where $\Gamma_{\sigma\sigma'}$ is real. The relations $\Gamma_{\sigma\sigma} = -w_{\sigma\sigma}$, and $\Gamma_{\sigma\bar{\sigma}} = -w_{\sigma\bar{\sigma}}$ can also be shown to hold to third order.

The calculation of the relaxation rate $\Gamma_1 = w_{\uparrow\downarrow} + w_{\downarrow\uparrow}$ to third order in terms of the parameters J and J' of the model (4.3) is straightforward. The result has already been quoted [see Eq. (3.14)].

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Thermal Conductivity of Paramagnetic Salts at Low Temperatures*

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We present a simple theory of the effect of impurity-induced changes in atomic force constants and changes in atomic mass on the lifetime of coupled spin-phonon modes in paramagnetic crystals. The result is then employed to study the effect of impurity scattering, boundary scattering, and scattering of the coupled modes by longitudinal fluctuations in spin density on the temperature dependence of the thermal conductivity, and the frequency distribution of the heat flux. The theory can account for the experimental data on MgO doped with Cr^{2+} reported recently by Challis, McConachie, and Williams and offers support for the interpretation of the data presented by these authors.

I. INTRODUCTION

When paramagnetic ions are introduced into insulating crystals, phonons may induce transitions between the Zeeman levels. This spin-phonon interaction thus gives rise to spin-lattice relaxation,[1] shifts of the g factor,[2] and a number of other phenomena. When the wavelength of the resonant phonons (i.e., phonons with energy $\hbar\omega$ equal to the Zeeman energy) is large compared to the mean spacing between the ions, Jacobsen and Stevens[3] have pointed out that the normal modes of the system are coupled spin-phonon modes, in which the motion of different spins is correlated through the phonon field. The resulting modes have properties similar in many respects to the coupled magnon-phonon modes considered earlier by Kittel.[4]

In the theory of coupled spin-phonon modes in paramagnets, one linearizes the equations of motion by replacing the combination $S_z u$ by $\langle S_z \rangle u$, where u is the phonon amplitude, S_z the z component of spin, and the angular bracket denotes the thermal coverage. The normal modes are well defined only so long as this approximation is valid. The finite lifetime of the normal mode that results when the correction term $(S_z - \langle S_z \rangle)u$ is retained in the equations of motion was studied in an earlier work.[5] This term gives rise to a scattering of the coupled mode by spatial fluctuations in the z component of the spin of the ions. Since this work, other authors have also studied the lifetime of the coupled modes from other points of view.[6]

One finds that the scattering produced by the fluctuations in S_z has a resonant character, in the sense that the scattering rate is strongest for modes with frequency in the vicinity of the Zeeman frequency ω_0. The width of the resonance is roughly equal to the width of the frequency regime within which the coupled modes contain a large admixture of spin motion.

Detailed experimental studies of the thermal conductivity of crystals of MgO doped with Cr and other transition-metal impurities have recently been completed by Challis and co-workers.[7,8] The experiments were carried out in the liquid-He temperature range, and the Cr concentration ranged from 10^{-6} to 10^{-3}, depending on the sample. Also, the dependence of the thermal conductivity on the magnitude and direction of the magnetic field was measured.[8]

These authors analyzed their data in zero magnetic field[7] by employing a phenomenological model with a Debye spectrum of phonons combined with a frequency-dependent relaxation time. They included three terms in their expression for the inverse relaxation time $\tau^{-1}(\omega)$: a frequency-independent boundary scattering term, an impurity scattering contribution proportional to ω^4, and a resonant term proportional to $\omega^2(\omega^2-\omega_0^2)^{-2}$, where ω_0 and the coefficients of the various terms were determined by comparison with the data. It was suggested that the resonance term may possibly have its

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origin in the scattering of the Jacobsen-Stevens coupled modes from the fluctuations in S_z, as described above. Also, a consistent interpretation of the data could be obtained by assuming the ω^4 impurity scattering and resonant scattering are associated with the same ion. From studies of the effect of x radiation on the crystal, it was inferred that the Cr^{2+} ion is responsible for the very strong resonant scattering; the value of ω_0 was deduced to be about 8°K, so the resonant scattering is associated with the coupling of the phonons to a level that is split off from the ground state in zero magnetic field. The presence of the resonant scattering term is also consistent with the magnetic field studies, since varying the Zeeman splitting of a second ion strongly coupled to phonons allows one to probe the frequency distribution of the heat flux.[8]

While we have concentrated our discussion on the work of Challis and co-workers, deGoer has also observed resonant scattering of a similar sort in Al_2O_3 doped with transition-metal impurities.[9] The data have been analyzed in a similar fashion.

If the normal modes of the crystal are mixed spin-phonon modes, then the contribution τ_I^{-1} to the relaxation rate from impurity scattering will not simply be proportional to ω^4. As the frequency of the mode enters the region where a strong admixture of spin motion is present, to compute τ_I^{-1} one must take account of the reduced phonon content of the mode, and the effect of the shift in wave vector from the value ω/c_s, where c_s is the velocity of sound. Also, one must take account of the effect of the change in density of states of the normal modes, and the change in group velocity to compute the frequency distribution of the heat flux, as Elliott and Parkinson have done.[6] These corrections will be especially important in systems in which the spins are strongly coupled to the phonons, since the modification of the normal modes is then important over a wide range of frequency.

The purpose of this note is to present the theory of the scattering of coupled spin-phonon modes by the changes in force constants and mass associated with the impurities. We do this by introducing appropriate phenomenological terms in the model Hamiltonian employed in earlier work. We include the scattering from longitudinal fluctuations in S_z in the theory, and rewrite this spin fluctuation contribution τ_{sf}^{-1} to the relaxation rate in a form convenient for computational purposes. We then present some numerical studies of the dependence of the thermal conductivity K on temperature and impurity concentration, along with computations of the frequency distribution of the heat flux. A wide variety of behaviors is obtained, depending on the relative values of the boundary scattering, impurity scattering or the spin fluctuation scattering rate. With the appropriate choice of parameters, we are able to reproduce the observed dependence of K on temperature, for the case of MgO doped with Cr^{2+}. We feel that some features of the data would be quite difficult to explain without invoking the coupled-mode picture.

II. CALCULATIONS OF RELAXATION RATES

We shall consider a phenomenological model of a single branch of a Debye phonon spectrum that is coupled to a number of paramagnetic impurities randomly distributed through the solid. The model may be applied to any two-level system coupled linearly to phonons, provided the Zeeman frequency is replaced by the separation between the energy levels. Following Ref. 5, we describe the phonons by a single scalar-boson field amplitude

$$\varphi(\mathbf{x})=\sum_{\mathbf{k}}\frac{1}{(2\rho_0\omega_{\mathbf{k}})^{1/2}}[a_{\mathbf{k}}+a_{-\mathbf{k}}^{\dagger}]e^{i\mathbf{k}\cdot\mathbf{x}} \tag{1}$$

and its canonically conjugate momentum

$$\pi(\mathbf{x})=i\sum_{\mathbf{k}}\tfrac{1}{2}(\rho_0\omega_{\mathbf{k}})^{1/2}[a_{\mathbf{k}}-a_{-\mathbf{k}}^{\dagger}]e^{i\mathbf{k}\cdot\mathbf{x}}. \tag{2}$$

In these expressions, ρ_0 is the density of the crystal, $\omega_{\mathbf{k}}=c_s k$ is the frequency of a phonon of wave vector $\mathbf{k}$, and we employ units with $\hbar=1$. The crystal is assumed to have unit volume. The variables $\varphi(\mathbf{x})$ and $\pi(\mathbf{x})$ satisfy the usual boson commutation relations

$$[\varphi(\mathbf{x}),\pi(\mathbf{x}')]=\delta(\mathbf{x}-\mathbf{x}'). \tag{3}$$

We then introduce the model Hamiltonian

$$H=\int d^3x\left(\frac{1}{\rho(\mathbf{x})}\pi^{\dagger}(\mathbf{x})\pi(\mathbf{x})+\tfrac{1}{2}\alpha(\mathbf{x})\nabla\varphi^{\dagger}(\mathbf{x})\cdot\nabla\varphi(\mathbf{x})\right)+\frac{\gamma}{c_s}\sum_{i=x,y,z}\int d^3x\,\pi(\mathbf{x})S_i(\mathbf{x})+\omega_0\int d^3x\,S_z(\mathbf{x}). \tag{4}$$

The first term is the contribution to H from the phonons. We assume the density of the medium varies with position, and the effective elastic modulus $\alpha(\mathbf{x})$ also varies with position. In this fashion we introduce the effect of mass and force constant changes produced by the paramagnetic impurities. We shall write

$$\rho(\mathbf{x})=\rho_0+\Delta M\sum_i\delta(\mathbf{x}-\mathbf{x}_i),$$

and a similar expression for $\alpha(\mathbf{x})$, where ΔM is the change in mass of the impurity located at the site $\mathbf{x}_i$.

The second term in Eq. (4) describes the coupling between the spins and the phonons. The operators $S_i(\mathbf{x})$ are the spin-density operators associated with the impurity system. Specifically, if $\mathcal{S}_i^{(n)}$ is the ith Cartesian coordinate of the spin located at $\mathbf{x}_n$, then

$$S_i(\mathbf{x})=\sum_n\mathcal{S}_i^{(n)}\delta(\mathbf{x}-\mathbf{x}_n),$$

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and the $S_i(\mathbf{x})$ obey the commutation relations

$$[S_i(\mathbf{x}),S_j(\mathbf{x}')]=i\epsilon_{ijk}S_k(\mathbf{x})\delta(\mathbf{x}-\mathbf{x}')\,,$$

where ϵ_{ijk} is the Levi-Civita symbol.

The last term in Eq. (4) is the Zeeman energy of the spin system.

We obtain the following equations of motion for the various operators:

$$\frac{\partial\varphi}{\partial t}=\frac{\pi}{\rho}+\frac{\gamma}{c_s}\sum_{i=x,y,z}S_i\,, \tag{5a}$$

$$\frac{\partial\pi}{\partial t}=\boldsymbol{\nabla}\cdot(\alpha\boldsymbol{\nabla}\varphi)\,, \tag{5b}$$

$$\frac{\partial S_x}{dt}=\frac{\gamma}{c_s}\pi(S_z-S_y)-\omega_0 S_y\,, \tag{5c}$$

$$\frac{\partial S_y}{dt}=\frac{\gamma}{c_s}\pi(S_x-S_z)+\omega_0 S_x\,, \tag{5d}$$

$$\frac{\partial S_z}{dt}=\frac{\gamma}{c_s}\pi(S_y-S_z)\,. \tag{5e}$$

We now write $\rho=\rho_0+\Delta\rho(\mathbf{x})$ and $\alpha=\alpha_0+\Delta\alpha(\mathbf{x})$. We suppose that the effect of $\Delta\rho$ and $\Delta\alpha$ may be treated by a perturbation approach. In this spirit, we rewrite Eq. (5a) in the form

$$\frac{\partial\varphi}{\partial t}=\frac{\pi}{\rho_0}-\frac{\Delta\rho}{\rho_0}\frac{\partial\varphi}{\partial t}+\frac{\gamma}{c_s}\sum_i S_i. \tag{5a$'$}$$

We neglect the term proportional to $\gamma\Delta\rho$, and terms of order $(\Delta\rho)^2$ and higher.

Following Ref. 5, we derive a single equation for the phonon amplitude φ. We replace S_z by the combination $\langle S_z\rangle+\{S_z-\langle S_z\rangle\}$ in order to separate out the terms that describe the scattering of the mode by the fluctuations in S_z. We also retain only terms first order in $\Delta\rho$ and $\Delta\alpha$, and neglect the contributions proportional to $S_{x,y}\nabla^2\varphi$ and $S_{x,y}\pi$. These latter terms have been found to give contributions to the relaxation rate of the coupled mode that are small compared to that from the $S_z-\langle S_z\rangle$ term in the resonance region.[5,6] We then obtain an equation of the form

$$\mathcal{L}_0\varphi+\mathcal{L}_s\varphi=0\,, \tag{6}$$

where we have the operators

$$\mathcal{L}_0=\left(\frac{\partial^2}{\partial t^2}+\omega_0^2\right)\left(\frac{\partial^2}{\partial t^2}+c_s^2\nabla^2\right)-\frac{2\gamma^2\omega_0\alpha_0}{c_s^2}\langle S_z\rangle\nabla^2 \tag{6$'$}$$

and

$$\mathcal{L}_s=-2\frac{\gamma^2\omega_0\alpha_0}{c_s^2}\{S_z-\langle S_z\rangle\}\nabla^2$$
$$-\left(\omega_0^2+\frac{\partial^2}{\partial t^2}\right)\left(\frac{\boldsymbol{\nabla}(\Delta\alpha)\cdot\boldsymbol{\nabla}}{\rho_0}+\frac{\Delta\alpha}{\rho_0}\nabla^2-\frac{\Delta\rho}{\rho_0}\frac{\partial^2}{\partial t^2}\right). \tag{6$''$}$$

The quantity $c_s^2=\alpha_0/\rho_0$ is the velocity of sound.

We obtain the dispersion relation of the coupled modes by ignoring the term $\mathcal{L}_s\varphi$ and looking at the solutions of $\mathcal{L}_0\varphi=0$. The dispersion relation for our model obtained by this means is found from the secular equation

$$(\omega^2-\omega_0^2)(\omega^2-c_s^2k^2)+(2\gamma^2\omega_0\alpha_0k^2/c_s^2)n_s\langle\mathcal{S}_z\rangle=0\,. \tag{7}$$

We have replaced the mean value of the spin density $\langle S_z\rangle$ by $n_s\langle\mathcal{S}_z\rangle$, where n_s is the number of ions per unit volume, and $\langle\mathcal{S}_z\rangle$ is the mean value of the z component of spin for one ion. We write this equation in a form that facilitates comparison with earlier work.[5] It will be convenient to rewrite Eq. (7) in the form

$$c_s^2k^2/\omega^2=\eta(\omega)\,, \tag{8}$$

where[10]

$$\eta(\omega)=\left(1+\frac{2\gamma^2\omega_0\alpha_0 n_s\langle\mathcal{S}_z\rangle}{c_s^4(\omega_0^2-\Omega^2)}\right)^{-1}. \tag{8$'$}$$

Notice that with our sign convention, $\langle S_z\rangle<0$.

The dispersion relation of the coupled modes is sketched in Fig. 1. The quantity Δ is given by

$$\Delta=\left(n_s\frac{\gamma^2\omega_0\alpha_0}{2c_s^4}|\langle\mathcal{S}_z\rangle|\right)^{1/2}. \tag{8$''$}$$

We can compute the lifetime of the mode by treating the terms in $\mathcal{L}_s\varphi$ by a perturbation theoretic technique.

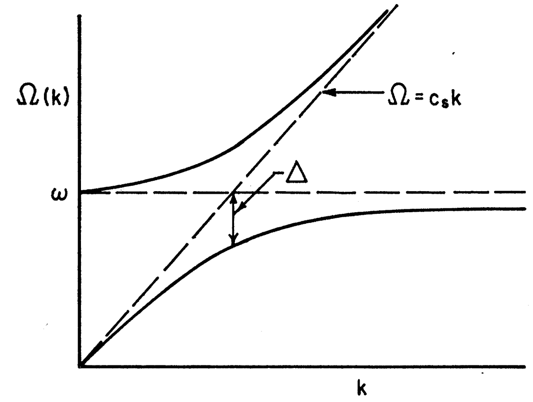

FIG. 1. Sketch of the dispersion relation of the coupled spin-phonon modes.

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[10] For the Hamiltonian of Eq. (1), notice that $\langle S_z\rangle$ is a negative quantity.

We shall follow the procedure employed previously.[5] We introduce a Green's function $G(\hat{r},t)$ that satisfies

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

and obeys the appropriate outgoing wave boundary condition. The amplitude of the scattered wave is then found from

$$\varphi_s(\mathbf{r},t)=\int G(\mathbf{r}-\mathbf{r}';t-t')\mathfrak{L}_s\varphi(\mathbf{r}',t')d^3r'\,dt'\,. \tag{9}$$

In Eq. (9), we suppose $\mathfrak{L}_s\varphi$ is nonzero only within a region of the crystal of finite spatial extent.

The details of the construction of the Green's function, and the evaluation of the integrals in Eq. (9) have been discussed elsewhere.[5] We should mention that one approximation we make is to ignore the time dependence of the fluctuations in S_z, i.e., we treat the scattering as if it were quasi-elastic. As we have argued previously,[5] this should be a reasonable approximation if Δ is large compared to the level width. This condition is a reasonable one if the spin-phonon coupling is large.

The amplitude φ_s of the scattered wave then assumes the form

$$\varphi_s=\frac{(V_s)^{1/2}}{4\pi^2}\,\frac{k_0V(k_0\hat{r}-\mathbf{k}_0)e^{-i\Omega_i(k_0)t}\varphi_0}{\Omega_i(k_0)v_i^G(k_0)[\Omega_1^2(k_0)-\Omega_2^2(k_0)]}\,\frac{e^{ik_0|\mathbf{r}|}}{|\mathbf{r}|}\,. \tag{10}$$

In Eq. (10), V_s is the volume of the region within which $\mathfrak{L}_s\varphi$ is nonzero, the incident wave is presumed to have wave vector $\mathbf{k}_0$ and frequency $\Omega_i(k_0)$. The index i is a branch index, with $i=1$ referring to the lower branch and $i=2$ to the upper branch of the dispersion curve, and $v_i^G(k_0)$ is the group velocity of the mode $(\mathbf{k}_0,i)$. Finally,

$$V(k_0\hat{r}-\mathbf{k}_0)=k_0^2(\hat{r}\cdot\hat{k}_0)\frac{\delta\alpha}{\rho_0}+\Omega_i^2(k_0)\frac{\delta\rho}{\rho_0}+\frac{2\gamma^2\omega_0\alpha_0}{c_s^2}\delta S_z\,. \tag{11}$$

In Eq. (11), $\delta\alpha$, $\delta\rho$, and δS_z are the Fourier transforms of the functions $\Delta\alpha(\mathbf{x})$, $\Delta\rho(\mathbf{x})$, and $\Delta S_z(\mathbf{x})$, respectively; the Fourier transforms are evaluated for the wave vector $k_0\hat{r}-\mathbf{k}_0$.

We then calculate the relaxation time of the mode, again following the earlier approach.[5] We do this by forming $|\varphi_s|^2$, and computing the energy flowing out of the volume V_s by integrating the appropriate quantity over solid angle. In this computation, one encounters the quantities $|\delta S_z(k_0\hat{r}-\mathbf{k}_0)|^2$, $|\delta\alpha(k_0\hat{r}-\mathbf{k}_0)|^2$, and $|\delta\rho(k_0\hat{r}-\mathbf{k}_0)|^2$ as well as cross terms between the three functions δS_z, $\delta\alpha$, and $\delta\rho$.

Consider $|\delta S_z(k_0\hat{r}-\mathbf{k}_0)|^2$. We have

$$\Delta S_z(\mathbf{x})=\sum_n(\mathcal{S}_z^{(n)}-\langle\mathcal{S}_z\rangle)\delta(\mathbf{x}-\mathbf{x}_n)$$
$$=\frac{1}{\sqrt{V_s}}\sum_{\mathbf{q}}\delta S_z(\mathbf{q})e^{+i\mathbf{q}\cdot\mathbf{x}}\,.$$

Thus

$$\delta S_z(\mathbf{q})=\frac{1}{\sqrt{V_s}}\sum_n(\mathcal{S}_z^{(n)}-\langle\mathcal{S}_z\rangle)e^{-i\mathbf{q}\cdot\mathbf{x}_n}\,.$$

We now form $|\delta S_z(\mathbf{q})|^2$ and average over the spatial positions of the impurities. For a two-level system, where $\langle S_z^2\rangle=S^2$, this gives

$$\langle|\delta S_z(\mathbf{q})|^2\rangle_{\mathrm{imp}}=n_s(\mathcal{S}^2-\langle\mathcal{S}_z\rangle^2)\quad\text{independent of }\mathbf{q}\,,$$

where $n_s=N_s/V_s$ is the number of spins/unit volume. It is this averaged expression for $|\delta S_z(q)|^2$ that we employ in the computation of the lifetime τ. One easily shows that the interference terms vanish:

$$\langle\delta S_z^*(\mathbf{q})\delta\alpha(\mathbf{q})\rangle_{\mathrm{imp}}=\langle\delta S_z^*(\mathbf{q})\delta\rho(\mathbf{q})\rangle_{\mathrm{imp}}\equiv0\,. \tag{12}$$

We write

$$\Delta\rho(\mathbf{x})=\Delta M\sum_n\delta(\mathbf{x}-\mathbf{x}_n)\,,$$

$$\Delta\alpha(\mathbf{x})=\Delta a\sum_n\delta(\mathbf{x}-\mathbf{x}_n)\,,$$

where ΔM is the change in mass of the impurity at $\mathbf{x}_n$, and Δa represents the change in the elastic properties of the crystal (the change in force constants) in the neighborhood of the impurity, for our simple model.

Then, following the discussion above, we find

$$\langle|\delta\rho(\mathbf{q})|^2\rangle_{\mathrm{imp}}=n_s(\Delta M)^2$$

and

$$\langle|\delta\alpha(\mathbf{q})|^2\rangle_{\mathrm{imp}}=n_s(\Delta a)^2\,.$$

The expression for the relaxation time then decomposes into two terms:

$$\frac{1}{\tau}=\frac{1}{\tau_{\mathrm{imp}}}+\frac{1}{\tau_{\mathrm{sf}}}\,,$$

where τ_{imp}^{-1} is the contribution from the scattering produced by the mass and force-constant changes, and τ_{sf}^{-1} is the contribution from the disorder in the z component of spin density. Equation (12) insures that there is no interference between these two contributions. Explicitly, one has

$$\frac{1}{\tau_{\mathrm{sf}}}=n_s\frac{\gamma^4\alpha_0^2\omega_0^2}{c_s^4\pi^3}\,\frac{k_0^6\{\mathcal{S}^2-\langle\mathcal{S}_z\rangle^2\}}{v_i^G(k_0)\Omega_i^2(k_0)[\Omega_1^2(k_0)-\Omega_2^2(k_0)]^2} \tag{13}$$

and

$$\frac{1}{\tau_{\mathrm{imp}}}=\frac{n_s}{4\pi^3\rho_0^2}\times\frac{k_0^2(\omega_0^2-\Omega_i^2(k_0))^2[\Omega_i^4(k_0)(\Delta M)^2+\frac{1}{3}k_0^4(\Delta a)^2]}{\Omega_i^2(k_0)v_i^G(k_0)[\Omega_1^2(k_0)-\Omega_2^2(k_0)]^2}\,. \tag{14}$$

The expression in Eq. (13) is the result for the scattering from longitudinal spin fluctuations described earlier,[5] except S^2 has been replaced by $S^2-\langle S_z\rangle^2$, as noted below,[11] and the host elastic constant α_0 appears explicitly. One sees that τ_{sf}^{-1} has a resonant form,[12] and is strong for incident frequencies within Δ of the Larmor frequency ω_0 of the spins. Also, when $c_sk_0 \ll \omega_0$, τ_{sf}^{-1} is proportional to k_0^4, while when $c_sk_0 \gg \omega_0$, τ_{sf}^{-1} approaches a constant value.

The defect scattering contribution to τ^{-1} is displayed in Eq. (14). There are several features of this result that should be discussed. First of all, the lack of a cross term involving the product $\Delta M \Delta a$ is a property of our particular model. The mass defect scattering has *s*-wave character, and the scattering from the changes in force constants (Δa) produces only *P*-wave scattering. Thus, there is no interference between the two for our model.

The expression for τ_{imp}^{-1} exhibits the well-known Ω^4 dependence on frequency, in the absence of spin-phonon coupling. Suppose we apply the expression to the lifetime of a mode on branch 1, the low frequency branch of the dispersion curve. As $\gamma \to 0$, $\Omega_2(k_0) \to \omega_0$ for $k_0 < \omega_0/c_s$, while $\Omega_1(k_0) \to c_sk_0$. Then

$$\lim_{\gamma \to 0} \frac{1}{\tau_{\mathrm{imp}}(k)} = \frac{n_sk_0^4}{4\pi^3\rho_0^2c_s^3}\left[(\Delta M)^2c_s^4 + \tfrac{1}{3}(\Delta a)^2\right].$$

The same limiting form applies to the lifetime of modes on the upper branch as $\gamma \to 0$, when $k_0 > \omega_0/c_s$.

It is interesting to note from Eq. (14) that the mass defect scattering is proportional to the fourth power of the *frequency* of the mode, while the scattering from force constant changes is proportional to the fourth power of the *wave vector*. This is reasonable from a physical point of view, since a change in mass affects the response of the crystal to a disturbance of finite frequency, but zero wave vector. A change in force constants, conversely, affects the response of the crystal to a disturbance of finite wave vector, even at zero frequency.

It is interesting to explore the form of τ_{imp}^{-1} as $k_0 \to \infty$ along branch 1, and also as $k_0 \to 0$ along branch 2. For the former case, after some algebra, one finds

$$\frac{1}{\tau_{\mathrm{imp}}} = \frac{n_s^2(\Delta a)^2k_0^5|\langle \mathcal{S}_z\rangle|\gamma^2\alpha_0}{2\pi^3\rho_0^2c_s^6\omega_0^3}.$$

There are three effects that combine to determine the behavior of τ_{imp}^{-1} in this region. First, the "phonon content" of the mode decreases, and this inhibits the ability of the wave to feel the effect of Δa or ΔM. At the same time, the wave vector of the mode is very much larger than for a pure phonon of the same frequency, and the density of final states increases. These latter two effects dominate the first.

As $k_0 \to 0$ along branch 2, one finds

$$\frac{1}{\tau_{\mathrm{imp}}} = \frac{n_s^2k_0\omega_0(\Delta M)^2}{4\pi^3\rho_0^2c_s^6}\alpha_0\gamma^2|\langle \mathcal{S}_z\rangle|.$$

In the small k_0 region, the mass defect scattering dominates, and $\tau_{\mathrm{imp}}^{-1} \to 0$ as $k_0 \to 0$.

III. THERMAL CONDUCTIVITY

In this section, we shall study the temperature dependence of the thermal conductivity for various values of the mean free time for impurity scattering, boundary scattering, and scattering from the spin fluctuations.

Before we present the results of our study, we rearrange the expressions for τ_{imp} and τ_{sf}. to place them in a form convenient for computational purposes. One of the difficulties with the general expressions given in the preceding section is that one requires the frequencies $\Omega_i(k_0)$ of the coupled modes explicitly in order to compute the relaxation rate. That is, one requires explicit solutions of the secular equation (7). While this presents no problem of principle, much more convenient expressions for τ_{imp} and τ_{sf} may be obtained. In effect, the relaxation rates may be expressed entirely in terms of the frequency $\Omega = \Omega_i(k_0)$ of the incident wave.

Consider, for example, the quantity

$$\Omega_2^2(k) - \Omega_1^2(k) = \left((\omega_0^2 - c_s^2k^2)^2 + \frac{8\gamma^2\omega_0\alpha_0k^2}{c_s^2}n_s|\langle \mathcal{S}_z\rangle|\right)^{1/2}.$$

By using Eq. (8), one may eliminate the wave vector $\mathbf{k}$ from the right-hand side of this equation, and express it entirely in terms of the frequency Ω. We find after a bit of algebra

$$\Omega_2^2(k) - \Omega_1^2(k) = |\omega_0^2 + [\eta(\Omega) - 2]\Omega^2|. \tag{15}$$

The explicit factors of k that appear in Eq. (13) and Eq. (14) may be eliminated by the use of Eq. (8). The group velocity v^G may be found by differentiating each side of Eq. (8) with respect to Ω. Rearranging a bit then gives

$$\frac{c_s^2}{v^Pv^G} = \eta + \tfrac{1}{2}\Omega\frac{\partial\eta}{\partial\Omega},$$

where $v^P = \Omega/k$ is the phase velocity of the wave. One then finds

$$v^G(\Omega) = \frac{c_s}{\sqrt{\eta}}\left|\frac{\Omega^2 - \omega_0^2}{(2-\eta)\Omega^2 - \omega_0^2}\right|. \tag{16}$$

The right-hand side of Eq. (16) is positive everywhere that $\eta > 0$, i.e., for all frequencies except in the forbidden region below ω_0. The use of these identities, along with Eq. (13) and Eq. (14) allow one to write the total

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[11] In Ref. 5, we displayed the result only for the high-temperature limit, where $\omega_0 \ll k_BT$. Then $\langle \mathcal{S}_z^2\rangle$ is small compared to $\mathcal{S}^2$, and one may ignore the factor of $\langle \mathcal{S}_z^2\rangle$.

[12] We have assumed that Δa and ΔM are associated with the same impurities that couple to the phonons to produce the mixed modes. However, if the defect scattering is produced by a second species, Eq. (14) still applies, provided the factor of n_s is replaced by the density of centers responsible for the mass and force constant changes.

relaxation rate in the form

$$\frac{1}{\tau}=\frac{1}{\tau_{\text{imp}}}+\frac{1}{\tau_{\text{sf}}}=\frac{n_s\Omega^4\eta^{7/2}}{4\pi^3c_s^7}\frac{[\{\omega_0^2-\Omega^2\}^2\{\frac{1}{3}(\Delta a/\rho_0)^2+c_s^4(\Delta M/\rho_0)^2\eta^2\}+4\gamma^4\omega_0^2\alpha_0^2(\mathcal{S}^2-\langle\mathcal{S}_z\rangle^2)c_s^{-4}]}{|\omega_0^2+(\eta-2)\Omega^2|\,|\Omega^2-\omega_0^2|}. \tag{17}$$

In an isotropic system, the thermal conductivity K is given by

$$K=\frac{1}{3V}\sum_{\mathbf{k}}\tau(\mathbf{k})v^G(\mathbf{k})^2C_k(T), \tag{18}$$

where $\tau(\mathbf{k})$ is the relaxation time of the mode of wave vector $\mathbf{k}$, and $C_k(T)$ is the specific heat of the mode. All of the quantities in Eq. (18) depend only on the frequency of the mode in our model. Thus, the sum over k can be converted to an integral over frequency. Note that the density of states associated with the coupled modes is

$$\rho(\omega)=\frac{Vk^2}{2\pi^2}\frac{dk}{d\omega}=\frac{V\eta\omega^2}{2\pi^2c_s^2v^G}.$$

Thus, one has

$$K=\int_0^\infty d\omega\,K(T,\omega), \tag{19}$$

where

$$K(T,\omega)=\frac{\eta\omega^2\tau(\omega)v^G(\omega)C(\omega,T)}{6\pi^2c_s^2}, \tag{19$'$}$$

and for $C(\omega,T)$ we use the boson result

$$C(\omega,T)=\frac{\hbar^2\omega^2}{k_BT^2}n(\omega)[1+n(\omega)],$$

where $n(\omega)=[\exp(\hbar\omega/k_BT)-1]^{-1}$.

Notice that all quantities in Eq. (19′) may be expressed in terms of $\eta(\omega)$, as we have seen.

We shall present numerical studies of the temperature of K, as well as the shape of the function $K(T,\omega)$, including the effect of boundary scattering as well as the impurity and spin fluctuation scattering described above. We note that Challis *et al.*[8] have pointed out that one may obtain direct information about the form of $K(T,\omega)$ by studying the magnetoresistance. In their case, the level responsible for the zero-field scattering is split off from the ground state by crystal-field effects. The resonant interaction of phonons with this pair of levels produces a minimum in the zero-field form of $K(T,\omega)$. If one now uses a magnetic field to sweep a Zeeman level associated with a second ion (say Fe^{2+}) in frequency, the change ΔK in the thermal conductivity is roughly $\Delta K=-K(T,\omega_0)\Delta\omega$, where $\Delta\omega$ is the width of the level associated with the second ion. This presumes the second ion couples strongly enough to the phonons to block the contribution to K of the modes in the band of width $\Delta\omega$ around ω_0. By these means, structure in the magnetic field dependence of K may be related to the frequency distribution of heat flux in zero field [i.e., the function $K(\omega,T)$] as well as the g factor of the second ion.

Since the impurity scattering present in the work on MgO [7,8] appears much stronger than that provided by the mass change ΔM alone, we have assumed all the scattering to be associated with changes in force constants near the impurity. We have thus taken ΔM equal to zero, and retain only the term in Δa. We introduce the parameters

$$A=(n_s/12\pi^3c_s^7)(\Delta a/\rho_0)^2$$

and

$$B=(n_s/\pi^3c_s^{11})\gamma^4\omega_0^2\alpha_0^2\mathcal{S}^2.$$

For some purposes, it is useful to note that A may be written in the form

$$A=(f_sV_c/12\pi^3c_s^3)(\Delta\alpha/\alpha_0)^2,$$

where V_c is the volume of the unit cell and $f_s=n_s/n$ is the concentration of spins. Then Eq. (17) becomes

$$\frac{1}{\tau}=\Omega^4\eta^{7/2}\frac{[(\omega_0^2-\Omega^2)^2A+(1-\langle\mathcal{S}_z\rangle^2/\mathcal{S}^2)B]}{|\omega_0^2+(\eta-2)\Omega^2|\,|\Omega^2-\omega_0^2|}. \tag{20}$$

Furthermore, let $\beta=2\gamma^2\omega_0\alpha_0n_s\mathcal{S}c_s^{-4}$. Then

$$\eta(\Omega)=\left(1+\frac{\beta|\langle\mathcal{S}_z\rangle|/\mathcal{S}}{\Omega^2-\omega_0^2}\right)^{-1}. \tag{21}$$

Notice that the parameters A, B, and β are all proportional to the concentration n_s of paramagnetic impurities.

To facilitate comparison with the recent analysis of the experimental data referred to earlier, we shall express all energies in temperature units (°K), and we let $\Omega=(k_BT/\hbar)x$ in Eqs. (20) and (21). In all of the discussion that follows, we have taken ω_0 to be 8°K, the value inferred by Challis *et al.* appropriate to the resonant scattering of phonons by Cr^{2+} in MgO, in zero magnetic field.

First consider the temperature dependence of the thermal conductivity. We first add in the effect of boundary scattering in a phenomenological fashion by adding to the inverse relaxation time of Eq. (20) a frequency-independent contribution τ_B^{-1}. We first examine the temperature dependence of K for various relative amounts of boundary scattering, impurity scattering, and spin fluctuation scattering. Then we present some curves of the variation of K with temperature, for various concentrations. We compare the last set of curves with the zero-field data of Challis *et al.*

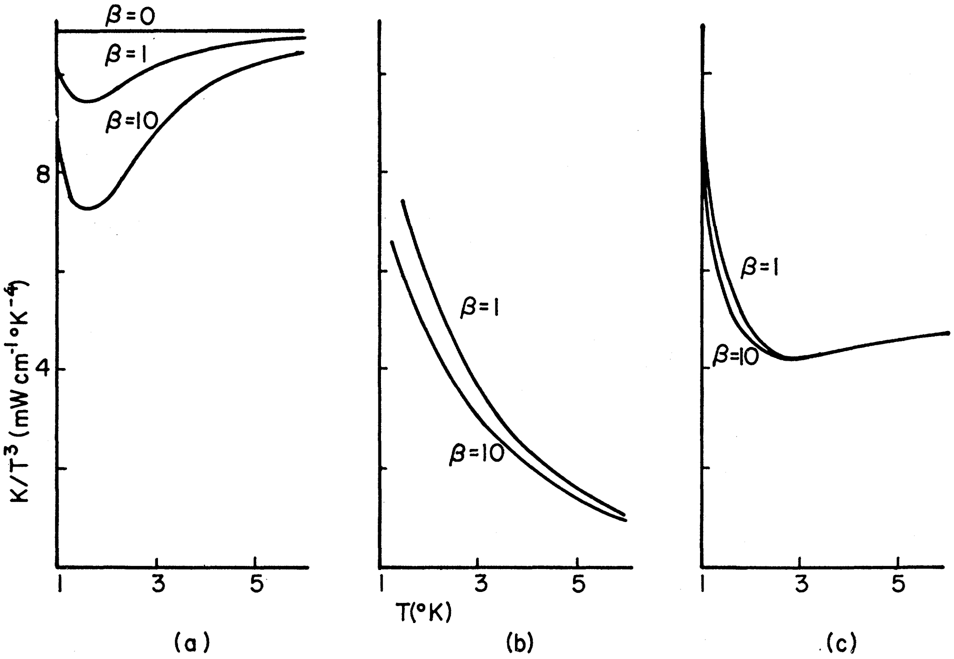

FIG. 2. Function K/T^3, plotted as a function of the temperature T for the case where (a) only boundary scattering is present, (b) boundary scattering and impurity scattering are both present, and (c) boundary scattering and scattering from longitudinal fluctuations in spin density are present. The values of the parameters employed in these calculations are discussed in the text.

In Fig. 2(a) we present the variation of the quantity K/T^3 with temperature, for various values of the spin-phonon coupling parameter β for the case where only boundary scattering is present. As Challis *et al.* point out,[7] the ratio K/T^3 can be thought of as being proportional to an average relaxation time $\bar{\tau}$. The dip in the K/T^3 apparent in Fig. 2(a) occurs when the peak of the blackbody specific-heat function

$$C(\omega,T)=(\hbar^2\omega^2/k_BT^2)n(\omega)[1+n(\omega)]$$

sweeps through the resonance frequency ω_0. In effect, the presence of the resonant level cuts a hole in the distribution of heat flux in frequency with a width the order of $[\beta\langle\mathrm{S}_z\rangle/\mathrm{S}]^{1/2}$.

In Fig. 2(b) we show the effect of introducing impurity scattering on the mean relaxation time K/T^3. We have chosen $\tau_B^{-1}=2.4\times10^{-6}$ sec^{-1}, the value employed in the earlier work.[7] The curves are calculated for the case where $A=200$°K^{-3}. For this value of A, τ_B^{-1} and contribution τ^{-1} from Eq. (20) with $B=0$ become equal when $\Omega\approx11$°K. Because of the strong frequency dependence of τ^{-1}, the impurity scattering completely dominates the boundary scattering for $\Omega>11$°K. One can see that K/T^3 is a strong monotonically decreasing function of temperature. At 2°K, for $\beta=10$°K^2, K/T^3 is depressed only by roughly 20% compared to its value with $A=0$ [Fig. 2(a)]. Larger values of A also produce values of K/T^3 that decrease sharply with T, as one would expect from physical considerations.

In Fig. 2(c), we illustrate the effect of scattering from the fluctuations in S_z on K/T^3. These curves are computed for $\beta=1$°K^2 and $\beta=10$°K^2. We have taken $A=0$ and $B=10^7$°K. For frequencies $\Omega\ll\omega_0$, τ_{sf}^{-1} is proportional to Ω^4, as in the case of impurity scattering. Thus, K/T^3 initially decreases, as in Fig. 2(b). When $\Omega\gg\omega_0$, an examination of Eq. (20) shows that τ_{sf}^{-1} becomes independent of Ω. Thus, when k_BT is large enough that most of the heat flux comes from phonons with $\Omega>\omega_0$, introduction of τ_{sf} is equivalent to introducing additional boundary scattering, as far as the dependence of K on T is concerned. As a consequence, K/T^3 becomes temperature-independent, with a value less than the value appropriate to boundary scattering alone. In Fig. 2(c), one sees a broad shallow minimum, with K/T^3 approaching the asymptotic value at the higher temperatures.

In Fig. 3(a), we reproduce some of the zero-field data of Ref. 7. Along side of this in Fig. 3(b) we present theoretical curves for different concentrations. The curves in Fig. 3(b) were calculated presuming that $A=15\beta$, and $B=10^7\beta$. The effect of changing n_s may then be introduced by changing β, since A, B, and β are all proportional to n_s. One can see that the theory reproduces the trends evident in the data. At the lowest concentrations, a broad plateau is present, and the plateau becomes difficult to pick out at the higher concentrations. The plateau has its origin in the scattering from fluctuations in S_z, as we saw in our discussion of the preceding paragraph, and the fall off is due to the presence of the impurity scattering.

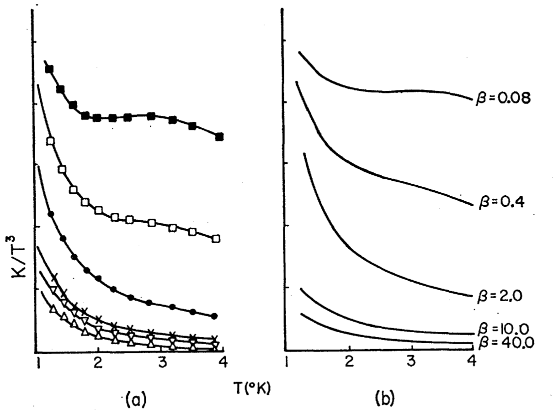

FIG. 3. (a) Experimental behavior of K/T^3 observed by Challis, McConachie, and Williams for Cr^{2+} doped MgO. (b) Some plots of K/T^3 for various ion concentrations obtained by supplementing the expression in Eq. (14) by a boundary scattering term.

There is one feature of the curves in Fig. 3 that is noteworthy. At small concentrations, the effect of the resonant scattering of the coupled modes from the spins is quite evident. At the higher concentrations, K/T^3 decreases smoothly and monotonically with T, very much as if only impurity scattering is present. We feel that it is difficult to see how this behavior can be realized within the framework of any theory that treats the resonant scattering as a single-ion phenomena, since such a model would produce a τ_I^{-1} and resonant relaxation rate which are both proportional to n_s, for the case where the impurity scattering is associated with the same ion as that responsible for the resonant scattering. The effect of the resonant scattering should then be evident even at high concentration. Intuitive arguments that suggest that in the coupled mode theory, the average effect of τ_{sf}^{-1} should vary with n_s less rapidly than τ_I^{-1} have been suggested elsewhere.[7]

The phenomenological analysis of Challis *et al.*,[7] while it involves expressions quite different than ours, also gives a good account of the data. If we identify their resonance term with our τ_{sf}^{-1}, then we also assign the various trends in the data to the same physical phenomena. We feel our work offers support for the analysis in Ref. 7, since our expressions follow from a simple microscopic model.

In Figs. 4–6, we plot the distribution in frequency of the heat flux for the cases described earlier. We write K/T^3 in the form

$$K/T^3=\int dx\, Q(x,T),$$

where x is a dimensionless measure of frequency, defined by the expression $\hbar\omega=xk_BT$. In these figures the function $Q(x,T)$ is plotted against the frequency ω, measured in °K. The quantity $Q(x,T)$ gives the distribution of the heat flux in frequency. Its relation to measurements of the magnetic field dependence of K was discussed above.

In Fig. 4, Q is plotted for the case where only boundary scattering is present, and $\beta=10$. In Fig. 5, the function Q is plotted when boundary scattering is present, and $A=200°\text{K}^{-3}$. This is the value of A employed in Fig. 2(b). The effect of the impurity scattering reduces the contribution to K of the phonons with frequency greater than ω_0. We note that these curves look very similar to the curves present in Fig. 11 of Ref. 7. In Fig. 6, we show Q when scattering from the spin fluctuations is present. We have taken $B=10^7$°K. Notice that as T increases, the contribution from the region below ω_0 is reduced, compared to its value in Fig. 4. As in the case of impurity scattering only (Fig. 5), the contribution from the region with frequency greater than ω_0 is sharply reduced. The peaks in the heat flux curves for $\Omega>\omega_0$ are sharp and well defined in Fig. 5. On Fig. 6, with only τ_B^{-1} and τ_{sf}^{-1} present, the peaks are much broader and flatter than those of Fig. 5.

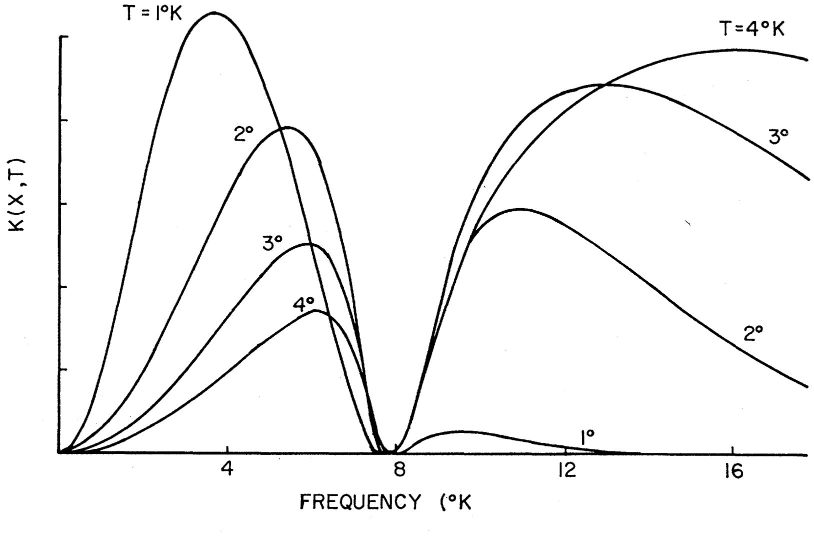

FIG. 4. Dependence of the distribution of heat flux $Q(x,T)$ on frequency for four temperatures. Only boundary scattering is present in this case.

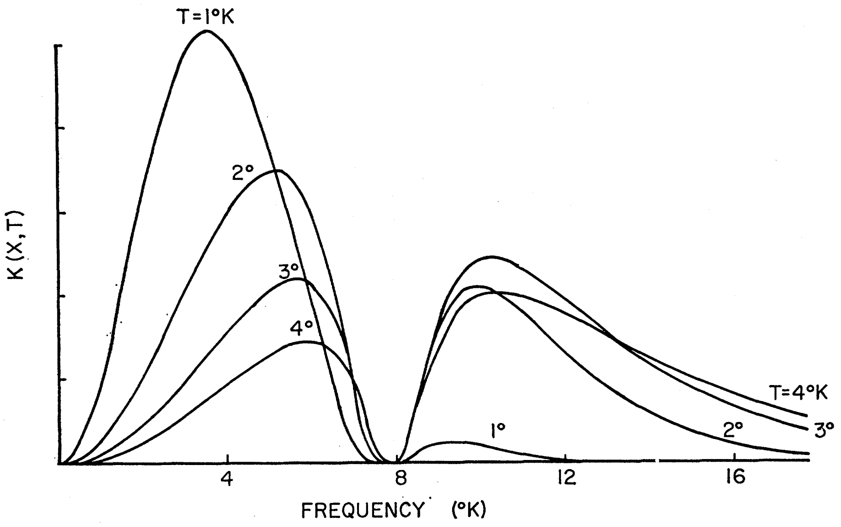

FIG. 5. Dependence of $Q(x,T)$ on frequency for four temperatures in the presence of boundary scattering, and scattering from force constant changes.

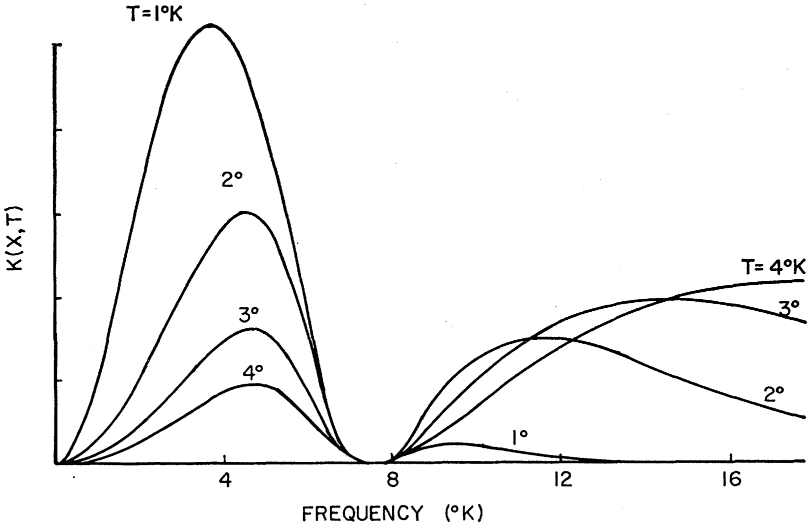

FIG. 6. Dependence of $Q(x,T)$ on frequency for four temperatures in the presence of boundary scattering, and scattering from fluctuations in S_z.

IV. SUMMARY

The results of Sec. III indicate that the coupled mode picture of excitations in paramagnetic spin system can give a good account of the data on MgO doped with Cr^{2+}. Our conclusions concerning the role of the various scattering mechanisms in producing features in the curves of K/T^3 versus T also agree with those of Challis *et al.*,[7] provided we identify the contribution to the scattering rate from longitudinal spin fluctuations with their resonance term. Of course, the details of our calculation are very different from the earlier phenomenological discussions.[7-9]

Some important questions concerning the validity of the coupled-mode picture remain open. As pointed out in earlier work,[7-9] the coupled mode picture is only strictly valid if the concentration of centers coupled to phonons in a resonant fashion is sufficiently high that a cube with a side one resonant phonon wavelength long contains many centers. For the case of Cr^{2+} in MgO, the wavelength of the resonant phonons is $\lambda = c_s/\nu$, where ν is the resonance frequency. If ω_0 is in the range of 8°K, then $\nu \cong 2\times10^{11}$ Hz, and $\lambda \cong 2\times10^{-6}$ cm, for $c_s = 5\times10^5$ cm/sec. The coupled-mode theory should thus apply only for concentrations greater than about 10^{17} spins/cm^3. In MgO, the number of lattice sites/unit volume is the order of 10^{23} cm^{-3}. Thus, so long as the concentration of paramagnetic centers exceeds the range of a few ppm, it appears that this criterion is met. The concentrations encountered in these experiments are all in the range of a few ppm or greater, so application of the theory at the low end of this range may be questionable.

A second assumption we have made is that the frequency Δ of Fig. 1 is larger compared to the intrinsic width of the resonant level. In this limit, one may treat the scattering from longitudinal fluctuations in S_z as a quasi-elastic scattering process. This assumption is difficult to assess at the present time. The large effect of small concentrations of the Cr^{2+} ion on the thermal conductivity of MgO, as well as ultrasonic attenuation studies[13] show that this ion is very strongly coupled to phonons. These data are thus consistent with a large value of Δ. To obtain information about the intrinsic width of the resonance level, one would need infrared studies of the region around 8°K, where resonant absorption of photons by the Cr^{2+} ion ought to occur.

Finally, as discussed earlier, the force constant changes associated with the impurity need to be very large to produce the values of A employed in this work. The same difficulty has been noted earlier.[7] Since one apparently needs to invoke the dynamic Jahn-Teller effect to explain the properties of Cr^{2+} in MgO,[14] this ion may scatter phonons very strongly.

We conclude by pointing out that studies of the dependence of the velocity of ultrasound on concentration of the Cr^{2+} and on temperature should contain useful information about the nature of these resonant centers. In the coupled mode theory, the observed velocity of sound $\tilde{c}_s$ at frequencies well below the resonance frequency ω_0 is related to the velocity of sound c_s in the undoped crystal in the following manner:

$$\frac{\tilde{c}_s}{c_s}=[\eta(0)]^{1/2}=\left(1-\frac{\beta|\langle \mathcal{S}_z\rangle|}{\mathcal{S}}\omega_0^{-2}\right)^{1/2}.$$

In our analysis, we have found that the experimental data are consistent with β in the range of 0.1 to $10°\mathrm{K}^2$, for the concentrations employed in the experimental work of Challis *et al.*[7] Particularly at the high end of the concentration range studied in this work, the coupled-mode theory predicts a substantial dependence of $\tilde{c}_s$ on concentration. Recall that β is proportional to the spin concentration n_s. Also, $\tilde{c}_s$ depends on temperature through the factor $\langle \mathcal{S}_z\rangle$ that appears in the last equation. A measurement of the temperature dependence of $\tilde{c}_s$ in a given sample should thus provide a measurement of $\langle \mathcal{S}_z\rangle$. In our computations, we have supposed that $|\langle \mathcal{S}_z\rangle/\mathcal{S}|=\tanh(\frac{1}{2}\hbar\omega_0/k_BT)$, the expression appropriate to a two-level system in thermal equilibrium. One should compute the value of $\langle \mathcal{S}_z\rangle$ in a self-consistent fashion, as Sears has discussed.[15] Corrections to the free-ion value of $\langle \mathcal{S}_z\rangle$ should become important when β/ω_0^2 becomes comparable to unity. An experimental study of the temperature dependence of the sound velocity in a sample containing a high concentration of Cr^{2+} should allow an assessment of the importance of corrections to $\langle \mathcal{S}_z\rangle$ from spin-phonon interactions. [For the Cr^{2+} ion in MgO, $\langle \mathcal{S}_z\rangle=\frac{1}{2}(N_+-N_-)$, where N_+ and N_- are the populations of the upper and lower resonanting levels, respectively. This quantity is not related to the magnetic susceptibility in any simple fashion.]

ACKNOWLEDGMENT

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[14] See the dlscussion and references in the paper by Marshall and Rampton, Ref. 13.

[15] V. F. Sears, Proc. Phys. Soc. (London) **84**, 951 (1964).