Lifetime of Coupled Spin-Phonon Excitations*

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In this paper we examine the lifetime of the normal modes of a system of noninteracting paramagnetic spins coupled to phonons. It is found that scattering from spatial fluctuations in the z component of the spin density is the most effective means of attenuating the excitations. If the spin-phonon coupling constant is sufficiently large, scattering from the spatial fluctuations in S_z may dominate absorption by the direct process. A simple argument suggests that the Cr^{4+} ion may couple to the lattice strongly enough for this to occur.

I. INTRODUCTION

IN recent years a number of authors have discussed the normal modes of coupled spin-phonon systems. Kittel[1] has studied the normal modes of a system of ferromagnetic spins coupled to phonons, while Jacobsen and Stevens[2] have examined the properties of noninteracting paramagnetic spins which are coupled to the lattice motion.

The elementary excitation spectrum of a spin system not coupled to the lattice may be described by a dispersion relation $\omega_s(k)$, where k is the wave vector of the excitation and $\hbar\omega_s(k)$ is the excitation energy. We may also describe the phonon spectrum of the lattice by a dispersion relation $\omega_p(k)$. In general these dispersion relations will intersect for some value of $k = k_c$. From Refs. 1 and 2, we find that the coupling between the phonons and the spin system leads to new dispersion relations which repel each other in the vicinity of k_c.

In Fig. 1 we sketch the dispersion curves which describe the normal modes of a system of paramagnetic spins coupled to acoustical phonons. We denote the Larmor frequency of the spins by ω_0 and the velocity of sound by c. In the vicinity of k_c, the normal modes contain a strong admixture of both spin and lattice motion. The dispersion relations of Fig. 1 describe a system of noninteracting spins and are, in essence, a special case of the more general relations obtained by Kittel[1] for a system of spins coupled by exchange interactions.

Measurements of the phase velocity[3] and the group velocity[4] of an ultrasonic wave propagating in MgO doped with Fe^{2+} have been performed. The measurements were performed with frequencies in the vicinity of the Larmor frequency and at liquid-helium temperatures. The experiments are consistent with the theoretical relations derived in Refs. 1 and 2.

In order to derive the excitation spectrum of Fig. 1, it is necessary to neglect fluctuations in the z component of the spin density as well as certain nonlinear terms in the equations of motion. The fluctuations in the spin density and the nonlinear terms will scatter the excitations and a finite mean free path will result.

In this paper we study the mean free path of the normal modes which results from the terms mentioned above. We find that scattering from the fluctuations in the z component of the spin density is the most effective means of damping the excitations.

If the spin-phonon coupling constant is sufficiently large, scattering from fluctuations in S_z may dominate absorption by means of the direct process. For a sample which contains 10^{19} spins/cm³, we estimate this may occur if the spin-phonon coupling constant $G > 10^{-12}$ ergs.[5]

A crude estimate indicates that the Cr^{4+} ion may couple to the lattice strongly enough for the scattering from spatial fluctuations in S_z to dominate the attenuation.

II. THE HAMILTONIAN AND THE EQUATIONS OF MOTION

We shall employ a spin-phonon interaction which is linear in the strain amplitude and the spin variables.
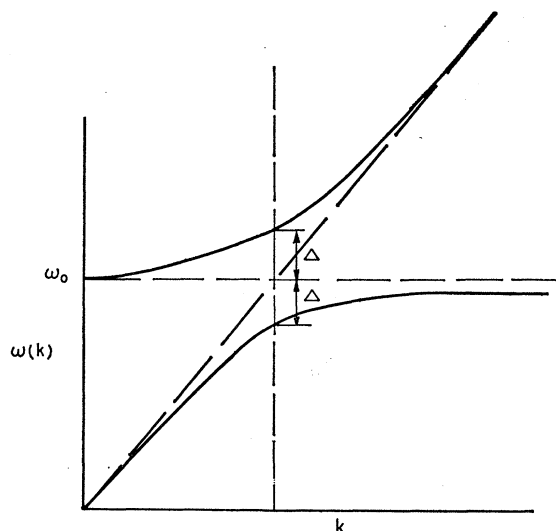

FIG. 1. The dispersion relations for a system of noninteracting spins coupled to acoustical phonons.

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[1] C. Kittel, Phys. Rev. **110**, 836 (1958).
[2] E. H. Jacobsen and K. W. H. Stevens, Phys. Rev. **129**, 2036 (1963).
[3] R. Guermeur, J. Joffrin, A. Levelut, and J. Penne, Phys. Letters **13**, 107 (1964).
[4] N. S. Shiren, Phys. Rev. **128**, 2103 (1962).
[5] We employ the notation of C. Kittel, Phys. Rev. Letters **1**, 5 (1958).

We expect that our conclusions would not be significantly altered if an interaction quadratic in the spin variables were employed.[6]

We simplify the problem further by neglecting the angular dependence in the spin-phonon coupling term, and we consider only acoustical phonons with the simple dispersion relation $\omega_k = ck$, where c is the velocity of sound.

For convenience we assume the system to have unit volume and unit density, and we choose units so that $\hbar = 1$.

Our Hamiltonian has the form

$$H = \sum_k \omega_k a_k^\dagger a_k$$

$$+ i\gamma \sum_{k,n} k(1/2\omega_k)^{1/2}[a_k - a_{-k}^\dagger]e^{ik\cdot x_n} s_x^{(n)}$$

$$+ i\gamma \sum_{k,n} k(1/2\omega_k)^{1/2}[a_k - a_{-k}^\dagger]e^{ik\cdot x_n} s_y^{(n)}$$

$$+ i\gamma \sum_{k,n} k(1/2\omega_k)^{1/2}[a_k - a_{-k}^\dagger]e^{ik\cdot x_n} s_z^{(n)}$$

$$+ \omega_0 \sum_n s_z^{(n)}. \quad (1)$$

The position of the spin n is denoted by x_n and the components of its spin are denoted by $s_i^{(n)}$. The phonon annihilation and creation operators are denoted by a_k and $a_{-k}^\dagger$, respectively. The operators satisfy the usual commutation relations

$$[s_i^{(n)}, s_j^{(m)}] = i\delta_{n,m}\epsilon_{ijk}s_k^{(n)} \quad \text{and} \quad [a_k, a_{k'}^\dagger] = i\delta_{kk'}.$$

We will find it useful to write the Hamiltonian in a different form. We follow the procedure of Herring and Kittel[7] by introducing the spin densities

$$S_i(r) = \sum_n s_i^{(n)}\delta(r - r_n).$$

One may easily show that the spin densities obey commutation relations of the form

$$[S_i(r), S_j(r')] = i\epsilon_{ijk}S_k(r)\delta(r - r'). \quad (2)$$

We also introduce the field variables

$$\varphi(r) = \sum_k (1/2\omega_k)^{1/2}[a_k + a_{-k}^\dagger]e^{-ik\cdot r},$$

and

$$\pi(r) = i\sum_k (\tfrac{1}{2}\omega_k)^{1/2}[a_k - a_{-k}^\dagger]e^{ik\cdot r}.$$

The variables $\varphi(r)$ and $\pi(r)$ satisfy the usual boson commutation relations

$$[\varphi(r), \pi(r')] = i\delta(r - r'). \quad (3)$$

The Hamiltonian of Eq. (1) may now be written

$$H = \int \{\tfrac{1}{2}\pi^\dagger(r)\pi(r) + \tfrac{1}{2}c^2 \nabla \varphi^\dagger(r)\cdot\nabla \varphi(r)\}d^3r$$

$$+ \frac{\gamma}{c}\sum_{i=x,y,z}\int \pi(r)S_i(r)d^3r + \omega_0 \int S_z(r)d^3r. \quad (4)$$

If we employ the Hamiltonian of Eq. (4) and the commutation relations of Eqs. (2) and (3), we find the following equations of motion:

$$\partial\varphi/\partial t = \pi^\dagger + (\gamma/c)\sum_{i=x,y,z} S_i;$$

$$\partial\pi/\partial t = c^2\nabla^2\varphi;$$

$$\partial S_x/\partial t = -\omega_0 S_y + (\gamma/c)\pi(S_z - S_y);$$

$$\partial S_y/\partial t = +\omega_0 S_x + (\gamma/c)\pi(S_x - S_z);$$

$$\partial S_z/\partial t = (\gamma/c)\pi(S_y - S_x). \quad (5)$$

We rearrange these equations and we find the equation which describes $\varphi(r,t)$. After some manipulation we obtain

$$\{(\partial^4/\partial t^4) + \omega_0^2(\partial^2/\partial t^2) - c^2(\partial^2/\partial t^2)\nabla^2$$
$$- c^2\omega_0^2\nabla^2 - 2\gamma^2\omega_0\langle S_z\rangle\nabla^2\}\varphi - 2\gamma^2\omega_0\{S_z - \langle S_z\rangle\}\nabla^2\varphi$$
$$+ \gamma^2\omega_0 S_x\{\nabla^2\varphi + c^{-2}\pi\} + \gamma^2\omega_0 S_y\{\nabla^2\varphi - c^{-2}\pi\} = 0. \quad (6)$$

We have neglected some terms of $o(\gamma^3)$ in the derivation of this result. In order to simplify the discussion which follows, we write Eq. (6) in the form

$$\mathcal{L}_0\varphi + \mathcal{L}_s\varphi = 0, \quad (7)$$

where $\mathcal{L}_0$ is the linear operator contained in the curly brackets of the first part of Eq. (6) and $\mathcal{L}_s\varphi$ denotes the nonlinear terms of the remainder.

Suppose we neglect the terms $\mathcal{L}_s\varphi$ for the moment. If we assume $\varphi = \varphi^{(0)} \exp[i(k\cdot r - \omega t)]$, then we find the secular equation

$$(\omega^2 - \omega_0^2)(\omega^2 - \omega_k^2) + 2\gamma^2\omega_0 k^2\langle S_z\rangle = 0. \quad (8)$$

Equation (7) has the same form as the dispersion relations discussed in Refs. 1 and 2. The two branches are sketched in Fig. 1. The quantity Δ indicated in Fig. 1 is given by

$$\Delta = ((\gamma^2\omega_0/2c^2)|\langle S_z\rangle|)^{1/2}. \quad (9)$$

The effect of spin-spin interactions may be included in a phenomenological manner by replacing the frequency ω in the equations of motion for S_x and S_y by $\omega + i\Gamma$, where Γ is the decay rate of the transverse components of the spin density. From this procedure[2,4] we find the usual expression for the lifetime from the direct process

$$1/\tau_d = (\pi\gamma^2\omega_k|\langle S_z\rangle|/2c^2)g(\omega - \omega_0), \quad (10)$$

where $g(\omega) = (\Gamma/\pi)/(\omega^2 + \Gamma^2)$.

We recall that $\langle S_z\rangle$ is the expectation value of the

[6] For example, consider an ion with spin $S=1$. If the ion is placed in a cubic environment, the states with $S_z = \pm 1$ will be split off from the state with $S_z = 0$ by the spin-orbit coupling in zero magnetic field. If we confine our attention to the manifold spanned by the states $S_z = \pm 1$, the quadratic form $S_i S_j$ may be replaced by a linear combination of Pauli matrices. The interaction is then linear in the effective spin variables.

The normal modes of a system of spin-one ions coupled to the lattice has been discussed in detail in Ref. 2 for the case when the three states $S_z = 0, \pm 1$ are degenerate in zero magnetic field.

[7] C. Herring and C. Kittel, Phys. Rev. 81, 869 (1951).

spin density, so that $\langle S_z \rangle = n \langle s_z \rangle$, where n is the number of spins per unit volume.

The nonlinear terms $\mathcal{L}_s \varphi$ of Eq. (7) allow the incident wave to interact with the thermal motion of the spin-lattice system. We shall compute the mean free path which results from these terms.

Since one is generally concerned with excitations of wavelength long compared to the mean separation of the spins, the field φ and the spin densities may be treated as macroscopic continuous fields. We consider temperatures sufficiently high that $kT > \omega_0$, so the spin system may be treated classically.

We will proceed by finding the Green's function $G(\mathbf{r}, t)$ which satisfies

$$\mathcal{L}_0 G(\mathbf{r}, t) = \delta(\mathbf{r}) \delta(t).$$

The scattered wave φ_S is then given by

$$\varphi_S(\mathbf{r}, t) = \int G(\mathbf{r} - \mathbf{r}'; t - t') \mathcal{L}_s \varphi(\mathbf{r}', t) d^3 r' dt'. \quad (11)$$

The integrand of Eq. (11) contains nonlinear terms of the form $S_i(\mathbf{r}', t') \varphi(\mathbf{r}', t')$. We write φ and the S_i's as a sum

$$\varphi(\mathbf{r}', t') = \varphi^{(0)} \exp[i(\mathbf{q} \cdot \mathbf{r}' - \Omega t')] + \varphi^{(\mathrm{th})}(\mathbf{r}', t'),$$

where φ_0 is the amplitude of the incident wave and $\varphi^{(\mathrm{th})}$ is the amplitude associated with the thermal motion. We retain terms linear in the impressed amplitudes $\varphi^{(0)}$, $S_i^{(0)}$.

If we assume $\mathcal{L}_s \varphi$ is nonvanishing only over a volume V_s of finite spatial extent,[8] we will find $\varphi_S(\mathbf{t}, t) \sim 1/|\mathbf{r}|$ far from the region V_s. We may then compute the energy per unit time which flows through a large sphere. This rate will be independent of the size of the sphere and will be proportional to V_s. We then find the mean free path of the incident wave.

Before we become involved in the details of the algebra, it will be useful to discuss qualitatively the contribution from various terms of $\mathcal{L}_s \varphi$ in order to sort out the part which scatters most strongly. For this purpose it will be useful to examine the form of the Green's function and also the structure of the integral of Eq. (11).

III. THE GREEN'S FUNCTION; COMPUTATION OF THE LIFETIME

We find the function $G(\mathbf{r}, t)$ which satisfies

$$\mathcal{L}_0 G(\mathbf{r}, t) = \delta(\mathbf{r}) \delta(t).$$

If we write (for a system of unit volume)

$$G(\mathbf{r}, t) = \sum_q \int \frac{d\Omega}{2\pi} \mathcal{G}(q, \Omega) e^{i\mathbf{q} \cdot \mathbf{r}} e^{-i\Omega t},$$

[8] The present discussion is patterned after the treatment of Rayleigh scattering by L. Landau and E. Lifshitz, *Electrodynamics of Continuous Media* (Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1960), Chap. XIV.

we find

$$\mathcal{G}(\mathbf{q}, \Omega) = [(\Omega^2 - \Omega_1^2(q))(\Omega^2 - \Omega_2^2(q))]^{-1},$$

where $\Omega_1(q)$ and $\Omega_2(q)$ are the two branches of the dispersion curve. Then

$$G(\mathbf{1}, t) = \sum_q \int \frac{d\Omega}{2\pi} \frac{e^{i\mathbf{q} \cdot \mathbf{r}} e^{-i\Omega t}}{[\Omega^2 - \Omega_1^2(q)][\Omega^2 - \Omega_2^2(q)]}.$$

Since $\Omega_1(q)$ and $\Omega_2(q)$ are independent of the direction of $\mathbf{q}$ in the present model, we may perform the integration over the direction of $\mathbf{q}$. It will be convenient to write the result in the form

$$G(\mathbf{r}, t) = \frac{1}{|\mathbf{r}|} \sum_q \int \frac{d\Omega e^{-i\Omega t}}{2\pi |\mathbf{q}|}$$

$$\times \frac{\sin|\mathbf{q}||\mathbf{r}|}{[\Omega^2 - \Omega_1^2(q)][\Omega^2 - \Omega_2^2(q)]}. \quad (12)$$

In the course of the calculation we shall arrange the poles of the integrand so that the scattered wave obeys the outgoing wave boundary conditions.

Suppose we send in a wave of wave vector $\mathbf{k}_0$ and frequency $\Omega_i(k_0)$. The subscript i is a branch index and may be either 1 or 2. The general form of $\mathcal{L}_s \varphi$ will then be

$$\mathcal{L}_s \varphi = \frac{1}{(V_s)^{1/2}} \sum_{k'} \int \frac{d\Omega'}{2\pi} V(\mathbf{k}', \Omega) e^{i(\mathbf{k}_0 + \mathbf{k}') \cdot \mathbf{r}} e^{-i(\Omega_i(k_0) + \Omega') t}. \quad (13)$$

The part $\exp[i(\mathbf{k}_0 \cdot \mathbf{r} - \Omega_i(k_0)t)]$ occurs because we have taken $\mathcal{L}_s \varphi$ to be proportional to the amplitude of the driving wave. The detailed form of $V(\mathbf{k}', \Omega')$ may be found by consulting the equation of motion Eq. (6).

We insert Eqs. (13) and (12) into the expression for the amplitude of the scattered wave. After some tedious but straightforward integrations, we find for $\mathbf{r}$ far outside the scattering volume V_s

$$\varphi_S(\mathbf{r}, t) = \frac{(V_s)^{1/2}}{4\pi^2 |\mathbf{r}|}$$

$$\times \left\{ \int_0^\infty \frac{k V(k\hat{r} - \mathbf{k}_0; \Omega_1(k) - \Omega_i(k_0))}{\Omega_1(k)[\Omega_1^2(k) - \Omega_2^2(k)]} e^{ikr} e^{-i\Omega_1(k)t} dk \right.$$

$$\left. + \int_0^\infty \frac{k V(k\hat{r} - \mathbf{k}_0; \Omega_2(k) - \Omega_i(k_0))}{\Omega_2(k)[\Omega_2^2(k) - \Omega_1^2(k)]} e^{ikr} e^{-i\Omega_2(k)t} dk \right\}. \quad (14)$$

With this expression we can assess the relative importance of the various terms of $\mathcal{L}_s \varphi$.

For definiteness we assume the incident wave $\mathbf{k}_0$ is on branch 1. We are also most interested in wave vectors $\mathbf{k}_0$ such that $\mathbf{k}_0$ is near ω_0/c.

If we set the index $i = 1$ in Eq. (14), we notice that

the integrand of the first term contains

$$V(k\hat{r}-\mathbf{k}_0;\Omega_1(k)-\Omega_1(k_0))$$

while the integrand of the second term contains

$$V(k\hat{r}-\mathbf{k}_0;\Omega_2(k)-\Omega_1(k_0)).$$

From the equation of motion, we see that all of the terms which contribute to $V(\mathbf{k},\omega)$ are of order γ^2. Hence $|V(\mathbf{k},\omega)|^2 \sim \gamma^4$ and the scattering will be weak unless we can find a term in V which allows the denominator $[\Omega_1^2-\Omega_2^2]$ to become small over an appreciable solid angle. The minimum value $[\Omega_1^2-\Omega_2^2]$ can assume is $4\omega_0\Delta \sim \gamma$. A process which allows the denominator to become small results in $\varphi_S \sim \gamma$ and the cross section $\sim \gamma^2$.

We now examine the various scattering terms. Consider first the last two terms of Eq. (6). These terms are proportional to $S_x(\mathbf{r},t)\varphi(\mathbf{r},t)$ and $S_y(\mathbf{r},t)\varphi(\mathbf{r},t)$, respectively. Since we assume the wave vector of the incident wave is near ω_0/c, the wave consists of approximately an equal admixture of spin and lattice motion. Let the amplitude of the spin motion associated with the incident wave be denoted by $S_x^{(0)}\exp[i(\mathbf{k}_0\cdot\mathbf{x}-\Omega_1(k_0)t)]$, $S_y^{(0)}\exp[i(\mathbf{k}_0\cdot\mathbf{x}-\Omega_1(k_0)t)]$ and let the amplitude of the lattice motion be denoted by $\varphi^{(0)}\exp[i\mathbf{k}_0\cdot\mathbf{x}-\Omega_1(k_0)t]$.

The last two terms of the equation of motion then lead to contributions to $V(\mathbf{k},\Omega)$ proportional to $S_x^{(\mathrm{th})}(\mathbf{k},\omega)\varphi^{(0)}$, $\varphi^{(\mathrm{th})}(\mathbf{k},\omega)S_x^{(0)}$, etc.

Since $S_x^{(\mathrm{th})}(\mathbf{k},\omega)$ has an appreciable amplitude only for frequencies $\sim\omega_0$, the frequency $\Omega_2(k)$ of the outgoing wave is $\sim\omega_0+\Omega_1(k_0)\approx 2\omega_0$. But then the denominator $\Omega_2^2(k)-\Omega_1^2(k)$ is of order ω_0^2 rather than $4\Delta\omega_0$. Consequently, terms of the form $S_x^{(\mathrm{th})}(\mathbf{k},\omega)\varphi^{(0)}$ or $S_y^{(\mathrm{th})}(\mathbf{k},\omega)\varphi^{(0)}$ result in only very weak scattering.

The terms of the form $\varphi^{(\mathrm{th})}(\mathbf{k},\omega)S_x^{(0)}$ also lead to a small cross section. There is strong scattering in the forward direction into a cone of half-angle $\sim\Delta/\omega_0$ (for $\Delta/\omega_0\ll 1$), however since the scattered energy is confined to a region of small angular extent, the total cross section is not large. A detailed calculation shows the cross section from this term is proportional to γ^3.

The only remaining term in the equation of motion is the term proportional to $S_z(\mathbf{r},t)-\langle S_x\rangle=\delta S_z(\mathbf{r},t)$. Consider the frequency dependence of the Fourier transform $\delta S_z(\mathbf{k},\omega)$. For a given $\mathbf{k}$, we expect $\delta S_z(\mathbf{k},\omega)$ to fall off rapidly as ω becomes larger than the spin-flip frequency Γ which results from spin-spin interactions.[9] Because $\Gamma\ll\Delta$,[10] we may consider $S_z(\mathbf{r},t)$ to be static in time for the purpose of evaluating the integrals of Eq. (14). We are then examining the scattering from static spatial fluctuations in S_z.

If we employ the above assumptions, only the first term of Eq. (6) contributes to φ_S. The quantity $V(k\hat{r}-\mathbf{k}_0;\Omega_1(k)-\Omega_1(k_0))$ is proportional to $\delta(\Omega_1(k)$

$-\Omega_1(k_0))$ and the integral over k may be performed. We find

$$\varphi_S(\mathbf{r},t)=\frac{(V_s)^{1/2}}{4\pi^2}$$

$$\times\frac{k_0 V(k_0\hat{r}-\mathbf{k}_0)e^{-i\Omega_1(k_0)t}}{\Omega_1(k_0)[\Omega_1^2(k_0)-\Omega_2^2(k_0)](\partial\Omega_1/\partial k)(k_0)}\frac{e^{ik_0|\mathbf{r}|}}{|\mathbf{r}|}.$$

From the equation of motion we find

$$V(\mathbf{q})=2\gamma^2\omega_0 k_0^2 S_z(\mathbf{q})\varphi_0.$$

Then

$$\varphi_S(\mathbf{r},t)=\frac{(V_s)^{1/2}}{2\pi^2}$$

$$\times\frac{\gamma^2\omega_0 k_0^3 S_z(k_0\hat{r}-\mathbf{k}_0)\varphi_0}{\Omega_1(k_0)(\partial\Omega_1/\partial k)(k_0)[\Omega^2(k_0)-\Omega_2^2(k)]}$$

$$\times\frac{e^{ik_0|\mathbf{r}|}}{|\mathbf{r}|}e^{-i\Omega_1(k_0)t}. \quad (15)$$

We may now compute the total energy/unit time which flows through a large sphere of radius R. From the Hamiltonian of Eq. (4) we know the energy density, and the group velocity of the outgoing wave is $\partial\Omega_1/\partial k$. To find the lifetime, we divide by the energy stored in the volume V_s. This procedure yields the following expression for the lifetime:

$$\frac{1}{\tau}=\frac{1}{\pi^3}\frac{\gamma^4\omega_0^2 k_0^6\int|S_z(k_0\hat{r}-\mathbf{k}_0)|^2(d\Omega(\hat{r})/4\pi)}{\Omega_1^2(k_0)(\partial\Omega_1/\partial k)(k_0)[\Omega_1^2(k_0)-\Omega_2^2(k_0)]^2}.$$

To complete the computation, we need an expression for $|S_z(\mathbf{q})|^2$. Now

$$S_z(\mathbf{r})=\sum_n s_z^{(n)}\delta(\mathbf{r}-\mathbf{r}_n)=[1/(V_s)^{1/2}]\sum_\mathbf{q} S_z(\mathbf{q})e^{i\mathbf{q}\cdot\mathbf{r}}.$$

From this we find

$$S_z(\mathbf{q})=[1/(V_s)^{1/2}]\sum_n s_z^{(n)}e^{-i\mathbf{q}\cdot\mathbf{r}_n},$$

so that

$$|S_z(\mathbf{q})|^2=(1/V_s)\sum_{n,m}s_z^{(n)}s_z^{(m)}e^{i\mathbf{q}\cdot(\mathbf{r}_m-\mathbf{r}_n)}. \quad (16)$$

We average Eq. (16) over an ensemble of systems and we assume no correlation between neighboring spins. This should be a valid procedure for our paramagnetic spin system if the temperature is sufficiently high. Then $\langle s_z^{(n)}s_z^{(m)}\rangle=s^2\delta_{nm}$ and $\langle|S_z(\mathbf{q})|^2\rangle_{\mathrm{av}}=(s^2/V_s)\times\sum_n 1=ns^2$, where n is the number of spins per unit volume.

Our expression for the lifetime becomes

$$\frac{1}{\tau}=\frac{1}{\pi^3}\frac{\gamma^4\omega_0^2 k_0^6 ns^2}{\Omega_1^2(k_0)(\partial\Omega_1/\partial k)(k_0)[\Omega_1^2(k_0)-\Omega_2^2(k_0)]^2}. \quad (17)$$

We apply Eq. (17) to an excitation of wave vector

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[9] In this argument we neglect spin-spin correlations through the phonon field. A simple estimate suggests that such correlations would not affect the conclusions of the argument for the systems of interest in the present paper.

[10] For example, for Fe^{2+}, $\Delta\sim 10^9$ rad/sec for a concentration of 10^{19} cm^{-3}, while Γ may be 10^6 or 10^7 sec^{-1}.

ω_0/c. Then

$$\frac{1}{\tau} \cong \frac{1}{8\pi^3} \frac{\gamma^4 \omega_0^4 n s^2}{c^7 \Delta^2} \cdot \qquad (18)$$

We recall that $\Delta^2 = (\gamma^2 n \omega_0 |\langle s_z \rangle|)/(2c^2)$.

The lifetime of Eq. (18) has the peculiar feature that it is independent of impurity concentration for $k_0 = \omega_0/c$. As we increase the impurity concentration we increase the strength of the scattering potential. At the same time the gap Δ increases, so the denominator becomes larger. The lifetime is rigorously independent of concentration only at the special point $k = \omega_0/c$; however, the lifetime will be approximately concentration-independent for[11] $|k - (\omega_0/c)| < (\Delta/c)$.

IV. NUMERICAL ESTIMATES

We estimate the order of magnitude of the lifetime of Eq. (18). We rewrite Eq. (18) in the form

$$\tau = \frac{8\pi^3}{\omega_0} \left(\frac{nc^3}{\omega_0^3}\right) \left(\frac{\omega_0}{\Delta}\right)^2 \frac{|\langle s_z \rangle|^2}{s^2} \cdot$$

We now estimate τ with the Cr^{4+} ion in mind. For this ion we are concerned with the $S_z = \pm 1$ levels. Since the measured g value[12] does not differ greatly from 2, we have $\omega_0 \sim 3 \times 10^{11}$ rad/sec for $H_0 = 10^4$ G. We assume $n = 10^{19}$ cm^{-3} and $c \cong 5 \times 10^5$ cm/sec. We suppose the spin-phonon coupling is sufficiently strong that $\Delta/\omega_0 \sim 0.1$. We shall see that this may not be an unreasonable assumption for Cr^{4+}. If we employ these numbers we find

$$\tau \cong 2 \times 10^{-6} |\langle s_z \rangle|^2/s^2 \text{ sec.} \qquad (19)$$

Thus, for the numbers stated above, this process may lead to a mean free path of the order of a millimeter.

We compare the lifetime of Eq. (19) with the lifetime from direct absorption given by Eq. (10). For our excitation of wave vector ω_0/c, we have $\Omega_1(k_0) - \omega_0 \gg \Gamma$ since $\Delta/\omega_0 \sim 0.1$. Thus

$$\frac{1}{\tau_d} \cong \frac{\gamma^2 \omega_0 n |\langle s_z \rangle|}{2c^2 \Delta^2} \Gamma = \Gamma.$$

Hence for $\Gamma = 10^6$ sec^{-1},

$$\tau/\tau_d \cong 2 |\langle s_z \rangle|^2/s^2.$$

If we assume a two-level spin system with a Larmor frequency of 3×10^{11} rad/sec, then $\langle s_z \rangle/s \sim \frac{1}{2}$ and $\tau/\tau_d \sim \frac{1}{2}$ for $T = 4°K$.

Thus our estimate suggests that scattering from fluctuations in S_z may dominate the direct absorption for a system described by the parameters employed above.

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[11] Notice that the right-hand side of this inequality vanishes as the concentration $n \to 0$. Hence the lifetime of an excitation with $k \neq k_0$ will vanish as $n \to 0$, since the volume of phase space over which the concentration-independent behavior occurs shrinks to zero.

[12] R. H. Hoskins and B. H. Soffer, Phys. Rev. 133, A490 (1964).

We now examine the assumption $\Delta/\omega_0 \sim 0.1$. In the present work, all of the calculations have been performed with a spin-phonon coupling linear in the spin variables. In Ref. 2 the dispersion relation for a spin-1 ion coupled to phonons by means of a coupling term quadratic in the spin variables. For frequencies in the vicinity of ω_0, the dispersion relations are similar to the expressions employed in the present paper, with

$$\Delta = (G^2 \omega_0 n \langle s^z \rangle / 8\hbar \rho c^2)^{1/2}. \qquad (20)$$

We have introduced $\hbar$ and the density ρ of the crystal explicitly. We employ the spin-phonon coupling constant G defined as in Ref. 5.

We use Eq. (20) and the values of ω_0, n, and c introduced earlier and we find the value of G for which $\Delta/\omega_0 \sim 0.1$. If $\rho = 2$ gm/cm^3, we obtain $G \cong (1 \times 10^{-12})/\langle s_z \rangle^{1/2}$. This is a very large value for the coupling constant.

The largest value of the spin-phonon coupling constant known to the present author is that of Fe^{2+} placed in MgO for which $G \sim 2 \times 10^{-13}$ ergs.[13,14] We present a simple argument which indicates that Cr^{4+} may couple to the lattice more strongly than Fe^{2+}. We denote the spin-phonon coupling constant of Cr^{4+} by G_C and the spin-phonon coupling constant of Fe^{2+} by G_F. We estimate the ratio G_C/G_F, and it is assumed that both ions are placed in a cubic environment.

If we expand the crystal field in terms of the normal coordinates of the nearest neighbors

$$V = \sum_\alpha V_\alpha Q_\alpha,$$

then it may be shown that the spin-phonon coupling constant is given by an expression of the form[15]

$$G_{ij}^{(\alpha)} = \lambda^2$$

$$\times \sum_{n,m}' \frac{\langle 0 | L_i | n \rangle \langle n | L_j | m \rangle \langle m | V_\alpha | 0 \rangle + \text{permutations}}{(E_n - E_0)(E_m - E_0)} \cdot$$

In the last equation, λ is the spin-orbit coupling parameter, L_i, L_j are orbital angular-momentum operators and $|0\rangle$ is the orbital wave function of the ground state.

The orbital ground state of both the Cr^{4+} ion (a d^2 configuration) and Fe^{2+} (a d^6 configuration) are triply degenerate in a perfect cubic field.[16] This degeneracy will be lifted by a Jahn-Teller distortion. Then the main contribution to G will come from matrix elements between the ground-state singlet and the two states

[13] G. D. Watkins and E. Feher, Bull. Am. Phys. Soc. 7, 29 (1962).

[14] N. S. Shiren, Magnetic and Electric Resonance and Relaxation, edited by J. Smidt (Interscience Publishers, Inc., New York, 1963).

[15] R. D. Mattuck and M. W. P. Strandberg, Phys. Rev. 119, 1204 (1960).

[16] See S. A. Al'tshuler, B. I. Kochelaev, and A. M. Leushin, Usp. Fiz. Nauk (U.S.S.R.) 75, 459 (1962) [English transl.: Soviet Phys.—Usp. 4, 880 (1962)].

split off by the Jahn-Teller distortion. The matrix elements $\langle j | V | 0 \rangle$ will be proportional to r^2, where r is the mean radius of the orbit.[17] Then

$$G \sim \lambda^2 r^2 / \delta^2.$$

The Jahn-Teller splitting δ is proportional to r^4. Then

$$\frac{G_C}{G_F} \sim \left(\frac{\lambda_C}{\lambda_F}\right)^2 \frac{r_F^6}{r_C^6}.$$

If the d-electron wave functions lie mostly outside the closed inner shells, we may imagine the d electrons move in a Coulomb field of some effective charge Z_{eff}. Then $r^2 \sim 1/Z_{eff}^2 \sim 1/I$, where I is the ionization potential. We then estimate

$$\frac{G_C}{G_F} \approx \left(\frac{\lambda_C}{\lambda_F}\right)^2 \left(\frac{I_C}{I_F}\right)^3.$$

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[17] Reference 16.

We employ the free-ion values for the ionization potential and the spin-orbit coupling parameter. From spectroscopic data[18] we find $\lambda_C/\lambda_F \sim 1.5$ and $I_C/I_F \sim 2.3$.[19]

This yields $G_C/G_F \approx 18$ or

$$G_C \approx 4 \times 10^{-12} \text{ ergs}.$$

This estimate indicates that Cr^{4+} should couple to the lattice strongly enough for the lifetime of the normal modes to be determined by scattering from fluctuations in S_z.

ACKNOWLEDGMENTS

[18] C. Moore, Natl. Bur. Std. (U.S.), Circ. No. 467 (1952), Vol. II, pp. 18–19, 60–61.
[19] If our assumption that the d electron moves in a field of an effective charge Z_{eff} is meaningful, then we should find $\lambda \sim Z_{eff}$, or $(\lambda_c/\lambda_F) \approx (I_c/I_F)^{1/2}$. This relation is well satisfied.

Trapped Hole Center Containing Fluorine in Magnesium Oxide*

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An intrinsic defect center readily induced in MgO by ionizing radiation is the positive hole localized on an oxygen atom adjacent to a positive ion vacancy (V_1 center). This has a tetragonal symmetry axis along [001] or equivalent directions. A similar ESR spectrum but with each line a hyperfine doublet was identified earlier as arising from the center $O^+ - [=] - H^+O$ (V_{OH} center). This paper describes a similar ESR spectrum of a trapped hole center (V_F) with smaller (anisotropic) hyperfine splitting than V_{OH}. It is best observed in single crystals, but it may be induced in powdered MgO by fluorine doping and heating. It thus appears that fluorine is the nucleus responsible for hyperfine splitting. The contact and dipolar splitting constants are, respectively: $a = 0.08$ G, $b = 0.33$ G. The proposed model for the V_F center is $O^+ - [=] - F^+$ (only deviations from normal site symmetry are shown).

INTRODUCTION

IN MgO crystals, a predominant intrinsic defect which may be induced by ionizing radiation is the hole trapped adjacent to a positive ion vacancy[1] (i.e., the V_1 center proposed by Seitz but not observed in the alkali halides). Uniform delocalization of the trapped hole over the six oxygen atoms surrounding the vacancy would give an isotropic ESR spectrum, whereas the spectrum observed has pure tetragonal symmetry. We have tended to regard the hole as strongly localized. However, Dr. T. E. Feuchtwang points out that there may be delocalization such that the hole density on the four oxygens girdling the vacancy and the axis is dif-

ferent from that of atoms on the axis.[2] In some MgO crystals there are "satellite" lines about but not centered upon the principal lines of the V_1 spectrum; it can easily be shown that these are not a part of the same line system. One group of three hyperfine doublets was recently shown by an electron-nuclear-double-resonance (ENDOR) study[3] to arise from a V_1-type center (V_{OH}) with the array: $-O^+ - [=] - H^+O$ along [001], [010], or [100]. (Only deviations from normal site charge are shown.) The infrared spectrum shows that the O-H stretching frequency is shifted from 3296 to 3323 cm^{-1} when a positive hole is trapped on the oxygen atom on the opposite side of the positive ion vacancy. The hyperfine splitting for V_{OH} is given by the expression $a + b(3\cos^2\theta - 1)$, where $a = 0.016$ G and $b = 0.848$ G.

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[1] J. E. Wertz, P. Auzins, J. H. E. Griffiths, and J. W. Orton, Disc. Faraday Soc. 28, 136 (1959).

[2] Dr. T. E. Feuchtwang (private communication).
[3] P. W. Kirklin, P. Auzins, and J. E. Wertz, J. Phys. Chem. Solids 26, 1067 (1965).