

## Virtual Phonon Effects in the Paramagnetic Resonance of MgO:Fe<sup>++</sup>†

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A change in the  $g$  value of the spin Hamiltonian of a single ion due to virtual emission of phonons and a line broadening due to the exchange of virtual phonons between spins are considered theoretically in the system MgO:Fe<sup>++</sup>. An experimental search for these effects has proved unsuccessful because of the excessive line broadening produced by the random strain fields of the available samples.

### INTRODUCTION

THE coupling of the magnetic moment of paramagnetic ions in crystals to the phonon field of the crystal has been extensively studied through its most prominent effect, the spin-lattice relaxation time of the paramagnetic ion. In analogy with the coupling of electrons to the electromagnetic field there will be other effects of this spin phonon coupling resulting from the virtual emission and absorption of phonons.

The virtual emission and absorption of phonons by an isolated spin gives an anomalous  $g$  value for the spin in close analogy to the anomalous moment of the free electron produced by the coupling to the electromagnetic field. This shift involves both a temperature-independent term and a temperature-dependent term. The temperature-dependent term could hopefully be observed experimentally.

The virtual exchange of phonons provides a mechanism of spin-spin coupling which, though weak, is of extremely long range and may contribute to resonance linewidths. This problem is treated here in more detail than in previous discussions,<sup>1-3</sup> with particular emphasis on dilute ion systems. Although specifically developed for the system MgO:Fe<sup>++</sup> which shows a particularly strong coupling, the theory is easily extended to other systems. The results of some unsuccessful experiments designed to observe these effects are also discussed.

### SPIN-LATTICE INTERACTION

Rather than develop the spin-strain or spin-phonon Hamiltonian from first principles in terms of product spin and orbital eigenfunctions, it is convenient to proceed directly to a spin Hamiltonian which is appropriate to Fe<sup>++</sup> in MgO and which operates on the  $S=1$  effective spin ground state manifold. The spin strain interaction can be written in terms of spin

raising and lowering operators as<sup>4</sup>

$$\begin{aligned} \mathcal{H} = & G_{11}Q_3(\mathbf{S} \cdot \mathbf{S} - 3S_z^2) \\ & + G_{11}Q_2\frac{1}{2}(S_+^2 + S_-^2) + G_{44}Q_4\frac{1}{2}i(S_-^2 - S_+^2) \\ & + G_{44}Q_5\frac{1}{2}[(S_+S_z + S_zS_+) + (S_-S_z + S_zS_-)] \\ & + G_{44}Q_6\frac{1}{2}i[(S_-S_z + S_zS_-) - (S_+S_z + S_zS_+)]. \quad (1) \end{aligned}$$

The  $Q$ 's are the noncubic symmetric normal modes of the 6 nearest neighbors of the paramagnetic ion as used by Van Vleck.<sup>5</sup> Using the interaction in this form amounts to neglecting the electrostatic interaction between all but nearest-neighbor ions. Watkins and Feher,<sup>4</sup> and Shiren,<sup>6</sup> using different techniques, have determined the constants of this Hamiltonian. The averages of their values in units of cm<sup>-1</sup> per unit strain are  $G_{11}=720$ ,  $G_{44}=460$ .

To convert this spin-strain interaction into a spin-lattice coupling, the  $Q$ 's or strains must be expressed in terms of phonons. The displacement from equilibrium of a nucleus embedded in a crystal lattice, caused by phonons, can be written

$$\mathbf{u}(\mathbf{r}) = (\hbar/2M)^{1/2} \sum_p \omega_p^{-1/2} \phi_p (a_p e^{i\mathbf{k}_p \cdot \mathbf{r}} + a_p^\dagger e^{-i\mathbf{k}_p \cdot \mathbf{r}}) \quad (2)$$

in terms of the normal modes  $p$ . Here  $\mathbf{r}$  is the position of a nucleus in the crystal lattice measured from some arbitrary point,  $M$  is the mass of the crystal, and  $\phi_p$  is the unit polarization vector for the mode  $p$ .  $a_p$  and  $a_p^\dagger$  are the annihilation and creation operators for the mode  $p$ .

To obtain magnitudes of the various effects without excessive computation the following simplifying assumptions are used. The Debye dispersion relation  $\omega_p = v|\mathbf{k}_p|$  is used freely and the optical modes of the crystal crudely included simply by appropriately choosing the Debye frequency to give the correct total number of modes. The longitudinal and transverse velocities of sound are assumed equal since detailed calculations have shown that no qualitatively new features are introduced by removing this assumption, and this velocity is taken to be isotropic. The substitutional iron ions are assumed not to alter the normal modes of the host crystal, and finally the long-wave-

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<sup>1</sup> Ko Sugihara, *J. Phys. Soc. Japan* **14**, 1231 (1959).

<sup>2</sup> R. H. Silsbee and D. H. McMahon, *Bull. Am. Phys. Soc.* **7**, 189 (1962).

<sup>3</sup> L. K. Aminov and B. I. Kochelaev, *Zh. Eksperim. i Teor. Fiz.* **42**, 1303 (1962) [English transl.: *Soviet Phys.—JETP* **15**, 903 (1962)].

<sup>4</sup> G. D. Watkins and E. Feher, *Bull. Am. Phys. Soc.* **7**, 29 (1962).

<sup>5</sup> J. H. Van Vleck, *J. Chem. Phys.* **7**, 72 (1939).

<sup>6</sup> N. S. Shiren, *Bull. Am. Phys. Soc.* **7**, 29 (1962).

length approximation is used to estimate the relative displacement of nuclei separated by a distance  $\delta\mathbf{r}$ ; i.e.,

$$\begin{aligned}\mathbf{u}(\mathbf{r}+\delta\mathbf{r})-\mathbf{u}(\mathbf{r}) &= [\delta\mathbf{r}\cdot\nabla\mathbf{u}(\mathbf{r})] \\ &= (\hbar/2M)^{1/2} \sum_p \omega_p^{-1/2} \phi_p(\mathbf{k}\cdot\delta\mathbf{r}) i (a_p e^{i\mathbf{k}\cdot\mathbf{r}} - a_p^\dagger e^{-i\mathbf{k}\cdot\mathbf{r}}).\end{aligned}$$

Although correct only for long wavelengths, this approximation should give a rough estimate of the coupling strength to all modes. For simplicity of notation, the mode index  $p$  is omitted from the wave vector  $\mathbf{k}$ , it being understood that for each  $p$  in the sum, the appropriate wave vector  $\mathbf{k}_p$  is to be used.

One can write the  $Q$ 's in terms of a normal coordinate expansion as

$$Q_j = \sum_p \left( \frac{\hbar\omega_p}{2Mv^2} \right)^{1/2} T_j^p i (a_p e^{i\mathbf{k}\cdot\mathbf{r}} - a_p^\dagger e^{-i\mathbf{k}\cdot\mathbf{r}}), \quad (3)$$

where  $j$  takes on values from 2 to 6, and where

$$\begin{aligned}T_2^p &= \frac{3}{4} (\phi_{px} K_{px} - \phi_{py} K_{py}), \\ T_3^p &= \frac{1}{4} (\phi_{px} K_{px} + \phi_{py} K_{py} - 2\phi_{pz} K_{pz}), \\ T_4^p &= (\phi_{py} K_{pz} + \phi_{pz} K_{py}), \\ T_5^p &= (\phi_{pz} K_{px} + \phi_{px} K_{pz}), \\ T_6^p &= (\phi_{py} K_{px} + \phi_{pz} K_{py}).\end{aligned}$$

The components of the unit polarization vector in the  $x, y, z$  direction are  $\phi_{px}, \phi_{py}, \phi_{pz}$ , respectively, and the components of the unit propagation vector in the  $x, y, z$  directions are  $K_x, K_y, K_z$ , respectively. Substitution of these expressions into Eq. (1) then gives the Hamiltonian describing the coupling of the spins to the lattice vibrations or phonon field.

#### SPIN-SELF-ENERGY TERMS

The shifts of the ground-state triplet level produced by the interaction Hamiltonian (1) are calculated in second order, assuming the system is in a magnetic field parallel to a crystal 100 axis giving a Zeeman splitting  $\hbar\omega_s = \hbar vk_s$ . Writing the phonon energy as  $\hbar\omega_p = \hbar vk$ , the energy shifts of the three Zeeman levels are, after summing over the three polarizations for each wave vector  $k$ ,

$$\begin{aligned}E_{\pm} &= \mp \frac{1}{2Mv^2} \sum_{\mathbf{k}} \left\{ \frac{(2n_k+1)k_s k}{k^2 - k_s^2} G_{44}^2 T_4^2 \right. \\ &\quad \left. + \frac{2(2n_k+1)k_s k}{k^2 - 4k_s^2} (G_{11}^2 T_2^2 + G_{44}^2 T_4^2) \right\}, \quad (4) \\ E_0 &= \frac{1}{2Mv^2} \sum_{\mathbf{k}} \frac{k_s^2}{k^2 - k_s^2} \{4G_{11}^2 T_2^2 + 3G_{44}^2 T_4^2\}.\end{aligned}$$

The  $T_i^2$ 's are sums over all polarizations, and averages over all equivalent directions of the vector  $\mathbf{k}$ ,

$$T_i^2 \equiv \langle \sum_{\text{pol}} (T_i^p)^2 \rangle_{\text{equiv } \mathbf{k}}. \quad (5)$$

Using the completeness relation for the polarization vectors,

$$\sum_{\text{pol}} \phi_{pi} \phi_{pj} = \delta_{ij} \quad i, j = x, y, z, \quad (6)$$

and assuming cubic symmetry, one has

$$T_2^2 = \frac{3}{8}, \quad T_3^2 = \frac{1}{8}, \quad T_4^2 = T_5^2 = T_6^2 = \frac{2}{3}.$$

In the evaluation of (4) shifts common to all three levels have been omitted since they do not alter the paramagnetic resonance spectrum.

These energy shifts are evaluated using the Debye approximation and the above identity. It is convenient also to define  $k_T = kT/\hbar v$  and to make the replacement

$$n_k = \frac{1}{e^{kT/\hbar v} - 1} \rightarrow \frac{k_T}{k} \frac{k_T^2}{k^2 + k_T^2},$$

which holds approximately for  $k \lesssim k_T$  and which allows the evaluation of (7) by contour integration. The result for  $k_s \ll k_T$  is

$$\begin{aligned}\sum_{\mathbf{k}} \frac{n_k k_s k}{k^2 - k_s^2} &\approx \frac{V}{4\pi^2} k_s k_T \int_{-\infty}^{\infty} \frac{k_T^2 k^2 dk}{(k^2 + k_T^2)(k^2 - k_s^2)} \\ &= (V/4\pi) k_s k_T^2 [1 + O(k_s^2/k_T^2)]. \quad (7)\end{aligned}$$

The other sums which occur are readily evaluated. If one neglects terms which are smaller in order of magnitude by the ratio of the Zeeman energy to the Debye energy, the results are

$$\begin{aligned}\sum_{\mathbf{k}} \frac{k_s^2}{k^2 - k_s^2} &\approx \frac{(6\pi^2)^{1/3} V k_s^2}{2\pi^2 a}, \\ \sum_{\mathbf{k}} \frac{k_s k}{k^2 - k_s^2} &\approx \frac{(6\pi^2)^{2/3} V k_s}{4\pi^2 a^2},\end{aligned}$$

where  $a$  is the cube root of the volume of the primitive cell. Using these sums, the energy shifts of the  $\Delta M = 1$  and  $\Delta M = 2$  transitions are

$$\begin{aligned}\delta E_{\Delta M=2} &= \frac{-(2G_{11}^2 T_2^2 + 3G_{44}^2 T_4^2)}{\rho v^2} \\ &\quad \times \left[ \frac{(6\pi^2)^{2/3} k_s}{4\pi^2 a^2} + \frac{k_s k_T^2}{2\pi} \right], \quad (8a)\end{aligned}$$

$$\begin{aligned}\delta E_{\Delta M=1} &= \frac{1}{2} \delta E_{\Delta M=2} \pm \frac{(4G_{11}^2 T_2^2 + 3G_{44}^2 T_4^2)}{\rho v^2} \\ &\quad \times \frac{(6\pi^2)^{1/3} k_s^2}{4\pi^2 a}, \quad (8b)\end{aligned}$$

where  $\rho$  is the crystal density.

For the system MgO:Fe<sup>2+</sup>, the fractional shift in field produced by these terms for the  $\Delta M = 1$  transition is

$$(\delta H/H) \sim 0.7 \times 10^{-2} + 1.3 \times 10^{-6} (T/4.2)^2 \pm 1.2 \times 10^{-6} (\nu),$$

where  $T$  is measured in degrees Kelvin and the microwave frequency  $\nu$  in gigacycles per second. The fractional shift in field for the  $\Delta M = 2$  transitions will be the same as above except that the last term is not present.

The leading term represents an appreciable negative  $g$  shift but unfortunately one cannot calculate the  $g$  values in absence of the spin-phonon coupling with sufficient precision to determine whether this shift is in fact observed. The observed  $g$  is lower than the simplest theory would suggest by about 4 times the prediction above but one can certainly not argue against various other possible sources of the discrepancy.<sup>7</sup> This shift is comparable in magnitude to that calculated for some rare-earth systems by Inoue.<sup>8</sup> The temperature-dependent term, though small, may be measurable since effects of thermal expansion would be expected to vary as a higher power of  $T$ . Finally, the last term represents an effective crystal field splitting proportional to the square of the Zeeman splitting which will not be observed since it is present only for the heavily strain-broadened  $\Delta M = 1$  line.

#### SPIN-SPIN COUPLING VIA PHONONS

For the virtual exchange of phonons, the intermediate state may again consist of the virtual emission or absorption of a phonon. In addition, one must distinguish between the time sequence of spin flips for an otherwise identical process. When one sums over all of the processes which connect a given initial and final state, the number of phonons per mode cancel leaving a temperature-independent coupling in contradiction to the results of Ref. 3. Writing down terms which conserve energy for the total process, the spin-spin interaction for spins separated by the distance  $R$  is

$$\begin{aligned} \mathcal{H} = & A(\mathbf{S} \cdot \mathbf{S}' - 3S_z S'_z)(\mathbf{S}' \cdot \mathbf{S}'' - 3S'_z S''_z) \\ & + \frac{1}{4}B[(S_{z-}S_{z-}' + S_{z-}S_{z-}'')(S_{z+}'S_{z+}'' + S_{z+}'S_{z+}''') \\ & + (S_{z+}S_{z+}' + S_{z+}S_{z+}'')(S_{z-}'S_{z-}'' + S_{z-}'S_{z-}''')] \\ & + \frac{1}{4}C[S_{z+}^2 S_{z-}'^2 + S_{z-}^2 S_{z+}'^2], \quad (9) \end{aligned}$$

where the primed quantities refer to the second spin, and where

$$\begin{aligned} A = & \frac{G_{11}^2}{Mv^2} \sum_k \sum_{\text{pol}} (T_3^p)^2 \cos(\mathbf{k} \cdot \mathbf{R}), \\ B = & \frac{G_{44}^2}{Mv^2} \sum_k \sum_{\text{pol}} \frac{k^2}{k^2 - k_s^2} [(T_5^p)^2 + (T_6^p)^2] \cos(\mathbf{k} \cdot \mathbf{R}), \quad (10) \\ C = & \frac{1}{Mv^2} \sum_k \sum_{\text{pol}} \frac{k^2}{k^2 - 4k_s^2} \\ & \times [G_{11}^2 (T_2^p)^2 + G_{44}^2 (T_4^p)^2] \cos(\mathbf{k} \cdot \mathbf{R}). \end{aligned}$$

It should be noted that a term in  $\sin(\mathbf{k} \cdot \mathbf{R})$  has been

<sup>7</sup> W. Low, *Paramagnetic Resonance in Solids* (Academic Press Inc., New York, 1960).

<sup>8</sup> M. Inoue, *Phys. Rev. Letters* **11**, 196 (1963).

omitted since, in the sum over modes, any terms odd in  $k$  will give canceling contributions.

The evaluation of these sums is discussed in the Appendix. Because the summand remains large throughout the Brillouin zone, the use of the Debye approximation gives spurious large oscillating terms [the terms  $\cos(\mathbf{k}_D \cdot \mathbf{R})$  and  $\sin(\mathbf{k}_D \cdot \mathbf{R})$  of Sugihara<sup>1</sup>] which result from the artificial cutoff of the integral at the Debye frequency. In the Appendix it is argued that there are no such oscillating terms for large  $R$  and a method for extracting the physically significant terms is outlined.

The results of the calculation outlined in the Appendix are

$$\begin{aligned} A = & \frac{-3 G_{11}^2 (3 \cos^2 \zeta - 1)}{64\pi \rho v^2 R^3}, \\ B = & \frac{G_{44}^2}{4\pi \rho v^2} \left\{ -(3 \cos^2 \zeta - 1) \left[ \frac{\cos k_s R}{R^3} + \frac{k_s \sin k_s R}{R^2} \right] \right. \\ & \left. + \frac{k_s^2 \cos k_s R}{R} (1 + \cos^2 \zeta) \right\}, \quad (11) \\ C = & \frac{(\frac{9}{16} G_{11}^2 + G_{44}^2)}{4\pi \rho v^2} \left\{ (3 \cos^2 \zeta - 1) \right. \\ & \times \left[ \frac{\cos 2k_s R}{R^3} + \frac{2k_s \sin 2k_s R}{R^2} \right] \\ & \left. + \frac{4k_s^2 \cos 2k_s R}{R} (1 - \cos^2 \zeta) \right\}. \end{aligned}$$

In these expressions  $\zeta$  is the angle between the vector  $R$  connecting the two spins and the applied field (assumed parallel to the [100] direction).

The most striking feature of these results is the long range,  $1/R$  dependence of the terms with  $(1 \pm \cos^2 \zeta)$  angular dependence. A finite phonon lifetime  $\tau$  will presumably limit the range by adding a factor  $\exp(-R/v\tau)$  but at low temperature the phonon mean-free paths are long and frequently limited by boundary scattering. Thus, although the magnitude of this coupling is small, because of its long range this term may give significant broadening of a resonance line.

Only the broadening of the  $\Delta M = 2$  transition is of experimental interest in the system MgO:Fe<sup>++</sup> because of the excessive strain broadening of the  $\Delta M = 1$  transition. This precludes the use of a rigorous calculation of moments from the interaction Hamiltonian given above. Further, the presence of residual strain fields can serve to make pairs of Fe<sup>++</sup> ions "unlike" in the sense of Van Vleck,<sup>9</sup> thus reducing the contributions of the  $B$  and  $C$  terms above to the line broadening. It should be noted that the  $A$  term is effective in broadening the  $\Delta M = 1$  transition but does not contribute to the breadth of the

<sup>9</sup> J. H. Van Vleck, *Phys. Rev.* **74**, 1168 (1948).

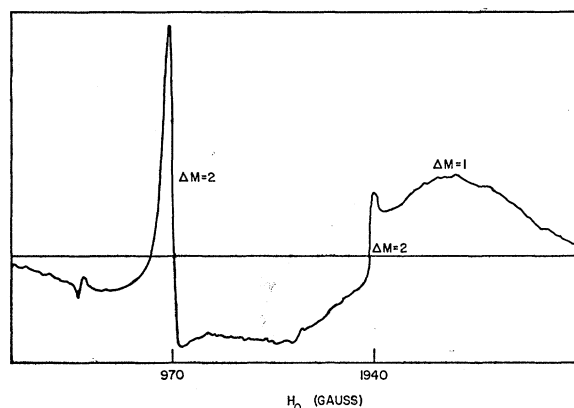


FIG. 1. Paramagnetic resonance spectrum of  $\text{Fe}^{++}$  in  $\text{MgO}$  at 9.5 Gc/sec. Magnetic field increases to the right.

$\Delta M=2$  transition as can be verified by a direct calculation of the energy levels for a spin pair. Despite these problems two observations are of interest concerning this phonon coupled interaction.

First, the terms varying as  $(1/R^3)$  may be compared with the strength of the normal dipolar coupling between  $\text{Fe}^{++}$  spins which has the same dependence on the separation of the spins for  $R \ll (1/k_s)$ . One has

$$\begin{aligned} \text{dipolar coupling} &\sim \frac{g^2 \beta^2}{R^3} \sim \frac{10^{-39}}{R^3} \text{ erg}, \\ \text{phonon coupling} &\sim \frac{G^2}{4\pi \rho v^2 R^3} \sim \frac{\frac{1}{2} \times 10^{-39}}{R^3} \text{ erg}. \end{aligned}$$

Thus, the two mechanisms are of comparable magnitude and one might hope to observe this breadth in systems of moderately high concentrations.

Second, the terms varying as  $1/R$ , because of their extreme range, may contribute to the observed line breadth. The  $C$  term, since it couples states which are made "unlike" only by second-order effects, will be the most important. The breadth due to this interaction may be estimated by summing the square of the interactions of one spin with all other spins in the crystal, distributed with a fractional density  $f$ . The result is

$$\langle \delta^2 \rangle \sim \frac{f}{a^3} \int_a^\infty C^2(R) d^3 R \sim \left( \frac{\frac{9}{16} G_{11}^2 + G_{44}^2}{\rho v^2} \right)^2 \frac{f k_s^4 L}{3a^3},$$

where  $L$  is the length of the sample. Using numerical values

$$\delta \sim 10^{10} (\omega/\omega_x)^2 (fL)^{1/2} \text{ rad/sec.}$$

This result predicts at X band, for a concentration of "like" spins of  $10^{-4}$ , and a crystal dimension of 1 mm, a breadth of about 1 G. This prediction is an upper limit of the broadening since the presence of strain fields will reduce the number of "like" spins and since the effective range  $L$  may be less than the macroscopic specimen size.

## EXPERIMENTAL RESULTS

The paramagnetic spectrum of  $\text{Fe}^{++}$  in  $\text{MgO}$  at 9.5 Gc/sec is illustrated in Fig. 1. The broad line at  $g=3.4$  is the normal  $\Delta M=1$  resonance. The  $\Delta M=2$  transition centered at  $g=3.4$  (1940 G) is a second-order process in which two rf quanta are absorbed by the spin system in rapid succession.<sup>10</sup> The intermediate state of perturbation theory almost conserves energy because of the presence of the center level of the ground state triplet. This near conservation of energy makes the process very likely. The other  $\Delta M=2$  resonance centered at  $g=6.8$  (970 G) is forbidden in a cubic field and occurs because strains cause small admixtures of the pure Zeeman eigenfunctions.<sup>7</sup> Because of this admixture, the rf field can induce a transition between the end levels of the triplet using only one photon. The presence of the  $\Delta M=2$  lines, showing only second-order strain broadening, suggests the possibility of observing the phonon coupled spin-spin interaction and the temperature dependence of the  $g$  factor deduced above.

The width of the derivative of the high-field edge of the  $\Delta M=2$  transition at  $g=6.8$  between the  $\frac{1}{4}$  and  $\frac{3}{4}$  height points was used as a sensitive measure of broadening. This parameter is designated by the symbol  $W_L$ . The dependence of  $W_L$  on spectrometer frequency  $\omega$  and on  $\text{Fe}^{++}$  concentration was used in attempt to observe broadening due to the exchange of virtual phonons.

$W_L$  versus  $\text{Fe}^{++}$  concentration measurements at 72 Gc/sec are illustrated in Fig. 2. This figure shows that the width parameter  $W_L$  is nearly independent of  $\text{Fe}^{++}$  concentration; the residual increase of  $W_L$  with concentration is very likely caused indirectly by an increase in the magnitude of the crystal strain with  $\text{Fe}^{++}$  concentration.

Measurements of  $W_L$  versus frequency give the results shown in Fig. 3. The increase in width at both high and low frequencies can be adequately explained in

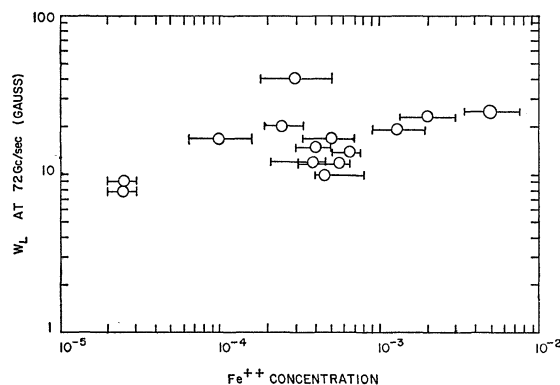


FIG. 2. Width  $W_L$  of the high-field edge of the derivative of the  $\Delta M=2$  transition at  $g=6.8$  as a function of  $\text{Fe}^{++}$  concentration. The data were taken at 72 Gc/sec.

<sup>10</sup> J. W. Orton, P. Auzins, and J. E. Wertz, Phys. Rev. Letters 4, 128 (1960).

terms of strain-width mechanisms.<sup>11</sup> At low frequencies, the strain-broadening mechanism for  $\Delta M = 2$  transitions is the second-order perturbation within the  $S = 1$  manifold

$$\delta E \sim \frac{(\text{strain})(\text{strain})}{(\text{Zeeman energy splitting})}.$$

At high frequencies the second-order strain perturbation through the next higher spin-orbit state,

$$\delta E \sim \frac{(\text{strain})(\text{Zeeman interaction})}{(\text{spin-orbit splitting})},$$

predominates. The cross-over point in width mechanisms is predicted to occur in the region of 10 Gc/sec.<sup>11</sup> Thus, although the observed widths are of the magnitude predicted as an upper bound, they appear adequately explained without appeal to the phonon coupled spin-spin interaction.

An attempt to observe the temperature-dependent  $g$  shift caused by the virtual emission of phonons was made at 24 Gc/sec using the  $\Delta M = 2$  transition at  $g = 3.4$ . This resonance had a width of 2 G in the sample used. The spectrometer was operated in the usual fashion, except that while slowly sweeping through the resonance, the temperature of the crystal was cycled in a square-wave fashion between 4 and 8°K at one cycle/min. Because the Boltzmann factor reduces the amplitude of the resonance signal at higher temperatures, one expects the temperature modulation to produce a modulation of the resonance signal at the same frequency. The maximum and minimum envelopes of the recorder trace give the line shape at the two temperatures. Thus, one has superimposed the resonance signal for two different temperatures and small deviations in  $g$  value are made visible. A picture of the resulting temperature modulated line is shown in Fig. 4.

The result of this experiment is that there is no temperature-dependent  $g$  shift greater than 0.05 G when

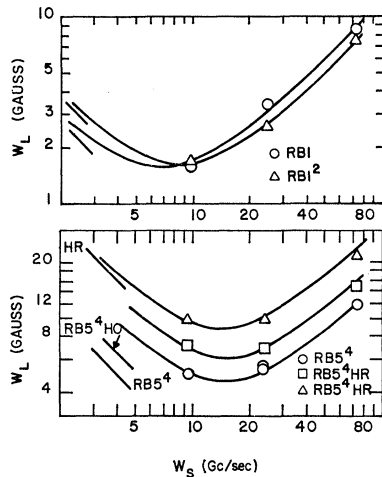
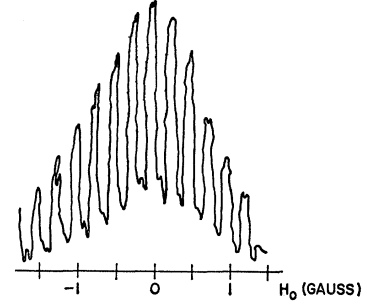


FIG. 3. Variation in the width parameter  $W_L$  as a function of spectrometer frequency.

<sup>11</sup> D. H. McMahon, Phys. Rev., 134, A128 (1964).

FIG. 4. Picture of the temperature modulated  $\Delta M = 2$  line centered at  $g = 3.4$ .



the temperature is varied between 4 and 8°K. The predicted shift under these circumstances is about 0.025 G. Thus, again the limitation of sensitivity resulting from the strain broadening of the lines prevented a satisfactory test of the theory. It would clearly be most desirable to have available crystals with an order of magnitude less strain broadening.

#### APPENDIX

This Appendix evaluates the sums (10). For each polarization branch of the acoustic modes, there is a sum of the form

$$g(\mathbf{R}) = \sum_{\mathbf{k}} F(\mathbf{k}) \cos(\mathbf{k} \cdot \mathbf{R}),$$

where the sum is to be taken over the first Brillouin zone. Contributions to the spin-spin coupling from the optical modes are not important and will be neglected. As noted in the body of the paper, since the summand remains large throughout the zone, the use of the Debye approximation gives terms in various powers of  $1/R$  which oscillate as  $\cos(\mathbf{k}_D \cdot \mathbf{R})$  or  $\sin(\mathbf{k}_D \cdot \mathbf{R})$ , which are not physically meaningful.

Suppose that the function  $F(\mathbf{k})$  had been evaluated without approximations. If one considers  $F(\mathbf{k})$  for  $\mathbf{k}$  not restricted to the first Brillouin zone, the correct  $F(\mathbf{k})$  is a periodic function of  $\mathbf{k}$  with the periods of the reciprocal lattice. It is not expected to show singular behavior at the zone boundary, although it is singular at points within the zone, namely at the origin through the angular dependence of the factors  $T^p$ , and on the surface  $\hbar\omega(\mathbf{k}) = \text{Zeeman energy}$ . Suppose  $F(\mathbf{k})$  is written as the sum of two terms,  $F_1(\mathbf{k}) + F_2(\mathbf{k})$ , where  $F_1(\mathbf{k})$  is periodic in  $\mathbf{k}$  and infinitely differentiable, and  $F_2(\mathbf{k})$  contains the singular behavior of  $F(\mathbf{k})$  and is small in the region on the zone boundary. That part of  $g(\mathbf{R})$  given by the Fourier transform of  $F_1(\mathbf{k})$  can be expressed, using integration by parts, as

$$\begin{aligned} g_1(\mathbf{R}) &= \int_{\text{B.Z.}} d^3k F_1(\mathbf{k}) \cos(\mathbf{k} \cdot \mathbf{R}), \\ &= \frac{\mathbf{R}}{R^2} \cdot \int d\mathbf{S}_k F_1(\mathbf{k}) \sin(\mathbf{k} \cdot \mathbf{R}) \\ &= \frac{\mathbf{R}}{R^2} \cdot \int_{\text{B.Z.}} \nabla F_1(\mathbf{k}) \sin(\mathbf{k} \cdot \mathbf{R}) d^3k, \end{aligned}$$

where the surface integral is taken over the surface of the Brillouin zone. Noting that on the surface of the zone  $\mathbf{k}$  may be written as

$$\mathbf{k} = \frac{1}{2}\mathbf{G} + \mathbf{k}_1,$$

where  $\mathbf{G}$  is the reciprocal lattice vector perpendicular to the zone face in question and  $\mathbf{k}_1$  is a vector lying in that face, and remembering that  $\mathbf{R}$  is a lattice vector,

$$\sin(\mathbf{k} \cdot \mathbf{R}) = \pm \sin(\mathbf{k}_1 \cdot \mathbf{R}).$$

The  $\pm$  sign depends on whether  $\frac{1}{2}\mathbf{G} \cdot \mathbf{R}$  is an even or odd multiple of  $\pi$ . Since  $F(\mathbf{k})$  is periodic in  $\mathbf{k}$  one can show that the integral over the pair of zone faces connected by  $\mathbf{G}$  is zero. For the two elements of area  $d\mathbf{S}_k$  connected by  $\mathbf{G}$ ,  $\sin(\mathbf{k} \cdot \mathbf{R})$  and  $F(\mathbf{k})$  will be the same, but the outward normals will be opposite and the contributions to the surface integral from the elements will cancel.

Similarly the surface integral vanishes in further iterations of the integration by parts. The  $n$ th iterate if  $n$  is even is

$$g_1(\mathbf{R}) = \pm \frac{1}{R^{2n}} \int_{\text{B.Z.}} (\mathbf{R} \cdot \nabla)^n F_1(\mathbf{k}) \cos(\mathbf{k} \cdot \mathbf{R}) d^3k.$$

Now suppose that  $F_1(\mathbf{k})$  is smooth in the sense that its  $n$ th gradient is of the order of  $F_1$  itself divided by the  $n$ th power of a typical  $k$  in the Brillouin zone, i.e., suppose that the typical scale of the variation of  $F_1$  is of the order of the dimension of the zone. Postulating that for all  $n$

$$|\nabla^n F_1(\mathbf{k})| < (ca)^n F_{1 \max}, \quad (13)$$

where  $a$  is the lattice constant,  $c$  a number of the order of unity and  $F_{1 \max}$  the maximum value of  $|F_1(\mathbf{k})|$ , one has the inequality

$$|g_1(\mathbf{R})| < \left(\frac{ca}{R}\right)^n F_{1 \max} \int_{\text{B.Z.}} d^3k.$$

Since  $n$  may be made arbitrarily large,  $g_1(\mathbf{R})$  must then be zero for all  $R > ca$  and the contribution of the term  $F_1(\mathbf{k})$  to the coupling must be of short range. It is then the portions of  $F$  which are singular which contribute to the long-range part of the coupling  $g(\mathbf{R})$ . It should be emphasized that the postulate (13) is an assumption which seems plausible but has not been justified. Finally, since  $F_2(\mathbf{k})$  was chosen not only to contain the singular portion of  $F(\mathbf{k})$ , but also to be small near the zone boundary, it is permissible to evaluate the transform of  $F_2(\mathbf{k})$  in the Debye approximation.

Now the summands of Eqs. (10) do not satisfy the periodicity requirement on  $F(\mathbf{k})$  because of the various approximations used in their derivation, but they do give, to a good approximation, the singular behavior of

the correct  $F(\mathbf{k})$ . Hence the summands will be broken up into one term which is infinitely differentiable within the zone and into two singular terms which are small at the zone surface. The first is a poor approximation to the  $F_1(\mathbf{k})$  above because it is not periodic in  $\mathbf{k}$ . Recognizing that had this term been derived without approximations, it would not have contributed to any long-range (powers of  $1/R$ ) interaction, it is discarded. The remaining contributions, which are reasonable approximations, are then evaluated in the Debye model.

Summing first over the polarization vectors, using the completeness relation (6), the sums become

$$A = \frac{G_{11}^2}{16Mv^2} \sum_{\mathbf{k}} (1 + 3K_z^2) \cos(\mathbf{k} \cdot \mathbf{R}), \quad (14a)$$

$$B = \frac{G_{44}^2}{Mv^2} \sum_{\mathbf{k}} (1 + K_z^2) \frac{k^2}{k^2 - k_s^2} \cos(\mathbf{k} \cdot \mathbf{R}), \quad (14b)$$

$$C = \frac{(9G_{11}^2 + 16G_{44}^2)}{16Mv^2} \sum_{\mathbf{k}} (1 - K_z^2) \frac{k^2}{k^2 - 4k_s^2} \cos(\mathbf{k} \cdot \mathbf{R}). \quad (14c)$$

As an example of the separation of the singular behavior, the sum (14b) may be written

$$B = \frac{G_{44}^2}{Mv^2} \sum_{\mathbf{k}} \cos(\mathbf{k} \cdot \mathbf{R}) \left\{ \left(1 + \frac{k_z^2}{\alpha^2 + k^2}\right) + \frac{\alpha^2 k_z^2}{k^2(\alpha^2 + k^2)} + \left(1 + \frac{k_z^2}{k^2}\right) \left(\frac{k_s^2}{k^2 - k_s^2}\right) \right\},$$

where the constant  $\alpha$  is chosen to be small compared with the reciprocal lattice constant. The first term is now dropped, as outlined above, and the remaining two terms integrated in spherical coordinates with the direction of  $R$  as polar axis. The integrals converge well for large  $k$  and the integral over  $k$  is extended to infinity since the contributions from outside the Debye sphere are small. The results are given as Eqs. (11) of the main text.

Note that the results given in the text are independent of the constant  $\alpha$  used to effect the separation of the summand; this result involves the neglect of terms of order  $e^{-\alpha R}$ , and hence is valid only if  $\alpha R \gg 1$ . Similarly, the term  $F_1(\mathbf{k})$  will have an  $n$ th derivative of order  $\alpha^n F$  and so the range of  $g_1(\mathbf{R})$  will be of order  $1/\alpha$  and can be neglected only for  $R \gg 1/\alpha$ . On the other hand, the extension of the integral over  $k$  to infinity is justified only if  $\alpha$  is small compared with the reciprocal lattice constant or if  $\alpha a \ll 1$ . Hence, the whole procedure outlined here is appropriate only for  $R \gg a$  and the results (11) represent an approximation valid only for large values of the separation between spins.