is the occupation number of phonons of energy $13.5 k$, where k is Boltzman's constant. Since atomic hydrogen has no excited electronic states below $50\,000\text{ cm}^{-1}$, we can rule out an Orbach² process as the source of this behavior. The purpose of this paper is to describe some defect models with low-lying vibrational states which could result in the observed temperature dependence.

The effect of temperature on electron spin-lattice relaxation times has been treated in detail by several authors.²⁻⁵ At very low temperatures, the reciprocal of the relaxation time $1/T_1$ is proportional to the absolute temperature. This is generally referred to as the region of the direct process. At these temperatures, the relaxation involves the emission and the absorption of phonons that have a frequency equal to the Zeeman

frequency of the spin system. As the temperature is raised, other relaxation mechanisms become important. One in particular is the inelastic scattering of phonons by the spin. This is generally referred to as the Raman process because of its analogy with the inelastic scattering of photons. Because of the frequency dependence of the scattering matrix elements and the fact that many pairs of phonons can be involved in the process, the temperature dependence of the relaxation rate due to Raman scattering varies as a high power of the temperature. In some cases it is proportional to $T^7 J_6(\Theta_D/T)$ in others to $T^9 J_8(\Theta_D/T)$ where⁶

$$J_n\left(\frac{\Theta_D}{T}\right) = \int_0^{\Theta_D/T} x^n \frac{e^x}{(e^x - 1)^2} dx,$$

and Θ_D denotes the Debye temperature of the lattice. The function $J_n(\Theta_D/T)$ is a constant for small T and is proportional to T^{1-n} for large T and $n > 1$. Therefore, all two-phonon relaxation processes vary as T^2 at high temperatures.

Only systems with an odd number of electrons (Kramer's systems) can exhibit the $T^9 J_8(\Theta_D/T)$ temperature dependence. The extra temperature dependence apparent in Kramer's systems at low temperatures is a consequence of the properties of both the dynamic crystalline electric field and the wave functions which result in matrix elements that are proportional to the frequency of the participating phonons.

If the paramagnetic defect has electronic energy levels that lie within the phonon spectrum, phonons can be absorbed and re-emitted as the electron makes

¹ D. W. Feldman, J. G. Castle, Jr., and G. R. Wagner, preceding paper, *Phys. Rev.* **145**, 237 (1966).

² R. Orbach, *Proc. Roy. Soc. (London)* **A264**, 458 (1961).

³ J. H. Van Vleck, *J. Chem. Phys.* **7**, 72 (1939); *Phys. Rev.* **57**, 426 (1940); **59**, 724 (1941); **59**, 730 (1941).

⁴ C. B. P. Finn, R. Orbach, and P. Wolf, *Proc. Phys. Soc. (London)* **77**, 261 (1961).

⁵ R. L. Peterson, *Phys. Rev.* **139**, A1151 (1965).

⁶ W. M. Rogers and R. L. Powell, *Natl. Bur. Std. (U.S.), Circ. No.* 595 (1958).

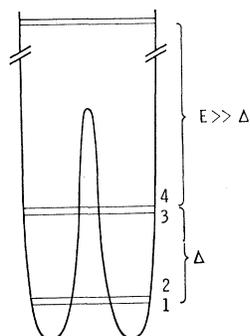


FIG. 1. The energy levels of the oscillator. The closely spaced pairs represent the Zeeman levels of the spin system. The separation Δ in temperature units is h (Planck's constant) times the tunneling frequency divided by Boltzmann's constant. The next excited state is assumed to be too high in energy to contribute to the relaxation process.

transitions between the ground state and the excited states. Orbach² recognized the importance of excited electron levels lying within the phonon spectrum. He showed that if an excited electronic level at an energy $k\Delta$ above the ground state is sharp, the temperature dependence of $1/T_1$ is given by

$$1/T_1 = AT + B[\exp(\Delta/T) - 1]^{-1} + CT^n J_{n-1}(\Theta_D/T),$$

where n is either 7 or 9 depending upon whether or not Van Vleck cancellation effects are important. If B is large enough, the second term dominates at intermediate temperatures but since it approaches a linear temperature dependence at high temperatures, the highest temperature region will still be dominated by the regular Raman process. If the excited electronic state is low enough and B is sufficiently large relative to A and C , both the exponential rise and the region of linear temperature dependence associated with the Orbach process will be observed. The point of interest here is that there is the possibility of a region at higher temperatures that is linear in T as well as the usual linear temperature dependence at low temperatures.

In analyzing the temperature dependence of a spin system that displays the feature of a linear region above an exponential region, one would generally have some knowledge of the excited states of the electronic system. If, as in atomic hydrogen centers, there is good reason to believe that no excited electronic states are close enough to the ground state for an Orbach process to exist, then we must look elsewhere for the source of the linear temperature dependence.

DEFECTS WITH TEMPERATURE-INDEPENDENT AMPLITUDES

In the high-temperature limit, the T^2 dependence of the normal Raman process is a consequence of the fact that the strain associated with both of the phonons involved is proportional to T . A linear temperature dependence may result if the paramagnetic defect is such that the amplitude of one of its vibrations (a localized mode) is very large (of the order of the interatomic spacing) and because of anharmonic forces approximately temperature-independent, and if the number of vibrational states of the defect does not increase with energy. The relaxation mechanism implied is similar

to that described by Orbach except that here, the low-lying excited states are vibrational rather than electronic. An important distinction must be made between these two types of excited states. The g values of excited electronic states are different (barring accident) from the g value of the ground state. Consequently, one only observes the spins in the ground multiplet and for a single low-lying excited state, one is led to a relaxation rate that is proportional to $[\exp(\Delta/T) - 1]^{-1}$. On the other hand, vibrational excitations do not affect the g value (in first order) and therefore all of the spins in the sample are observed. This fact leads to a somewhat different temperature dependence than that obtained when one observed only the spins in the ground multiplet.

We will describe two examples of defects with large temperature-independent vibrational amplitudes and derive the temperature dependence of $1/T_1$ for each. As in the calculation of Finn *et al.*⁴ we will treat the transitions between the states of the defect in first order.

The Tunneling Oscillator

Imagine a paramagnetic ion with $S = \frac{1}{2}$ trapped in a double well such as that shown in Fig. 1. We will assume that all excited states above the first antisymmetric state have sufficiently high energies that we need not consider them. The splitting $k\Delta$ between the symmetric ground state and the antisymmetric excited state determines the tunneling frequency. The amplitude of oscillation in this case is the separation between the well minima and to the extent that the change in the separation due to a change in temperature can be neglected when compared with the separation, the amplitude of oscillation is temperature-independent. Including spin, there are only four states of interest for the tunneling particle and they are marked 1, 2, 3, and 4 in Fig. 1. In the absence of the spin-lattice coupling energy, the energy difference between states 1 and 2 as well as that between states 3 and 4 is the Zeeman energy of the spin. Both levels 4 and 2 are "spin-up" levels while levels 3 and 1 are "spin-down" levels.

Since the vibrational states of the defect are assumed to be more tightly coupled to the lattice than are the spin states, the vibrational excitation is expected to remain in thermal equilibrium with the lattice while the spins relax. Therefore, since the spin parts of states 1 and 3 are identical, as are the spin parts of states 2 and 4, the following constraint on the populations of the states will prevail:

$$N_3/N_1 = N_4/N_2 = e^{-\Delta/T}. \quad (1a)$$

This is equivalent to

$$N_1 + N_2 = \frac{1}{1 + e^{-\Delta/T}} N, \quad (1b)$$

and

$$N_3 + N_4 = \frac{e^{-\Delta/T}}{1 + e^{-\Delta/T}} N,$$

where $N = N_1 + N_2 + N_3 + N_4$ is the total number of spins.

Let W_{ij} be the rate coefficient for transitions from level i to level j due to the absorption or emission of a lattice phonon, and let N_i represent the population of level i . Direct spin-flip processes, i.e., $4 \leftrightarrow 3$ and $2 \leftrightarrow 1$ will be neglected, being much slower because of the low density of the corresponding lattice phonons. The rate equations for the remaining transitions reduce to

$$d(\delta N)/dt = -2[W_{41}N_4 + W_{23}N_2 - W_{14}N_1 - W_{32}N_3], \quad (2)$$

where $(\delta N) = N_4 + N_2 - N_3 - N_1$. Notice that this is a rate equation for all of the spins in the sample, not just those in the ground multiplet as in the case of the Orbach process. The probability that the tunneling particle makes a downward transition in Fig. 1 is proportional to $[n(\Delta) + 1]$ while the upward transition probability is proportional to $n(\Delta)$, where $n(\Delta) = [\exp(\Delta/T) - 1]^{-1}$ is the number of quanta in the lattice mode of energy $k\Delta$. The coefficients W_{ij} are then given by

$$\begin{aligned} W_{41} &= W_{32} = W[n(\Delta) + 1], \\ W_{14} &= W_{23} = Wn(\Delta), \end{aligned} \quad (3)$$

where we have neglected the Zeeman energy relative to $k\Delta$. The factor W contains the matrix element of the position coordinate of the tunneling particle as well as the spin matrix elements and is temperature-independent. Substituting Eqs. (1a) and (3) into Eq. (2) we find

$$d(\delta N)/dt = -4W(N_1 - N_2)[\exp(\Delta/T) - 1]^{-1}. \quad (4)$$

But $N_2 - N_1 = (\delta N)_1$ is the difference in the population of the spin states when the tunneling particle is in its ground vibrational state. Using Eq. (1a) and the definition of δN , we find

$$(\delta N)_1 = \delta N [1 + \exp(-\Delta/T)]^{-1}. \quad (5)$$

Substituting Eq. (5) into Eq. (4), we get

$$d(\delta N)/dt = -G(\delta N), \quad (6a)$$

where

$$\begin{aligned} G &= 4W[\exp(\Delta/T) - \exp(-\Delta/T)]^{-1} \\ &= 2W \operatorname{csch}(\Delta/T). \end{aligned} \quad (6b)$$

The function $\operatorname{csch}(\Delta/T)$ is compared in Fig. 3 with other functions to be derived below.

The Square Well

Another type of defect that has a localized motion which is nearly temperature-independent is that of a particle trapped in a square well. Imagine a solid in which there are large voids that are much longer in one dimension than in the other two so that for all temperatures to be considered, the occupied vibrational states correspond to motion of the particle in the long dimension. The energy levels of a particle of mass M

in an infinite well of dimension $2a$ are given by $E_i = i^2\hbar^2/32Ma^2$, $i = 1, 2, 3, \dots$.

In the tunneling model, there were only two vibrational states between which transitions occurred. The specific form of the interaction coupling the defect states and the rest of the lattice was not critical since a change in the form could only change the magnitude of the temperature-dependent function and not the temperature function itself. In the square well, however, there are a large number of vibrational states of the defect, therefore the matrix elements of the interaction must be taken between many pairs of states. Since the splitting between the energy levels of a square well increases with energy, i.e., $E_{i+1} - E_i = (2i+1)\hbar^2/32Ma^2$, lattice vibrations at all of these frequencies are involved in the spin-flipping process. As in Raman scattering in perfect crystals the total relaxation rate for the square-well defect involves a sum over all the contributing vibrational modes. The dependence of each individual transition upon its frequency is therefore important in determining the ultimate temperature dependence of the total transition probability.

There are two principal mechanisms by which the spin can be flipped. The first and simplest is a modulated magnetic dipole-dipole interaction with some nearby rapidly relaxing spin center and the second is a modulated electric field. One might expect the electric-field modulation to be weak if the excited states of the paramagnetic center are at very high energies relative to the ground state. We will first discuss the magnetic-field case.

Magnetic Dipole-Dipole Interaction

The spin states of the paramagnetic ion can be coupled together directly by a magnetic dipole-dipole coupling to another spin system. Because the interaction energy falls off as $1/R^3$ where R is the separation between the two dipoles, the probability of the modulation of this interaction inducing spin transitions falls off as $1/R^8$. In order to be effective, then, the dipoles must be fairly close together. We will assume that the dipole embedded in the lattice is close enough to the square well that the two can be considered to have the same amplitude and sufficiently alike phases that their relative displacements can be ignored. We will further assume that the square well and the nearby dipole behave as a particle in a Debye continuum so that the density of lattice states can be handled in a simple manner. With these restrictions the spin-lattice interaction, expanded in powers of the relative displacements of the paramagnetic ion (x_1) and the square well (x_2), is

$$V = V_0 + V_x(x_1 - x_2) + V_{xx}(x_1 - x_2)^2 + \dots \quad (7)$$

The linear term in Eq. (7) is responsible for the emission or absorption of phonons at the Zeeman frequency, i.e.,

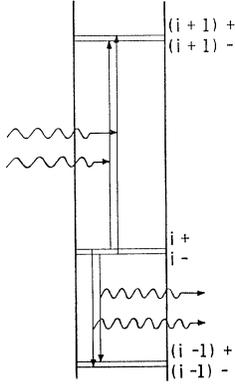


FIG. 2. Spin-flipping transitions in which lattice quanta are annihilated while the square-well particle makes an upward transition (wavy arrows entering from the left) and those in which lattice quanta are created while the square-well particle makes a downward transition (wavy arrows leaving to the right). The + and - signs denote the up and down spin states, respectively.

the direct process.⁷ The quadratic term contains a component that is bilinear in x_1 and x_2 . Because of this term, energy can be coupled into and out of the square well. The coefficients V_x , etc. are operators that contain the spin coordinates of the interacting systems. The phenomenological potential that is responsible for the spin transitions at temperatures above the direct-process region is

$$H' = Cx_1x_2. \quad (8)$$

We must now calculate the transition probabilities between the lattice plus square-well eigenstates.

Let us define $(N_+)_i$ to be the population of the i th square-well state with spin up and $(N_-)_i$, the population of the corresponding state with spin down. Once again we will use the first-order theory discussed earlier for the tunneling model. W_{ij} will be the transition probability per unit time from state i to state j . Figure 2 illustrates some of the transitions considered. The solid arrows indicate transitions of the square-well particle in which the spin is flipped. The wavy lines entering from the left represent lattice quanta destroyed in the process while those leaving to the right represent lattice quanta created in the process. The rate equation for each of the spin-square-well states $(N_{\pm})_i$ is

$$d(N_{\pm})_i/dt = -\sum_l (W_{i,i+2l+1} + W_{i,i-2l-1})(N_{\pm})_i + \sum_l W_{i+2l+1,i}(N^{\mp})_{i+2l+1} + \sum_l W_{i-2l-1,i}(N^{\mp})_{i-2l-1}. \quad (9)$$

We have left off the terms that correspond to transitions in which the spin does not flip since they cancel in summing over all of the square-well levels. A transition due to a perturbation linear in the amplitude of a particle in an infinite square well vanishes unless the change in level number is odd; hence the appearance in Eq. (9) of transitions to states differing in number by $(2l+1)$. As in the tunneling model we now require that the vibrational energy of the square-well particle remain in thermal equilibrium with the lattice. This

restriction is imposed by setting

$$(N_+)_i = [e^{-E_i/kT} / \sum_i e^{-E_i/kT}] N_+, \quad (10)$$

and

$$(N_-)_i = [e^{-E_i/kT} / \sum_i e^{-E_i/kT}] N_-,$$

where N_+ and N_- are the total number of spins in the up and down states, respectively. Substituting these into Eq. (9), summing over all the square-well levels and subtracting the resulting equation for N_- from the equation for N_+ , we get

$$d(\delta N)/dt = -W(\delta N),$$

where

$$W = [\sum_i e^{-E_i/kT}]^{-1} \left\{ \sum_{l,i} [(W_{i,i+2l+1} + W_{i,i-2l-1}) e^{-E_i/kT} + W_{i-2l-1,i} e^{-E_{i-2l-1}/kT} + W_{i+2l+1,i} e^{-E_{i+2l+1}/kT}] \right\}. \quad (11a)$$

Since the energy levels have a lower limit, a change of summation variable shows that the third and fourth sums in the numerator are equal, respectively, to the first and second sums, in which case

$$W = 2 \sum_{l,i} (W_{i,i+2l+1} + W_{i,i-2l-1}) \times e^{-E_i/kT} / \sum_i e^{-E_i/kT}. \quad (11b)$$

If we consider the lattice and the square-well particles to be initially in one of their respective eigenstates, the transition probabilities between the square-well states will be proportional to

$$W_{ij} = C^2 |\langle \psi_i | x_1 | \psi_j \rangle|^2 |\langle \Phi_i | x_2 | \Phi_j \rangle|^2 \rho(E_i - E_j), \quad (12)$$

where $\rho(E_i - E_j)$ is the phonon density at the frequency corresponding to the difference in energy between the square-well levels ψ_i and ψ_j . Φ_i and Φ_j are harmonic-oscillator lattice eigenfunctions differing in energy by one quantum, of frequency $(E_i - E_j)/\hbar$. Throughout the discussion we neglect the Zeeman energy of the spins relative to the energy splittings of the square-well states. The matrix elements of x_2 are proportional $\omega^{-1/2} n(\omega)^{1/2}$ or $\omega^{-1/2} (n(\omega) + 1)^{1/2}$ depending upon whether a phonon of frequency ω is destroyed or created, respectively, in the transition and $n(\omega)$ is the occupation number of the mode of that frequency. We see then that

$$W_{ij} \propto P_{ij} [n(E_i - E_j) + 1], \quad j < i; \\ P_{ij} n(E_j - E_i), \quad j > i; \quad (13)$$

where

$$P_{ij} = |\langle \psi_i | x_1 | \psi_j \rangle|^2 \rho(E_i - E_j) |E_i - E_j|^{-1}.$$

Substituting Eq. (13) into Eq. (11b) we find that the sums over the two terms in Eq. (11b) are equal and

therefore that

$$W \propto \left[\sum_i e^{-E_i/kT} \right]^{-1} \times \sum_{i,i} \frac{\rho(E_{i+2l+1}-E_i) |\langle \psi_{i+2l+1} | x_1 | \psi_i \rangle|^2 e^{-E_i/kT}}{|E_{i+2l+1}-E_i| \{ \exp[(E_{i+2l+1}-E_i)/kT] - 1 \}} \quad (14)$$

The normalized eigenfunction corresponding to the n th level of the infinite square well is

$$\psi_n = \frac{1}{2} a^{-1/2} \left[\exp\left(\frac{in\pi x}{2a}\right) - (-1)^n \exp\left(-\frac{in\pi x}{2a}\right) \right].$$

It is straightforward to show that

$$|\langle \psi_{i+2l+1} | x | \psi_i \rangle|^2 = \frac{16a^2}{\pi^4} [(2l+1)^{-2} - (2l+2i+1)^{-2}]^2. \quad (15)$$

The specific form of the density of states $\rho(\omega)$ for the lattice with the square well is subject to speculation. We propose, however, that the number of phonons in the important wavelength region, i.e., long compared with the size of the square well, would not be strongly perturbed by the presence of the defect. We then say that $\rho(\omega)$ is proportional to ω^2 as in the Debye model for a lattice. Substituting Eq. (15) into Eq. (14), and replacing $\rho(E_{i+1}-E_i)$ by $(E_{i+1}-E_i)^2$ and E_i by $i^2\Theta$, where $\Theta k = h^2/32Ma^2$, we find that the temperature dependence of the spin lattice relaxation rate for the atom in a square well is proportional to

$$M_1 = \left[\sum_i e^{-i^2\Theta/T} \right]^{-1} \left\{ \sum_{i,i} (2i+2l+1)(2l+1) \times [(2l+1)^{-2} - (2l+2i+1)^{-2}]^2 \times \frac{\exp(-i^2\Theta/T)}{\exp[(2i+2l+1)(2l+1)\Theta/T] - 1} \right\}. \quad (16)$$

The function M_1 is plotted in Fig. 3.

Electric-Field Modulation

According to Kramers theorem, two states of half-integral angular momentum that transform into one another under the operation of time reversal, cannot be coupled together by an electric field. For this reason, the direct process, wherein a spin is flipped and a single phonon is created or destroyed, can only occur if the external magnetic field removes the time-reversal symmetry. Under these circumstances, the initial and final spin states are a mixture of states of different character with respect to time reversal and therefore can be coupled together. The extent to which time-reversal symmetry is removed is proportional to the magnetic-

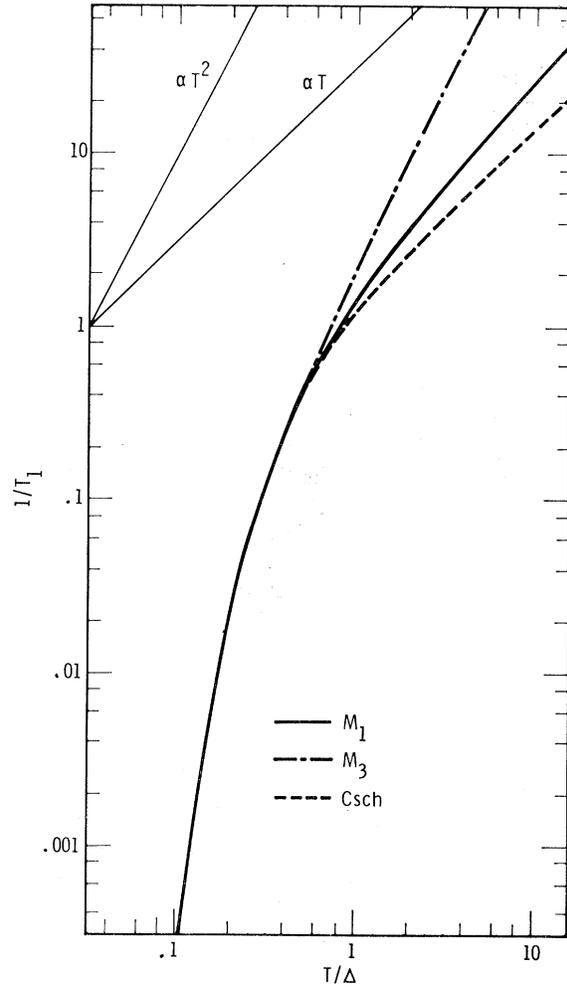


Fig. 3. The temperature dependence of the reciprocal of the spin-lattice relaxation time $1/T_1$ for the defect models considered. M_1 and M_3 are associated with the square-well defect while the hyperbolic cosecant is associated with the tunneling oscillator. The parameter Δ is $1/k$ times the energy of the first excited state above the ground state where k is Boltzmann's constant.

field strength H . Hence the transition matrix elements are proportional to H . Time-reversal symmetry does not preclude electric fields from coupling together states that do not transform into each other under the time-reversal operation. A consequence of this is that an electric field in second order can couple states together that are Kramers conjugates, i.e., transform into each other under time reversal. Orbach² has shown that, if the mixing of excited states due to the external magnetic field is small, after summing over the intermediate states involved in the second-order process, the contributions from each excited Kramers pair almost cancel. This is similar to the "Van Vleck cancellation" and is a consequence of time-reversal symmetry. The resulting matrix elements are proportional to the sum of the frequencies of the participating phonons. On the other hand, if the mixing of the excited states due to the

external magnetic field cannot be neglected the cancellation just mentioned is avoided by an amount proportional to the field. The resulting matrix elements in this case are independent of frequency but depend linearly upon the magnetic field. We have, then, that the matrix elements for a spin flip in a Kramers system may be

- (a) proportional to the frequency of the participating phonons or
- (b) independent of the frequency of the phonons but proportional to the magnetic-field intensity H .

If the electric field in the neighborhood of the spin site is due to a set of point charges, fixed relative to the square-well position, we can expand it as in Eq. (7). Ignoring the direct process, the high-temperature relaxation will be due to the linear term in second order. Since excited electronic states must be mixed with the ground state, the quadratic term in first order cannot make any contribution here. The interaction Hamiltonian that is responsible for the spin flips can again be written as in Eq. (8) except that now the coefficient C may be dependent upon the frequency of the phonons depending upon whether or not the mixing of states by the magnetic field is important. If the magnetic-field mixing is important, the matrix elements of C are independent of frequency and the spin-lattice relaxation rate is again proportional to M_1 given by Eq. (16) and to H^2 . If however the magnetic-field effects are not important the matrix elements of the spin transitions are proportional to the frequency and so each transition probability W_{ij} [Eq. (13)] will contain an extra factor $(E_i - E_j)^2$ (neglecting factors of \hbar). The final form of the temperature dependence in this case is

$$M_3 = \left[\sum_i \exp(-i^2\Theta/T) \right]^{-1} \left\{ \sum_{l,i} (2i+2l+1)^3 (2l+1)^3 \right. \\ \times [(2l+1)^{-2} - (2l+2i+1)^{-2}]^2 \\ \left. \times \frac{\exp(-i^2\Theta/T)}{\exp[(2i+2l+1)(2l+1)\Theta/T] - 1} \right\}. \quad (17)$$

This function is plotted in Fig. 3 with a suitable scaling factor to enable easy comparison with the other functions.

We have considered magnetic and electric interactions that may be responsible for transitions between the spin states of the particle trapped in the box. Another interaction by means of which the spin could be flipped is the collision of the particle with the walls. According to our model, the particle encounters delta-function forces at the walls. These sudden forces could mix excited electronic states with the ground just as the usual action at a distance electric fields that we have just considered. The mean force of the walls on the particle is equal to the energy of the particle divided by the length of the well. We can estimate this force

by assuming that the well length is 10 Å and in the high-temperature limit the energy of the particle is kT . At 100°K the mean force is equal to that felt by a unit charge in an electric field of roughly 10^5 V/cm. The field of a unit charge at a distance of 10 Å, on the other hand, is about 10^7 V/cm. It is probable, therefore, that the fields due to surrounding charges would be more effective in flipping the spin than would collisions with the walls.

DISCUSSION

In Fig. 3 we have plotted on a log-log scale the two different square-well relaxation functions $M_1(\Delta/T)$ and $M_3(\Delta/T)$ and the tunneling-model function $\text{csch}(\Delta/T)$. The energy of the first excited state of each defect is $k\Delta$ above the ground state. In each case the vertical scale has been adjusted so that they can be compared. The lines in the upper left corner of the figure represent functions, one of which varies linearly, the other quadratically with temperature. Observe that in the high-temperature limit, M_1 and the hyperbolic cosecant vary as T while M_3 varies as T^2 . The data for the spin lattice relaxation rate of atomic hydrogen in fused quartz, reported in the preceding paper, is fairly well described by the function M_1 with $\Delta = 13.5^\circ\text{K}$. The first excited state of the square well of width $2a$ lies at $k\Delta = 3\hbar^2/32Ma^2$ above the ground state. Substituting the mass of hydrogen and this value of Δ , one finds a width equal to about 7 Å. Holes of this size are not out of the question in fused quartz.

If instead of a one-dimensional square-well potential we had chosen a three-dimensional box, we would have derived a relaxation rate that is a superposition of terms like M_1 or M_3 , i.e., to second order in the relative displacements of the square-well particle and the surrounding ions the three-dimensional well is simply a superposition of three one-dimensional square wells. The complete analysis of the three-dimensional square well to higher order has not been carried out. It is felt, however, that if the terms higher than second order in the relative displacements are important, then the three-dimensional well would result in a faster rate than the one-dimensional well because the density of states for the 3-D well increases with energy (equivalent to the increase in degeneracy of a 3-D harmonic oscillator with increasing quantum number of the level). One important factor for deriving a linear (or quadratic as the case may be) temperature dependence at high temperatures in the one-dimensional well is the fact the density of states is independent of energy.

The features of the models presented here that, in the high-temperature limit, are responsible for the relatively slow temperature dependence of the processes considered are the existence of a temperature-independent vibrational amplitude of the defect as well as a density of defect states that does not increase with energy. These features may be common to a number of other defect models. For instance an asymmetric charged

rigid rotor embedded in a lattice would satisfy the requirement of having a large temperature-independent charge displacement, changes in which could be effective in relaxing a paramagnetic center somewhere nearby. The energy levels of a rigid rotor are proportional to $n(n+1)$ which for large n resembles the square-well energy-level distribution.

The E' center in quartz,⁷ which is an electron trapped at a silicon atom next to an oxygen divacancy may behave like a particle in a square well. The two missing oxygen atoms free the silicon atom to swing in a large arc about the line joining the remaining two oxygens. For the E' center and for complex defects in general, it is probable that the frequency of the localized motion gets lower and lower, the motion becomes more and more like a particle in a square well. It is clear that the amplitude cannot remain harmonic for extremely low frequencies because the amplitude of a harmonic oscillator is proportional to $\omega^{-1/2}$ as $\omega \rightarrow 0$. Large anharmonicities must therefore become important at very low frequencies.

SUMMARY

A paramagnetic center which is involved in a vibration whose amplitude is independent of temperature, e.g., a particle moving in a large square well, or a

⁷ J. G. Castle and D. W. Feldman, *Phys. Rev.* **137**, A671 (1965); *J. Appl. Phys.* **36**, 124 (1965).

particle tunneling through a barrier between two stable positions, can have a spin-lattice relaxation rate that varies linearly with temperature at high temperatures and drops off exponentially with the reciprocal of the temperature at low temperatures. The linear temperature dependence for the tunneling model is a consequence of a single excited vibrational state. The process is analogous to an Orbach process. The temperature dependence differs from that of an Orbach process because spins in the excited state are observed while in the Orbach process one observes only ground-state spins. If the relaxation mechanism in the square-well case is due to a magnetic interaction with some other nearby dipole, the relaxation rate is linear in temperature at high temperatures. In order to obtain a linear variation in a Kramer's system using an electric-field modulation, it is necessary to require that the external magnetic field couple the excited states of the defect together resulting in spin-flip matrix elements that are not proportional to the frequency of the participating phonons. If this is not probable then the electric-field modulation in a Kramers system leads to a T^2 dependence at high temperatures.

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Density Effect for the Ionization Loss of Charged Particles*

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The reduction in the ionization loss of charged particles due to the polarization of the medium (density effect) has been evaluated for several substances. An approximate semiempirical expression for the mean excitation potential I as a function of the atomic number Z has been obtained.

THE density effect correction for the ionization loss of charged particles¹⁻⁶ has been previously evaluated for various substances.⁴⁻⁶ The purpose of the present paper is to give the results of additional calculations for the following materials: silicon, germanium, liquid hydrogen, propane and freon (CF_3Br). The first two substances are of interest in connection

with solid-state detectors, while an evaluation of the density effect for liquid hydrogen, propane, and freon should be useful in connection with the observation of ionization densities in bubble chambers. We have also obtained a semiempirical expression for the mean excitation potential I (as a function of Z) which enters into the Bethe-Bloch formula for the ionization loss.^{7,8}

*Work performed under the auspices of the U. S. Atomic Energy Commission.

¹ E. Fermi, *Phys. Rev.* **57**, 485 (1940).

² G. C. Wick, *Nuovo Cimento* **1**, 302 (1943).

³ O. Halpern and H. Hall, *Phys. Rev.* **73**, 477 (1948).

⁴ R. M. Sternheimer, *Phys. Rev.* **88**, 851 (1952).

⁵ R. M. Sternheimer, *Phys. Rev.* **91**, 256 (1953).

⁶ R. M. Sternheimer, *Phys. Rev.* **103**, 511 (1956).

⁷ A review of expressions for the ionization loss and of the experimental verification of the density effect has been given by R. M. Sternheimer, in *Methods of Experimental Physics*, edited by L. C. L. Yuan and C. S. Wu (Academic Press Inc., New York, 1961), Vol. 5A, pp. 4-55.

⁸ See also the review article of U. Fano, *Ann. Rev. Nucl. Sci.* **13**, 1 (1963).