

## Spin-Phonon Interaction in Paramagnetic Crystals\*

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(Received November 16, 1959)

A general theory of the spin-phonon interaction, which is applicable to any iron group spin not in an  $S$  state, is developed. The theory employs a perturbation treatment that has a more direct physical meaning than techniques previously used and that leads to more accurate results. These results are presented in the form of an equivalent spin-phonon interaction Hamiltonian involving sums over products of spin operators and phonon creation-annihilation operators. The interaction between any two spin levels can then be calculated by using the spin wave functions associated with the usual "spin Hamiltonian." It is shown that, owing to the dominant role played by the quadratic term in the above interaction, odd half-integer iron group spins ( $S > \frac{1}{2}$ ) obey quadrupole selection rules. A formula is derived for order-of-magnitude calculations of the interaction strength. It is shown that acoustic experiments should provide the ideal way to test this theory in detail, and two methods of checking the quadrupole rule are proposed. Experimental results are reported on observed acoustic saturation in MgO doped with  $\text{Cr}^{+++}$ , on the absence of saturation between low-field Kramers doublets in ruby, and an apparent saturation effect in  $F$ -center quartz.

### 1. INTRODUCTION

THE spin-phonon interaction plays the central role in the interpretation of paramagnetic relaxation phenomena.<sup>1-3</sup> According to current hypothesis, the process occurs through modulation of the crystalline electric field.<sup>1,2</sup> Our first objective here is to present a theory of this interaction, which, although it introduces no new physical assumptions, has the following advantages: (a) It utilizes a perturbation procedure which we believe has more direct physical meaning than methods employed in the past and which produces more accurate results. (b) It is more general than previous theories, being applicable to any non- $S$ -state ion in the iron group. (c) As a result of this generality,

it is possible to prove that iron group spins ( $S > \frac{1}{2}$ ) obey quadrupole selection rules. The second objective shall be to analyze the methods best suited to test the theory in detail. This will start with a calculation of the transition probabilities for direct and Raman interactions between a spin and a thermal phonon field, and between a spin and a monochromatic phonon wave. Then it will be demonstrated that, although relaxation experiments are generally inadequate for any proposed test, acoustic experiments should provide the desired information. Our final objective shall be to describe the results of an acoustical investigation of a preliminary nature, which appears to give some partial confirmation of the theory.

### 2. EQUIVALENT SPIN-PHONON INTERACTION HAMILTONIAN

#### A. Total Hamiltonian of Spin Plus Phonon Field

The model we shall use is illustrated in Fig. 1, which shows a paramagnetic ion surrounded by a few nearest neighbors that produce an electrostatic field at the ion site. In the unperturbed system, the nearest neighbors are assumed stationary. If we allow these neighbors to vibrate (since they are part of the lattice), the crystalline electric field will be modulated, will perturb the orbital motion of the paramagnetic electrons, and will induce spin transitions by means of spin-orbit interaction. The following assumptions are made:

(a) All effects of spin-spin interaction except for energy level broadening are neglected. Presumably in a sufficiently dilute crystal these effects will be small.

(b) The effects of local lattice distortion produced by the presence of the paramagnetic ion are omitted. In the case of  $F$ -center electrons, which have considerable charge density at the nearest neighbor sites, this distortion is not negligible, and is, further, a function of electronic excited state. It is thus of enormous importance in the interaction of  $F$  centers with phonons. In our case, it is assumed that, since the paramagnetic

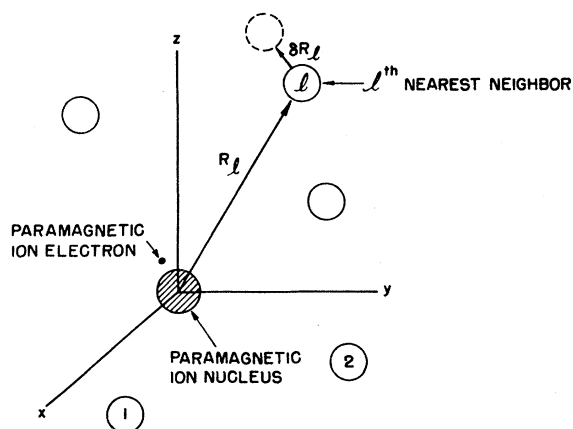


FIG. 1. Paramagnetic ion in crystal electric field of nearest neighbors.

\* This work was supported in part by the U. S. Army (Signal Corps), the U. S. Air Force (Office of Scientific Research, Air Research and Development Command), and the U. S. Navy (Office of Naval Research).

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<sup>1</sup> J. H. Van Vleck, *Phys. Rev.* **57**, 426 (1940).

<sup>2</sup> R. Kronig, *Physica* **6**, 33 (1939).

<sup>3</sup> C. J. Gorter, *Paramagnetic Relaxation* (Elsevier Publishing Company, Inc., Amsterdam, 1947).

electrons are closely associated with the paramagnetic nucleus, the corresponding effect should be small.<sup>4</sup>

(c) The crystalline field potential is assumed to be smaller than the free ion potential, but greater than the spin-orbit energy. Thus the theory applies to iron group ions but not to rare earth ions.

(d) The theory does not apply to ions for which the ground state is  $L=0$ .

With these assumptions in mind, we can write the total Hamiltonian in the form

$$\mathcal{H} = \mathcal{H}_L + \mathcal{H}_0 + V + 2\beta \mathbf{S} \cdot \mathbf{H} + \lambda \mathbf{L} \cdot \mathbf{S} + \beta \mathbf{L} \cdot \mathbf{H}. \quad (1)$$

In this equation,  $\beta$  is the Bohr magneton,  $\lambda$  is the spin-orbit coupling parameter,  $S$  and  $L$  are the spin and orbital angular moments of the paramagnetic ion,  $H$  is the external dc magnetic field,  $V$  is the energy of the ion due to the crystalline electric field,  $\mathcal{H}_0$  is the energy of the free ion, and  $\mathcal{H}_L$  represents the lattice energy. The lattice Hamiltonian can be written<sup>5</sup>

$$\mathcal{H}_L = \sum_p \hbar \omega_p (a_p^\dagger a_p + \frac{1}{2}), \quad (2)$$

where  $a_p^\dagger$ ,  $a_p$  are the phonon creation and annihilation operators. They have the properties that

$$a_p^\dagger |\cdots n_p \cdots\rangle = (n_p + 1)^{\frac{1}{2}} |\cdots n_p + 1 \cdots\rangle, \quad (3)$$

$$a_p |\cdots n_p \cdots\rangle = (n_p)^{\frac{1}{2}} |\cdots n_p - 1 \cdots\rangle. \quad (4)$$

The  $p$  index represents the phonon mode and branch number. The mode-branch frequency is designated by  $\omega_p$ . If we designate the equilibrium position of an atom in the lattice by  $\mathbf{r}$  and the displacement of this atom from equilibrium by  $u_{r\alpha}$  ( $\alpha = x, y, \text{ or } z$ ), then  $u_{r\alpha}$  can be expanded in normal lattice modes as<sup>5</sup>

$$u_{r\alpha} = \left(\frac{2\hbar}{M}\right)^{\frac{1}{2}} \sum_p \frac{1}{(\omega_p)^{\frac{1}{2}}} \phi_{p\alpha} (a_p + a_p^\dagger) \cos(\mathbf{k}_p \cdot \mathbf{r} + \Delta_p), \quad (5)$$

where  $M$  is the crystal mass,  $\phi_{p\alpha}$  is the  $\alpha$ th component of the unit polarization vector for mode-branch  $p$ ,  $\mathbf{k}_p$  is the propagation vector for mode-branch  $p$ , and  $\Delta_p$  is an arbitrary phase factor. In what follows, we shall assume for simplicity that the lattice is dispersionless and isotropic, with the result that all phonons have the same velocity,  $v$ , and thus we can describe the density of states by the Debye formula

$$\begin{aligned} \rho(\nu) &= \frac{dn}{d\nu} = \frac{12\pi V \nu^2}{v^3} \quad \text{if } \nu \leq \left(\frac{3N}{4\pi V}\right)^{\frac{1}{3}} v \\ &= 0 \quad \text{if } \nu > \left(\frac{3N}{4\pi V}\right)^{\frac{1}{3}} v. \end{aligned} \quad (6)$$

We shall also make use of the fact that the average number of phonons in mode  $p$  when the crystal is in

<sup>4</sup> J. Korringa, Department of Physics and Astronomy, Ohio State University, Columbus, Ohio (unpublished).

<sup>5</sup> P. G. Klemens, *Solid-State Physics* (Academic Press, Inc., New York, 1958), Vol. 7, p. 1.

thermal equilibrium at temperature  $T$  is given by

$$\bar{n}_p = (e^{\hbar \omega_p / kT} - 1)^{-1}. \quad (7)$$

In order to show the interaction between the spin and lattice explicitly, we expand the crystal field potential,  $V$ , in a power series in the normal displacements ( $Q_f$ ) of the ion nearest neighbors.<sup>6</sup>

$$V = V_0 + \sum_f \frac{\partial V}{\partial Q_f} Q_f + \frac{1}{2} \sum_{ff'} \frac{\partial^2 V}{\partial Q_f \partial Q_{f'}} Q_f Q_{f'} + \cdots, \quad (8)$$

where the  $Q_f$ 's can be related to the ordinary displacements of the neighbors ( $\delta R_{l\alpha}$ ) by

$$Q_f = \sum_{l\alpha} B_{fl\alpha} \delta R_{l\alpha}. \quad (9)$$

The  $\delta R_{l\alpha}$  can in turn be expanded in normal lattice modes by means of Eq. (5). In doing this, we make the approximation that the phonon wavelength is considerably greater than the dimensions of the cluster of nearest neighbors, so that  $\mathbf{k}_p \cdot \mathbf{r} \ll 1$  (assuming, for simplicity, that the spin nucleus is located at the origin). Because only nearest neighbor displacements relative to the spin nucleus will be effective in modulating the crystalline field, Eq. (5) reduces to

$$\delta R_{l\alpha} = \left(\frac{2\hbar}{M}\right)^{\frac{1}{2}} \sum_p \frac{(\omega_p)^{\frac{1}{2}}}{v} \phi_{p\alpha} (a_p + a_p^\dagger) \mathbf{K}_p \cdot \mathbf{R}_l \sin \Delta_k, \quad (10)$$

where  $\mathbf{K}_p$  is the unit vector in the  $\mathbf{k}_p$  direction, and we have used  $|\mathbf{k}_p| = \omega_p/v$ . Substituting Eqs. (10) and (9) into Eq. (8), we find

$$V = V_0 + \sum_{fp} V^f A^{fp} \mathcal{O}_p + \sum_{ff'pq} V^{ff'} A^{fp} A^{f'q} \mathcal{O}_p \mathcal{O}_q + \cdots, \quad (11)$$

where

$$V^f = \frac{\partial V}{\partial Q_f}; \quad V^{ff'} = \frac{1}{2} \frac{\partial^2 V}{\partial Q_f \partial Q_{f'}}; \quad \mathcal{O}_p = a_p + a_p^\dagger, \quad (12)$$

$$A^{fp} = \left(\frac{2\hbar \omega_p}{M v^2}\right)^{\frac{1}{2}} \sin \Delta_p \sum_{l\alpha} B_{fl\alpha} \mathbf{K}_p \cdot \mathbf{R}_l.$$

Utilizing Eqs. (1), (2), and (11), we find for the total Hamiltonian:

$$\begin{aligned} \mathcal{H} = & \sum_p \hbar \omega_p (a_p^\dagger a_p + \frac{1}{2}) + \mathcal{H}_0 + V_0 \\ & + 2\beta \mathbf{S} \cdot \mathbf{H} + \lambda \mathbf{L} \cdot \mathbf{S} + \beta \mathbf{L} \cdot \mathbf{H} + \sum_{fp} V^f A^{fp} \mathcal{O}_p \\ & + \sum_{ff'pq} V^{ff'} A^{fp} A^{f'q} \mathcal{O}_p \mathcal{O}_q. \end{aligned} \quad (13)$$

We now divide  $\mathcal{H}$  into  $\mathcal{H}_{\text{lattice}}$ ,  $\mathcal{H}_{\text{spin}}$  and  $\mathcal{H}_{\text{interaction}}$ . Examining the terms, we find that  $\sum_p \hbar \omega_p (a_p^\dagger a_p + \frac{1}{2})$  has only lattice coordinates;  $[H_0 + V_0 + 2\beta \mathbf{S} \cdot \mathbf{H} + \lambda \mathbf{L} \cdot \mathbf{S} + \beta \mathbf{L} \cdot \mathbf{H}]$  involves only paramagnetic electron co-

<sup>6</sup> J. H. Van Vleck, J. Chem. Phys. 7, 72 (1939).

ordinates; and  $\sum_{fp} V^f A^{fp} \mathcal{O}_p + \sum_{ff'pq} V^{ff'} A^{fp} A^{f'q} \mathcal{O}_p \mathcal{O}_q$  involves mixed coordinates. The term in electron coordinates is precisely the one that gives rise to the spin Hamiltonian that describes the energy levels that are observed in the laboratory. In relaxation experiments, we are interested in phonon-induced transitions between these pairs of spin levels. Hence, it seems reasonable to set

$$\mathcal{H}_{\text{lattice}} = \sum_p \hbar \omega_p (a_p^\dagger a_p + \frac{1}{2}), \quad (14)$$

$$\mathcal{H}_{\text{spin}} = \mathcal{H}_0 + V_0 + 2\beta \mathbf{S} \cdot \mathbf{H} + \lambda \mathbf{L} \cdot \mathbf{S} + \beta \mathbf{L} \cdot \mathbf{H}, \quad (15)$$

and to consider

$$\mathcal{H}_{\text{interaction}} = \sum_{fp} V^f A^{fp} \mathcal{O}_p + \sum_{ff'pq} V^{ff'} A^{fp} A^{f'q} \mathcal{O}_p \mathcal{O}_q, \quad (16)$$

as inducing energy-conserving exchanges of quanta between  $\mathcal{H}_{\text{spin}}$  and  $\mathcal{H}_{\text{lattice}}$ . The calculation would involve diagonalizing  $\mathcal{H}_{\text{spin}}$  to some appropriate order (the second order would suffice—this would produce the spin Hamiltonian), finding its energy levels  $E_k$  and corresponding state vectors  $\psi_k$ , and computing the appropriate matrix elements of  $\mathcal{H}_{\text{interaction}}$  between simultaneous eigenstates of  $\mathcal{H}_{\text{spin}}$  and  $\mathcal{H}_{\text{lattice}}$ .

In reference 1, this is not done; instead, the Hamiltonian is broken into

$$\mathcal{H}_{\text{lattice}} = \sum_p \hbar \omega_p (a_p^\dagger a_p + \frac{1}{2}), \quad (17)$$

$$\mathcal{H}_{\text{spin}}' = \mathcal{H}_0 + V_0 + 2\beta \mathbf{S} \cdot \mathbf{H}, \quad (18)$$

and

$$\mathcal{H}_{\text{interaction}}' = \lambda \mathbf{L} \cdot \mathbf{S} + \beta \mathbf{L} \cdot \mathbf{H} + \sum_{fp} V^f A^{fp} \mathcal{O}_p + \sum_{ff'pq} V^{ff'} A^{fp} A^{f'q} \mathcal{O}_p \mathcal{O}_q + \dots \quad (19)$$

is considering as inducing quantum exchange between

$\mathcal{H}_{\text{spin}}$  and  $\mathcal{H}_{\text{lattice}}$ . The  $\mathcal{H}_{\text{spin}}$  is now only part of what we mean physically when we talk about the spin system, since the large  $\lambda \mathbf{L} \cdot \mathbf{S} + \beta \mathbf{L} \cdot \mathbf{H}$  term has been left out. It might be claimed that this procedure should lead to the same result as ours, but in a higher order of perturbation theory. This is true, but the procedure would have to be different from that used in reference 1. We examine this question in the next section.

## B. Comparison of Alternative Perturbation Procedures

For our purposes, it is convenient to use a formalism employed by Karplus and Schwinger<sup>7</sup> which is entirely equivalent to the "variation of constants" procedure. We start with the time-dependent equation

$$\mathcal{H}(t)\psi = (\hbar/i)(\partial\psi/\partial t), \quad (20)$$

which has the formal solution

$$\psi(t) = \exp[(it/\hbar)\mathcal{H}(t)]\psi(0). \quad (21)$$

Let  $\mathcal{H} = \mathcal{H}^0 + \mathcal{H}'$  (where  $\mathcal{H}'$  and  $\mathcal{H}^0$  are independent of  $t$ , and  $\mathcal{H}' \ll \mathcal{H}^0$ ), and let  $\chi_n$  and  $E_n$  be the eigensolutions of  $\mathcal{H}^0$ . Suppose that the system is in an arbitrary state,  $|\alpha\rangle$ , at  $t=0$ , and that we wish to know the probability amplitude of some other state,  $|\beta\rangle$ , orthogonal to  $|\alpha\rangle$ , at time  $t$ . This is evidently

$$A_{\alpha \rightarrow \beta}(t) = \langle \beta | \exp[(it/\hbar)(\mathcal{H}^0 + \mathcal{H}')] | \alpha \rangle. \quad (22)$$

In the simple case where  $|\alpha\rangle$  is an eigenstate of  $\mathcal{H}^0 + \mathcal{H}'$ , we find that no transitions can occur, since  $A=0$  for  $|\alpha\rangle \neq |\beta\rangle$ . If  $|\alpha\rangle$  is not an eigenstate of  $\mathcal{H}^0 + \mathcal{H}'$ , transitions will take place. In particular, if  $|\alpha\rangle$  happens to be an eigenstate of  $\mathcal{H}^0$ , say  $\chi_a$ , and  $|\beta\rangle = \chi_b$ , then by carrying out the expansion of the exponential operator, it can be shown that Eq. (22) yields the same result as the variation of constants method, that is,

$$A_{a \rightarrow b}(t) = \left[ \langle \chi_b | \mathcal{H}' | \chi_a \rangle + \sum_n \frac{\langle \chi_b | \mathcal{H}' | \chi_n \rangle \langle \chi_n | \mathcal{H}' | \chi_a \rangle}{E_n - E_a} + \dots \right] \exp[(it/\hbar)E_b] \left[ \frac{\exp[(it/\hbar)(E_a - E_b)] - 1}{E_a - E_b} \right]. \quad (23)$$

[If  $|\alpha\rangle$  and  $|\beta\rangle$  are not eigenstates of  $\mathcal{H}^0 + \mathcal{H}'$ , or of  $\mathcal{H}^0$ , but are related to the  $\chi_a$ 's by a unitary transformation, the expansion can be carried out as shown in Eqs. (29)–(34).] We now apply this formalism to our problem. Define

$$\mathcal{H}^u = \mathcal{H}_{\text{lattice}} + \mathcal{H}_0 + V_0 + 2\beta \mathbf{S} \cdot \mathbf{H}, \quad (24a)$$

$$P = \lambda \mathbf{L} \cdot \mathbf{S} + \beta \mathbf{L} \cdot \mathbf{H}, \quad (24b)$$

$$V = \sum_{fp} V^f A^{fp} \mathcal{O}_p + \sum_{ff'pq} V^{ff'} A^{fp} A^{f'q} \mathcal{O}_p \mathcal{O}_q. \quad (24c)$$

In our procedure we use

$$\mathcal{H}^0 = \mathcal{H}^u + P; \quad \mathcal{H}' = V, \quad (25)$$

with  $\psi_k$ ,  $E_k$  as eigensolutions of  $\mathcal{H}^u + P$ , whereas in reference 1,

$$\mathcal{H}^0 = \mathcal{H}^u; \quad \mathcal{H}' = P + V, \quad (26)$$

with  $\phi_k$ ,  $E_k$  as eigensolutions of  $\mathcal{H}^u$ . Substituting Eqs. (25) and (26) separately into Eqs. (22) and (23), we find,

<sup>7</sup> R. Karplus and J. Schwinger, Phys. Rev. **73**, 1024 (1948).

by using our representation,

$$A_{k \rightarrow k'}(t) = \langle \psi_{k'} | \exp[(it/\hbar)(\mathcal{H}^u + P + V)] | \psi_k \rangle = \left( \langle \psi_{k'} | V | \psi_k \rangle + \sum_{k^2} \frac{\langle \psi_{k'} | V | \psi_{k^2} \rangle \langle \psi_{k^2} | V | \psi_k \rangle}{\mathcal{E}_{k^2} - \mathcal{E}_k} + \dots \right) \times \exp[(it/\hbar)\mathcal{E}_{k'}] \left( \frac{\exp[(it/\hbar)(\mathcal{E}_k - \mathcal{E}_{k'})] - 1}{\mathcal{E}_k - \mathcal{E}_{k'}} \right). \quad (27)$$

If the representation of reference 1 is used, then

$$A_{n \rightarrow n'}(t) = \langle \phi_{n'} | \exp[(it/\hbar)(\mathcal{H}^u + P + V)] | \phi_n \rangle = \left( \langle \phi_{n'} | P + V | \phi_n \rangle + \sum_{n^2} \frac{\langle \phi_{n'} | P + V | \phi_{n^2} \rangle \langle \phi_{n^2} | P + V | \phi_n \rangle}{E_{n^2} - E_n} + \dots \right) \times \exp[(it/\hbar)E_{n'}] \left( \frac{\exp[(it/\hbar)(E_n - E_{n'})] - 1}{E_n - E_{n'}} \right). \quad (28)$$

It is clear that, as it stands, Eq. (28) cannot be directly interpreted physically since it does not deal with the transitions between the spin energy levels observed in paramagnetic resonance experiments. Furthermore, there is no simple way in which the expansion in Eq. (28) can be used to obtain transition probability amplitudes for transitions between the true paramagnetic spin states,  $\psi_k$  and  $\psi_{k'}$ . Of course, it is possible to obtain an expansion for  $A_{k \rightarrow k'}$  purely in terms of  $\phi_n$ 's and  $E_n$ 's, and we proceed to do this.

The unitary transformation connecting  $\psi_k$  and  $\phi_n$  is

$$\psi_k = \sum_n S_{kn} \phi_n. \quad (29)$$

Substituting Eq. (29) in Eq. (27), we find

$$\langle \psi_{k'} | \exp[(it/\hbar)(\mathcal{H}^u + P + V)] | \psi_k \rangle = \langle \phi_{k'} | S^{-1} \exp[(it/\hbar)(\mathcal{H}^u + P + V)] S | \phi_k \rangle, \quad (30)$$

$$A_{k \rightarrow k'}(t) = [\langle \phi_{k'} | S^{-1}(P + V)S | \phi_k \rangle + \langle \phi_{k'} | S^{-1}\mathcal{H}^u S - \mathcal{H}^u | \phi_k \rangle + \sum \dots]$$

We thus see that, although Eq. (30) expresses the fact that there is a unitary transformation connecting the two methods, there is no simple way of getting from the expansion of Eq. (28) to that of Eq. (34) if we look at the perturbation expansions themselves. If one chooses to work in terms of the eigenstates  $\phi_n$  of the system  $\mathcal{H}^u$ , as in reference 1, but wishes to obtain probabilities for transitions between the true "spin" eigenstates, one is forced to use the more complicated expansion, Eq. (34). We prefer to employ Eq. (27), and we claim that Eq. (28) cannot be used rigorously to calculate spin transitions. Equation (28) will, however, give the proper order of magnitude for the results.

We would like to point out here that the fundamental difficulty in the method of reference 1 does not lie in the choice of unperturbed system [i.e., the  $\mathcal{H}^0$  in Eq. (22)] but rather in the wrong choice of initial and final states ( $|\alpha\rangle$  and  $|\beta\rangle$ ). What one chooses as the unperturbed system is a matter of convenience (such

where  $S$  is defined from the  $S_{kn}$  by

$$\langle \phi_k | S | \phi_n \rangle = S_{kn}. \quad (31)$$

(Note that for purposes of identifying the subscripts, we can label  $\psi_k$  and  $\mathcal{E}_k$  in such a manner that they evolve continuously out of  $\phi_k$  and  $E_k$ , as  $P$  increases from 0.) We can obtain a perturbation expansion for the right-hand side of Eq. (30) as follows:

$$\begin{aligned} S^{-1} \exp[(it/\hbar)(\mathcal{H}^u + P + V)] S \\ = \exp[(it/\hbar)S^{-1}(\mathcal{H}^u + P + V)S] \\ = \exp[(it/\hbar)(\mathcal{H}^u + G)], \end{aligned} \quad (32)$$

where

$$G = S^{-1}(P + V)S + S^{-1}\mathcal{H}^u S - \mathcal{H}^u. \quad (33)$$

Hence we find

$$\times \exp[(it/\hbar)E_{k'}] \left( \frac{\exp[(it/\hbar)(E_k - E_{k'})] - 1}{E_k - E_{k'}} \right). \quad (34)$$

as simplicity, rapidity of convergence, and so on), but the selection of initial and final states must be dictated by the physical nature of the problem. This becomes clear from Eq. (22) when we note that  $A_{\alpha \rightarrow \beta}(t)$  is independent of the way in which  $\mathcal{H}$  is broken up into  $\mathcal{H}^0$  and  $\mathcal{H}'$ , but depends greatly on the choice of  $|\alpha\rangle$  and  $|\beta\rangle$ . For example, Eqs. (27) and (34) represent the same choice of initial and final states and are therefore physically equal; however, the unperturbed system ( $\mathcal{H}^0 = \mathcal{H}^u$ ) chosen in Eq. (34) is less convenient than that ( $\mathcal{H}^0 = \mathcal{H}^u + P$ ) employed in Eq. (27). On the other hand, Eq. (28) is incorrect because it deals with initial and final states that are not physically meaningful.

### C. Derivation of Equivalent Spin-Phonon-Interaction Hamiltonian

We now carry out the procedure outlined at the end of Sec. 2-A. For the preliminary diagonalization of

$\mathcal{H}_{\text{spin}}$  [see Eq. (15)] we introduce the following notation:

(a)  $\mathcal{H}_{\text{spin}} = \mathcal{H}^A + P.$

(b)  $P = \lambda \mathbf{L} \cdot \mathbf{S} + \beta \mathbf{L} \cdot \mathbf{H}.$

(c)  $\mathcal{H}^A = \mathcal{H}_0 + V_0 + 2\beta \mathbf{S} \cdot \mathbf{H}.$

(d)  $\phi_m, \phi_n, \dots$  denote any eigenstates of  $\mathcal{H}^A$ . The symbol  $\phi_m$ , for example, represents  $|m, s\rangle$  where  $m$  denotes the electronic eigenstate of  $\mathcal{H}_0$ , and  $s$  denotes the spin eigenstate of  $2\beta \mathbf{H} \cdot \mathbf{S}$ ;  $s$  is a mixture of  $m_s$  states.

(e)  $\phi_a, \phi_b, \dots$  denote only those eigenstates of  $\mathcal{H}^A$  associated with the ground electronic state.

(f)  $\phi_\alpha, \phi_\beta, \dots$  denote only those eigenstates of  $\mathcal{H}^A$  associated with the excited electronic states.

(g)  $\psi_k$  is one of the exact eigenstates of  $\mathcal{H}^A + P$ . It is a mixture of the  $\phi_m$ 's.

The Schrödinger equation for the unperturbed problem is

$$\mathcal{H}^A \phi_m = E_m \phi_m, \quad (35)$$

whereas for the perturbed problem,

$$\mathcal{H} \psi_k = (\mathcal{H}^A + P) \psi_k = E_k \psi_k. \quad (36)$$

Let us focus our attention on the unperturbed ground states,  $\phi_a, \phi_b, \dots$ , which describe the pure spin-Zeeman levels. When  $P$  is introduced, these states are mixed among themselves, and also a small amount of the  $\phi_\alpha$ 's is mixed in. Thus we have

$$\psi_k = \sum_n C_{kn} \phi_n. \quad (37)$$

Because  $\langle a | P | b \rangle = 0$  as the result of quenching of orbital angular momentum in the ground state,  $P$  affects the  $\phi_a$ 's only through its interaction with the  $\phi_\alpha$ 's. Applying the method of Löwdin,<sup>8</sup> we find that the new ground-state levels can be obtained by solving

$$\sum_a C_{ka} [U_{ba} - \delta_{ba} E_k] = 0, \quad (38)$$

and the wave functions can be obtained from

$$\psi_k = \sum_a C_{ka} \phi_a + \sum_\alpha \left[ \sum_a C_{ka} \left( \frac{U_{a\alpha}}{E_k - E_\alpha} \right) \right] \phi_\alpha, \quad (39)$$

where

$$U_{ma} = \mathcal{H}_{ma}^A + P_{ma} + \sum_\alpha \frac{{}'P_{ma} {}'P_{\alpha a}}{E_k - E_\alpha} + \sum_{\alpha\beta} \frac{{}'P_{ma} {}'P_{\alpha\beta} {}'P_{\beta a}}{(E_k - E_\alpha)(E_k - E_\beta)} + \dots \quad (40)$$

(The prime on the  $P$ 's means off-diagonal elements only, and we have  $E_\alpha = \mathcal{H}_{\alpha\alpha}^A$ .) Thus, in this method, the problem is restricted to the ground states, the influence of the excited states being brought in by the "effective"

Hamiltonian,  $U_{ba}$ . When carried out to second order,  $U_{ba}$  is the spin Hamiltonian.

We next write  $\psi_k$  to second order, including normalization

$$\psi_k = \sum_a C_{ka} \left[ \left( 1 - \frac{1}{2} \sum_{bb'} C_{kb'} {}^*C_{kb'} \frac{P_{ba} P_{\alpha b'}}{E_k - E_\alpha} \right) \phi_a + \sum_\alpha \frac{P_{a\alpha} \phi_\alpha}{E_k - E_\alpha} + \sum_{\alpha\beta} \frac{{}'P_{\alpha\beta} P_{\beta a} \phi_\alpha}{(E_k - E_\alpha)(E_k - E_\beta)} \right]. \quad (41)$$

These, then, are the eigenstates of  $\mathcal{H}_{\text{spin}}$  [Eq. (15)]. If we call  $\gamma_L$  the eigenstates of  $\mathcal{H}_{\text{lattice}}$ , the total system eigenstate is  $\Psi_{kL} = \psi_k \gamma_L$ . We can now compute the matrix elements in Eq. (27) to obtain effective interaction Hamiltonians for direct and Raman interactions.

#### Direct Interaction

In a direct interaction, we require only one phonon operator. The relevant matrix element is

$$\begin{aligned} \langle k' L' | V | k L \rangle &= \sum_{a a'} C_{k' a'} {}^*C_{ka} \left[ \sum_\alpha \left( \frac{V_{L' L a' \alpha} P_{\alpha a}}{E_k - E_\alpha} + \frac{P_{a' \alpha} V_{L' L a \alpha}}{E_{k'} - E_\alpha} \right) \right. \\ &\quad + \sum_{\alpha\beta} \left( \frac{P_{a' \alpha} V_{L' L a \beta} P_{\beta a}}{(E_{k'} - E_\alpha)(E_k - E_\beta)} + \frac{V_{L' L a' \alpha} {}'P_{\alpha\beta} P_{\beta a}}{(E_k - E_\alpha)(E_k - E_\beta)} \right. \\ &\quad \left. \left. + \frac{P_{a' \alpha} {}'P_{\alpha\beta} V_{L' L a \alpha}}{(E_{k'} - E_\alpha)(E_k - E_\beta)} \right) \right], \quad (42) \end{aligned}$$

where we have used  $P_{\alpha\beta} {}^* = P_{\beta\alpha}$ . The term in  $V_{L' L a' \alpha}$  and the terms that result from normalization vanish because of the orthogonality condition

$$\sum_{a a'} C_{k' a'} {}^*C_{ka} = \delta_{k' k}, \quad (43)$$

and because  $V$  is diagonal in  $a$ .

We can evaluate Eq. (42) by using the definitions in Eq. (34) and the one-phonon part of Eq. (24c). In the calculation, we make use of the commutativity of  $L_i$  and  $S_i$ , and employ the fact<sup>9</sup> that  $\langle n' | L_i | n \rangle = -\langle n | L_i | n' \rangle$ . In Eq. (42), in the first summation in braces, it is necessary to take into account small differences in denominators, but not in the second summation. (Note that a "Van Vleck cancellation"<sup>10</sup> takes place in the first summation, thus greatly reducing its order of magnitude.) The final result is presented in terms of the following equivalent Hamiltonian involving spin and phonon operators:

$$\mathcal{H}_{\text{direct}} = \sum_{p, f, i > j} A^{fp} (a_p^\dagger + a_p) \{ 2\beta \lambda \mathcal{E}_i^f [g_{kk'} S_i + g(S_i \mathcal{E} - \mathcal{E} S_i)] + 2\beta \lambda \mathcal{E}_{ij}^f (S_i H_j + S_j H_i) + \lambda^2 \mathcal{E}_{ij}^f (S_i S_j + S_j S_i) \}, \quad (44)$$

<sup>8</sup> P. O. Löwdin, J. Chem. Phys. **19**, 1396 (1951).

<sup>9</sup> M. H. L. Pryce, Proc. Phys. Soc. (London) **A63**, 25 (1950).

<sup>10</sup> E. Abrahams, Phys. Rev. **107**, 491 (1957).

where

$$\begin{aligned}\mathcal{L}_i^f &= \sum_{n \neq 0} \frac{\langle 0 | V^f | n \rangle \langle n | L_i | 0 \rangle}{(E_n - E_0)^2}, \\ \mathcal{L}_{ij}^f &= \sum_{n, n' \neq 0} \frac{(\langle 0 | L_i | n \rangle \langle n | L_j | n' \rangle \langle n' | V^f | 0 \rangle + \langle 0 | L_i V^f L_j | 0 \rangle + \langle 0 | V^f L_i L_j | 0 \rangle)}{(E_n - E_0)(E_{n'} - E_0)}, \\ g_{kk'} &= (E_k - E_{k'}) / \beta H; \quad \langle s' | \mathcal{E} | s \rangle = \delta_{ss'} E_{s'}, \\ g &= \text{electron } g \text{ factor.}\end{aligned}\quad (45)$$

In Eq. (44), it is to be understood that  $\mathcal{H}_{\text{direct}}$  gives the phonon-spin interaction between two energy eigenstates  $k, k'$  of the spin Hamiltonian [ $U_{ba}$  in Eq. (40) carried to the second order], and that the correct eigenfunctions to use are the spin Hamiltonian eigenfunctions:

$$\psi_k = \sum_a C_{ka} \phi_a = \sum_s C_{ks} \phi_s, \quad (46)$$

where  $\phi_s$  is an eigenstate of  $2\beta \mathbf{H} \cdot \mathbf{S}$ . Note that we have thus reduced the calculation of the interaction matrix from a problem involving the complicated wave functions of Eq. (41) to one using the simple wave functions of Eq. (46). The reason is, of course, that the effect of the excited electronic states has been taken out of the wave functions of Eq. (41) and compressed into the  $\mathcal{L}$  tensors in Eq. (44). This is precisely the type of notation that is used to display the spin Hamiltonian, and, in fact, Eq. (44) is simply the phonon-spin Hamiltonian for direct interactions.

If this calculation is performed by the method of reference 1, the terms in  $\mathcal{L}_{ij}^f$  in Eq. (44) are the same, but the quantity in square brackets multiplying the  $\mathcal{L}_i^f$  is changed to  $2S_i$ . We also note that the  $\text{Ti}^{+++}$  and  $\text{Cr}^{+++}$  calculations of reference 1 are special cases of Eq. (44).

#### Raman Interaction

The Raman interaction requires two-phonon operators, and these can come from the term in  $V^{ff'}$

[Eq. (24c)] or from two  $V^f$  terms in the second order of perturbation theory.

The former category gives rise to the equivalent Hamiltonian

$$\begin{aligned}\mathcal{H}_{\text{Raman}}^{\text{I}} &= \sum_{\substack{ff'pq \\ i > j}} A^{fp} A^{f'q} (a_p^\dagger + a_p) (a_q^\dagger + a_q) \{ 2\beta \lambda H \mathcal{L}_i^{ff'} \\ &\quad \times [\mathcal{L}_{kk'} S_i + g(S_i \mathcal{E} - \mathcal{E} S_i)] + 2\beta \lambda \mathcal{L}_{ij}^{ff'} (S_i H_j + H_i S_j) \\ &\quad + \lambda^2 \mathcal{L}_{ij}^{ff'} (S_i S_j + S_j S_i) \}, \quad (47)\end{aligned}$$

where all terms are the same as those in Eq. (44), except that in the  $\mathcal{L}$ 's [Eq. (45)]  $V^f$  is replaced by  $V^{ff'}$ .

Terms in the latter category must be obtained by calculating the second-order matrix element as expressed in Eq. (27)

$$\langle k' L' | V | k L \rangle^{\text{II}} = \sum_{k^2 L^2} \frac{\langle k' L' | V | k^2 L^2 \rangle \langle k^2 L^2 | V | k L \rangle}{(E_{k^2 L^2} - E_{kL})}. \quad (48)$$

In the summation,  $|k^2 L^2\rangle$  can be either an excited state or one of the ground states. Consider the former case first. We can use the expression in Eq. (41) for the wave function, with appropriate reinterpretation of the indices. We then write an equation similar to Eq. (42), from which the ( $k^2 L^2$ =excited state) Raman terms can be computed. In abbreviated form, this equation is

$$\begin{aligned}\langle k' L' | V | k L \rangle^{\text{II}} &= \sum_{aa'} C_{k'a'}^* C_{ka} \sum_{k^2 L^2 AB} \frac{C_{k^2 B}^* C_{k^2 A}}{E_{k^2 L^2} - E_{kL}} \left[ V_{L'L^2 a' A} V_{L^2 L B a} - V_{L'L^2 a' A} V_{L^2 L B a} \sum_{\alpha b b'} \left( C_{k^2 b}^* C_{k^2 b'} \frac{P_{ba} P_{\alpha b'}}{(E_{k^2} - E_{\alpha})^2} \right) \right. \\ &\quad \left. + \sum_{\omega} \left( \frac{V_{L'L^2 a' A} V_{L^2 L B \omega} P_{\omega a}}{(E_k - E_{\omega})} + 3 \text{ similar terms} \right) + \sum_{\gamma \omega} \left( \frac{V_{L'L^2 a' \gamma} P_{\gamma A} V_{L^2 L B \omega} P_{\omega a}}{(E_{k^2} - E_{\gamma})(E_k - E_{\omega})} + 9 \text{ similar terms} \right) \right]. \quad (49)\end{aligned}$$

The simplest terms here are those involving two  $P$ 's and two  $V$ 's in the numerator, since we do not have to consider small differences in energy denominators, and can use the fact that, within a given excited cluster,  $\sum_{k^2} C_{k^2 B}^* C_{k^2 A} = \delta_{BA}$ . We find that

$$\mathcal{H}_{\text{Raman}}^{\text{II}} = \sum_{\substack{ff'pq \\ i > j}} A^{fp} A^{f'q} (a_p^\dagger + a_p) (a_q^\dagger + a_q) \mathfrak{M}_{ij}^{ff'} [2\beta \lambda (S_i H_j + S_j H_i) + \lambda^2 (S_i S_j + S_j S_i)], \quad (50)$$

where

$$\begin{aligned}\mathfrak{M}_{ij}^{ff'} &= \sum_{n' n^2 n^3} \left[ \frac{\langle 0 | L_i V^f V^{f'} L_j + V^f V^{f'} L_i L_j + L_i L_j V^f V^{f'} | 0 \rangle}{(E_{n'} - E_0)(E_{n^2} - E_0)(E_{n^3} - E_0)} + \langle 0 | V^f L_i L_j V^{f'} | 0 \rangle \right. \\ &\quad \left. \times \left( \frac{1}{(E_{n'} - E_{n^2})(E_{n'} - E_{n^3})} + \frac{1}{(E_{n^2} - E_{n'}) (E_{n^3} - E_{n^2})} + \frac{1}{(E_{n^2} - E_{n'}) (E_{n^3} - E_{n^2})} \right) \right]. \quad (51)\end{aligned}$$

Consider next the term with two  $V$ 's. Such a term vanishes in the method of reference 1 because there, the  $C_{k^2A}$  are equal to unity or to zero, and because of the considerations discussed in relation to Eq. (43). In our method, this term produces an important contribution which may be written

$$\mathfrak{H}_{\text{Raman}}^{\text{III}} = \sum_{\substack{ff'pq \\ i > j}} A^{fp} A^{f'q} (a_p^\dagger + a_p) (a_q^\dagger + a_q) \sum_{n^2} \frac{\langle 0 | V^f | n^2 \rangle \langle n^2 | V^f | 0 \rangle}{(E_{n^2} - E_0)^2} C_{n^2}, \quad (52)$$

where  $C_{n^2}$  is a spin-type operator defined by

$$\langle s' | C_{n^2} | s \rangle = 2 \sum_{k^2} C_{k^2 n^2 s'}^* C_{k^2 n^2 s} (E_{k^2} - E_{n^2}). \quad (53)$$

The sum is over all  $k^2$ 's (excited spin states) that are associated with a given  $n^2$  (excited pure electronic state).

The fourth Raman term comes from the normalization, and it is

$$\mathfrak{H}_{\text{Raman}}^{\text{IV}} = - \sum_{\substack{ff'pq \\ i > j}} A^{fp} A^{f'q} (a_p^\dagger + a_p) (a_q^\dagger + a_q) \sum_{n^2} \frac{\langle 0 | V^f | n^2 \rangle \langle n^2 | V^f | 0 \rangle}{(E_n - E_0)} D_{n^2}, \quad (54)$$

where  $D_{n^2}$  is the spin-type operator given by

$$\langle s' | D_{n^2} | s \rangle = \sum_{\substack{k^2 n^2 s' s \\ i > j}} C_{k^2 n^2 s'}^* C_{k^2 n^2 s} C_{k^2 n^2 s'}^* C_{k^2 n^2 s} \frac{\langle n^2 | L_i L_j | n^2 \rangle}{(E_{n^2} - E_n)^2} \langle s' | 2\beta \lambda (S_i H_j + S_j H_i) + \lambda^2 (S_i S_j + S_j S_i) | s \rangle. \quad (55)$$

Next we have the contribution from the terms involving two  $V$ 's and one  $P$ :

$$\mathfrak{H}_{\text{Raman}}^{\text{V}} = \sum_{ff'pqi} A^{fp} A^{f'q} (a_p^\dagger + a_p) (a_q^\dagger + a_q) [S_i \mathfrak{G}_i^{ff'} + (S_i \mathfrak{H}_i^{ff'} - \mathfrak{H}_i^{ff'} S_i)], \quad (56)$$

where

$$\mathfrak{G}_i^{ff'} = \lambda h \frac{(\nu_p + \nu_q)}{2} \sum_{nn'} \left( \frac{\langle 0 | V^f L_i V^{f'} - V^{f'} L_i V^f | 0 \rangle}{(E_n - E_0)^2 (E_n - E_{n'})} + \frac{\langle 0 | V^f V^{f'} L_i - V^{f'} V^f L_i | 0 \rangle}{(E_n - E_0)^2 (E_0 - E_{n'})} \right) + 2g_{kk'} \lambda \beta H \sum_{nn'} \frac{\langle 0 | V^f V^{f'} L_i | 0 \rangle}{(E_0 - E_{n'})^2 (E_n - E_0)}, \quad (57)$$

$$\mathfrak{H}_i^{ff'} = 2g\beta H \lambda \mathcal{E} \sum_{nn'} \frac{\langle 0 | V^{f'} L_i V^f | 0 \rangle}{(E_n - E_{n'}) (E_n - E_0)^2} + \lambda \sum_{nn'} C_{n^2} \left[ \frac{\langle 0 | V^{f'} L_i V^f | 0 \rangle}{(E_{n^2} - E_{n'}) (E_{n^2} - E_0)} \times \left( \frac{1}{(E_{n^2} - E_{n'})} + \frac{1}{(E_{n^2} - E_0)} \right) + \frac{\langle 0 | V^f V^{f'} L_i | 0 \rangle}{(E_n - E_{n'}) (E_{n^2} - E_0)^2} \right]. \quad (58)$$

The  $\mathcal{E}$  and  $C_{n^2}$  operators are defined in Eqs. (45) and (53), respectively, and  $\nu_p$  and  $\nu_q$  are the frequencies of the incident and scattered phonons.

The last important term is the one obtained from Eq. (48) when  $|k^2 L^2\rangle$  is one of the ground states. This term can be constructed by using the equivalent operator of Eq. (44), and the result is

$$\mathfrak{H}_{\text{Raman}}^{\text{VI}} = \sum_{\substack{ff'pq \\ i > j, i' > j'}} A^{fp} A^{f'q} (a_p^\dagger + a_p) (a_q^\dagger + a_q) \sum_{k^2} \left( \frac{\phi_{ij}^f \zeta_{k^2} \phi_{i'j'}^{f'}}{h(\nu_{k^2k} + \nu_q)} + \frac{\phi_{ij}^{f'} \zeta_{k^2} \phi_{i'j'}^f}{h(\nu_{k^2k} - \nu_p)} \right), \quad (59)$$

where  $\phi_{ij}^f$  is the operator in braces in Eq. (44) and  $\zeta_{k^2}$  is the operator defined by

$$\langle s' | \zeta_{k^2} | s \rangle = C_{k^2 0s}^* C_{k^2 0s}. \quad (60)$$

If either of the two denominators vanishes, we must use the considerations of Schiff,<sup>11</sup> and carry out a contour integration by using the line-shape factor to

<sup>11</sup> L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1949).

obtain the density of states. The final result is that Eq. (59) is still valid if we replace the zero denominator by  $h\nu_{\frac{1}{2}}$ , where  $\nu_{\frac{1}{2}}$  is the half-width of the ground-state energy levels.

#### D. Quadrupole Selection Rule in Direct Interactions

Examination of Eq. (44) shows that it constitutes a multipole expansion of the interaction in terms of spin

operators, the terms linear in  $S_i$  being dipolar, and those quadratic in  $S_i$  being quadrupolar. Since  $\mathcal{L}_i^f \sim \mathcal{L}_{ij}^f$ , the ratio of these two types of terms is of the order of  $\lambda^2/4\beta\lambda H$ . Taking as a typical case  $H=10^4$  gauss and  $\lambda=100 \text{ cm}^{-1}=2\times 10^{-14} \text{ erg}$ , we find that the quadrupole term dominates by a factor of 50 when the spin anticommutator is of the order of unity. [This is caused essentially by the "Van Vleck cancellation" in the dipolar term mentioned in connection with Eq. (42).] Thus, the direct phonon-spin interaction will obey quadrupole selection rules. This means that for odd half-integer spin systems of  $S>\frac{1}{2}$ , the spin-phonon transitions are "approximately" forbidden between any pair of orthogonal spin states,  $|1\rangle, |2\rangle$ , of the form

$$\begin{aligned} |1\rangle &= a|m_s\rangle + b|-m_s\rangle, \\ |2\rangle &= c|m_s\rangle + d|-m_s\rangle, \\ \langle 1|2\rangle &= 0. \end{aligned} \quad (61)$$

This is easily shown from the properties of the  $S_+$ ,  $S_-$ ,  $S_z$  operators.

### E. Order-of-Magnitude Formulas for $\mathcal{H}_{\text{spin-phonon}}$

We derive here simple expressions for computing the order of magnitude of the spin-phonon interaction. Consider first  $A^{fp}$ . From Eq. (9), the  $B_{fl\alpha}$  are of the order of 1. The  $\phi_{k\alpha}$  are of the order of 1,  $K_p \sim 1$ ,  $R_i \sim R$  (average interatomic separation) and we take  $\sin\Delta_p \sim 1$  (since we always average over its square). Thus

$$A^{fp} \sim (2h\nu_p/Mv^2)^{\frac{1}{2}}R. \quad (62)$$

For the phonon operators we have  $a_p \sim (n_p)^{\frac{1}{2}}$ , and  $a_p^\dagger \sim (n_p+1)^{\frac{1}{2}}$ . The  $L_i$  matrix elements are of the order of 1. To estimate the size of the  $V^f$  and  $V^{ff'}$  matrix elements, we consider the simple case of a paramagnetic nucleus at the origin with two nearest neighbors of charge  $e$  lying at  $x=\pm R$ . The potential energy of the paramagnetic electron at point  $r$  is

$$V = \frac{e^2}{R-r} + \frac{e^2}{R+r}. \quad (63)$$

Suppose there is a normal displacement in which each neighbor moves out a short distance,  $Q_f$ . Replacing  $R$  by  $R+Q_f$  and expanding to second order in  $Q_f$ , we obtain

$$\begin{aligned} V &= e^2 \left( \frac{1}{R-r} + \frac{1}{R+r} \right) - e^2 \left( \frac{1}{(R-r)^2} + \frac{1}{(R+r)^2} \right) Q_f \\ &\quad + e^2 \left( \frac{1}{(R-r)^3} + \frac{1}{(R+r)^3} \right) Q_f^2 + \dots \end{aligned} \quad (64)$$

Using Eqs. (8) and (12), and expanding in a power

series in  $r$  we find

$$\begin{aligned} V^f &= \frac{2e^2}{R^2} + \frac{6e^2r^2}{R^4} + \dots, \\ V^{ff'} &= \frac{2e^2}{R^3} + \frac{12e^2r^2}{R^5} + \dots. \end{aligned} \quad (65)$$

We assume that the constant terms are already part of the lattice Hamiltonian, since they involve only lattice coordinates. (The rigorous analysis of such a procedure requires techniques like those used by Korringa.<sup>4</sup>) For  $r$  we use the ionic radius,  $r_0$ , thus obtaining the estimate

$$\begin{aligned} \langle n|V^f|n'\rangle &\sim 6e^2r_0^2/R^4, \\ \langle n|V^{ff'}|n'\rangle &\sim 12e^2r_0^2/R^5. \end{aligned} \quad (66)$$

Using these results, we obtain the following crude formulas for order-of-magnitude calculations:

$$\mathcal{H}_{\text{direct}} \sim \left( \frac{2h\nu_p n_p}{Mv^2} \right)^{\frac{1}{2}} \frac{6e^2r_0^2}{\Delta^2 R^3} (2\beta\lambda H S_i + \lambda^2 S_A), \quad (67)$$

$$\begin{aligned} \mathcal{H}_{\text{Raman}} &\sim \frac{2h}{Mv^2} [n_p \nu_p (n_q+1) \nu_q]^{\frac{1}{2}} \frac{36e^4 r_0^4}{\Delta^3 R^6} \\ &\quad \times \left( [2\beta\lambda H + \frac{1}{2}\lambda h(\nu_p + \nu_q)] S_i + \lambda^2 S_A' \right. \\ &\quad \left. + \epsilon_x \Delta + \frac{(2\beta\lambda H S_i + \lambda^2 S_A')^2}{\Delta h(\nu_k - \nu_p)} \right), \end{aligned} \quad (68)$$

where  $S_A$  is the spin anticommutator,  $\epsilon_x$  is of the order of the level splittings in excited states, and  $S_A' \sim 1$ , if  $S>\frac{1}{2}$  and  $S_A'=0$  if  $S=\frac{1}{2}$ . Equations (67) and (68) assume an average over phonons of all propagation directions, polarizations, and phases.

## 3. POSSIBLE EXPERIMENTS

### A. Calculation of Four Different Spin-Phonon Processes

The feasibility of any proposed test of our general theory depends on the relative sizes of four transition probabilities—direct relaxation ( $W_{\text{DR}}$ ), Raman relaxation ( $W_{\text{RR}}$ ), direct interaction between spin and monochromatic phonon ( $W_{\text{DM}}$ ), and Raman interaction between spin and monochromatic phonon ( $W_{\text{RM}}$ ). We consider these in turn.

#### Direct Process Relaxation ( $W_{\text{DR}}$ )

In this case, the spin interacts with all thermal phonons in a frequency interval determined by the spin shape factor  $g(\nu-\nu_r)$ , where  $\nu_r = \nu_{k',k} = \text{resonance frequency}$ . The transition probability is:

$$W_{\text{DR}} = (1/\hbar^2) |\langle p'k'|\mathcal{H}_{\text{direct}}|pk\rangle|^2 \rho(\nu_r), \quad (69)$$



where  $\rho$  is the density of states in the phonon field. For an emission process, we find, using Eqs. (67) and (6), that

$$W_{DR} = \frac{1}{\hbar^2} \frac{2\hbar\nu_r}{Mv^2} \langle n_r + 1 \rangle_{av} \frac{36e^4 r_0^4}{\Delta^4 R^6} \times |2\beta\lambda HS_i + \lambda^2 S_A|^2_{k'k} \frac{12\pi V \nu_r^2}{v^3}. \quad (70)$$

The contribution to  $W_{DR}$  from  $n_r$  (in  $\langle n_r + 1 \rangle_{av}$ ) is the induced emission probability, whereas the contribution from the 1 gives the spontaneous emission probability. Since  $n_r \approx kT/\hbar\nu_r$  in most cases of interest, we find for the induced emission or absorption

$$W_{DR} \sim \frac{3456\pi^3 kT \nu_r^2}{\hbar^2 (M/V) v^5} \frac{e^4 r_0^4}{\Delta^4 R^6} |2\lambda\beta HS_i + \lambda^2 S_A|^2_{k'k}. \quad (71)$$

#### Raman Process Relaxation

The transition here involves thermal phonons of all frequencies, and the probability is given by

$$W_{RR} = \int_0^{\nu_D} d\nu_p |\langle p'q'k' | \mathcal{H}_{Raman} | pqk \rangle|^2 \times \rho(\nu_p) \rho(\nu_p - \nu_r), \quad (72)$$

where  $\nu_D$  is the Debye cutoff frequency. Actual integration and numerical evaluation for typical cases reveal that the contribution of the last term in braces in Eq. (68) is small since the minimum value ( $=\hbar\nu_{\frac{1}{2}}$ ) of the denominator is finite and it has a  $1/\nu_p$  dependence for high values of  $\nu_p$ . The  $2\beta\lambda H$  term also produces negligible effect. Making the approximation  $\nu_p \gg \nu_r$  we find, for sufficiently low temperatures,

$$W_{RR} \sim \frac{2304\pi^4}{(M/V)^2 v^{10}} \frac{(36)^2 e^8 r_0^8}{\Delta^6 R^{12}} \times \int_0^{\nu_D} |\epsilon_x \Delta + \lambda^2 S_A' + \lambda \hbar \nu_p|^2_{k'k} \times \nu_p^6 e^{(-\hbar\nu_p)/(kT)} d\nu_p. \quad (73)$$

If we take  $\epsilon_x \sim 1 \text{ cm}^{-1}$ ,  $\Delta \sim 10^4 \text{ cm}^{-1}$ ,  $\lambda \sim 10^2 \text{ cm}^{-1}$ , and  $\hbar\nu_D \sim 10^2 - 10^3 \text{ cm}^{-1}$  as typical values, we see that all terms in the integrand may make roughly the same contribution. For simplicity we use only the  $(\epsilon_x \Delta + \lambda^2 S_A')$  term, while recognizing the highly schematic nature of the result:

$$W_{RR} \sim \frac{2304\pi^4}{(M/V)^2 v^{10}} \frac{(36)^2 e^8 r_0^8}{\Delta^6 R^{12}} (\epsilon_x \Delta + \lambda^2 S_A')^2 \left(\frac{k}{\hbar}\right)^7 T^7. \quad (74)$$

(Note that if the other term dominates, a  $T^9$  dependence results.)

#### Direct Interaction Between Spin and Monochromatic Phonon

For this process, the transition probability is

$$W_{DM} = (1/\hbar^2) |\langle p'k' | \mathcal{H}_{direct} | pk \rangle|^2 g(\nu_p - \nu_r), \quad (75)$$

where  $g$  is the line-shape factor. Before estimating  $W_{DM}$ , we introduce some other quantities of utility:

(a) Energy density in  $n$ -phonon wave

$$\mathcal{E} = \frac{n_p \hbar \nu_p}{V} \left( \frac{\text{ergs}}{\text{cm}^3} \right). \quad (76)$$

(b) Wave intensity

$$I = \mathcal{E}_v = \frac{n_p \hbar \nu_p}{V} v \left( \frac{\text{ergs}}{\text{cm}^3 \cdot \text{sec}} \right). \quad (77)$$

(c) Power absorbed by the wave from spin system, if no saturation is assumed, when  $\hbar\nu_r \ll kT$  with  $N$  spins/cm<sup>3</sup>

$$P = \frac{N}{(2S+1)} \frac{(2\pi\nu_r)^3}{kT} |\langle p'k' | \mathcal{H}_{direct} | pk \rangle|^2 g(\nu_p - \nu_r). \quad (78)$$

The maximum power absorbed is given by setting  $g = g_{\max} \sim 1/\nu_{\frac{1}{2}}$ , where  $\nu_{\frac{1}{2}}$  is the linewidth.

(d) Phonon attenuation coefficient

$$\sigma (\text{cm}^{-1}) = \frac{P}{I} = \frac{4\pi^2 N \nu_r^2 V}{(2S+1) \nu_p n_p \hbar k T v} \times |\langle p'k' | \mathcal{H}_{direct} | pk \rangle|^2 g(\nu_p - \nu_r). \quad (79)$$

(e) Phonon relaxation time (resulting from interaction with spins)

$$\tau_{ps} = (1/\sigma v) (\text{sec}). \quad (80)$$

Using these formulas as well as Eq. (67), we obtain for  $W_{DM}(\max)$  and  $\sigma(\max)$ :

$$W_{DM} \sim \frac{8\pi^2 \mathcal{E}}{\hbar^2 (M/V) v^2} \frac{36e^4 r_0^4}{\Delta^4 R^6} |2\beta\lambda HS_i + \lambda^2 S_A|^2_{k'k} \frac{1}{\nu_{\frac{1}{2}}}, \quad (81)$$

$$\sigma_{DM} \sim \frac{8\pi^2 N \nu_r^2}{(2S+1) k T v^3 (M/V)} \frac{36e^4 r_0^4}{\Delta^4 R^6} \times |2\beta\lambda HS_i + \lambda^2 S_A|^2_{k'k} \frac{1}{\nu_{\frac{1}{2}}}. \quad (82)$$

#### Raman Interaction Between Spin and Monochromatic Phonon

In this case we have the following expression for the transition probability:

$$W_{RM} = (1/\hbar^2) |\langle p'k' | \mathcal{H}_{Raman} | pk \rangle|^2 \rho(\nu_p - \nu_r). \quad (83)$$

With the aid of Eqs. (6), (68), and (79), we obtain

$$W_{RM} \sim \frac{192\pi^3 \mathcal{E} k T}{(M/V)^2 h^2 v^7} \frac{(36)^2 e^8 r_0^8}{\Delta^6 R^{12}} (\nu_p - \nu_r)^2$$

$$\times \left| \left[ 2\beta \lambda H + \frac{1}{2} \lambda h (\nu_p + \nu_q) \right] S_i + \lambda^2 S_A' + \epsilon_x \Delta \right. \\ \left. + \frac{(2\beta \lambda H S_i + \lambda^2 S_A')^2}{\Delta h (\nu_k^2 k - \nu_p)} \right|_{k'k}, \quad (84)$$

$$\sigma_{RM} \sim \frac{N}{2S+1} \frac{h^2 \nu_p \nu_r W_{RM}}{k T \mathcal{E} v}. \quad (85)$$

### B. Inadequacy of Relaxation and rf Saturation Experiments

In order to check the theory, we need to obtain measurements of  $|\langle p'k' | \mathcal{H}_{int} | pk \rangle|^2$ , that is, of  $W_{p'k'pk}$ . The methods in most widespread use at present are relaxation and rf saturation. They both suffer from the defect that a single observation (of a relaxation time or a saturation coefficient) gives a number that involves all pairs of energy levels,  $k, k'$ , and all phonons  $p, p'$  (all directions, polarizations, and frequencies). This means that a large number of measurements would be required in order to obtain a particular  $W_{p'k'pk}$ .

As a simple illustration of the difficulty, consider a four-level system in which we attempt to measure  $W_{12}$  by saturating levels 1 and 2 with rf energy. The differential equations for the spin populations are:

$$\dot{N}_i = \sum_{j \neq i} [-N_i (W_{ij} + \lambda_{ij} V_r) + N_j (W_{ji} + \lambda_{ji} V_r)], \quad (86)$$

where  $i, j = 1, 2, 3, 4$ ;  $\lambda_{12} = \lambda_{21} = 1$ , and all other  $\lambda$ 's = 0;  $V_r$  is the rf-induced spin transition probability;  $W_{ij}$  is the total phonon-spin transition probability between levels  $i, j$ ; and  $N_i$  is the population of the  $i$ th level, and is subject to the constraint  $N = \sum_i N_i$ , where  $N$  = total number of spins. It can be shown that the ratio of the population difference, with  $V_r \neq 0$ , to the equilibrium population difference ( $V_r = 0$ ) is

$$\frac{N_1 - N_2}{(N_1 - N_2)_{\text{equil}}} = \frac{1}{1 + V_r / W_{\text{eff}}}, \quad (87)$$

where

$$W_{\text{eff}} = \frac{aie + bfg + dhc - bdi - ceg - fha}{(e + b + a + d)i - (f + c)(h + g)}, \quad (88)$$

and  $a = W_{12} + W_{13} + W_{14} + W_{41}$ ,  $b = W_{41} - W_{21}$ ,  $c = W_{41} - W_{31}$ ,  $d = W_{42} - W_{12}$ ,  $e = W_{21} + W_{23} + W_{24} + W_{42}$ ,  $f = W_{42} - W_{32}$ ,  $g = W_{43} - W_{13}$ ,  $h = W_{43} - W_{23}$ , and  $i = W_{31} + W_{32} + W_{34} + W_{43}$ . Clearly, then, the measurement of  $W_{\text{eff}}$  is in no sense a measurement of  $W_{12}$ . For example, consider the case of ruby in a weak magnetic field ( $< 40$  gauss). Let the  $+\frac{1}{2}$ ,  $-\frac{1}{2}$  Kramers doublet be levels 1 and 2, and let the  $+\frac{3}{2}$ ,  $-\frac{3}{2}$  doublet be levels 3

and 4. Because of the quadrupole selection rule, we can take  $W_{12} \sim W_{21} \sim W_{34} \sim W_{43} \sim 0$ , and since the other  $W$ 's are approximately equal, we immediately find that  $W_{\text{eff}} \sim W_{13} \sim W_{14} \sim W_{23}$ , and so on. Thus, the saturation observation gives  $W_{13}$  instead of  $W_{12}$ .

### C. Possible Acoustic Experiments

Acoustic techniques for investigating spin-phonon interactions have the obvious advantage that they permit direct measurement of  $W_{p'k'pk}$ , since one has control over phonon frequency, direction, and polarization. The first proposal for such experiments was made in 1953 by Kastler,<sup>12</sup> and subsequently Al'tshuler<sup>13</sup> did order-of-magnitude calculations of  $\sigma$  for titanium cesium alum, chrome alum, some rare earths, and S-state ions. Several acoustic experiments were performed on nuclear spins,<sup>14-16</sup> and in 1959, Jacobsen et al.<sup>17</sup> saturated Mn and  $F$ -center spin resonances in quartz by using microwave phonons. The present authors<sup>18</sup> have briefly reported low-frequency acoustic saturation of the  $\text{Cr}^{+++}$  resonance in MgO and of the  $F$ -center resonance in crystalline quartz.

We proceed now to examine some possible acoustic experiments in the light of the preceding discussion. These experiments are of two types: measurements of the attenuation coefficient,  $\sigma$ , and determination of the saturation coefficient,  $\gamma$ ;  $\gamma$  is defined by

$$\frac{N_1 - N_2}{(N_1 - N_2)_{\text{equil}}} = \frac{1}{1 + \gamma}; \quad \gamma = \frac{W_{\text{acoustic}}}{W_{\text{eff}}}, \quad (89)$$

[see Eq. (87) for rf saturation]. We shall first compute rough values for  $\sigma$  and  $\gamma$  in ruby, and then examine the case of MgO doped with  $\text{Cr}^{+++}$ . In both cases we assume the following crude figures for evaluating the order-of-magnitude formulas:  $M/V = 3$  g/cm<sup>3</sup>,  $R \sim 2 \times 10^{-8}$  cm,  $r_0 \sim 0.5 \times 10^{-8}$  cm,  $v \sim 2.5 \times 10^5$  cm/sec,  $\lambda \sim 100$  cm<sup>-1</sup> ( $= 2 \times 10^{-14}$  erg), and  $\Delta \sim 10^4$  cm<sup>-1</sup> ( $= 2 \times 10^{-12}$  erg). We take  $T = 4^\circ\text{K}$  and  $\nu_{\frac{1}{2}}(\text{ruby}) \sim 5 \times 10^7$  cps,  $\nu_{\frac{1}{2}}(\text{MgO}) \sim 10^7$  cps, and  $N \sim 10^{20}$  spins/cm<sup>3</sup>. We use  $\mathcal{E} \sim 10$  ergs/cm<sup>3</sup> as a phonon energy density at  $\nu_p = 10^7$  cps; no figures are available at present for the microwave phonon region.

The results for ruby are summarized in Table I. [In the calculation of  $\gamma$ , we have made use of conclusions drawn from Eqs. (87) and (88).] From this table we see that  $\sigma$  should be easy to measure in the microwave region, but not at lower frequencies, and that  $\gamma$  should

<sup>12</sup> A. Kastler, *Experientia* **8**, 1 (1952).

<sup>13</sup> S. A. Al'tshuler, *Zhur. Eksp. i Teoret. Fiz.* **24**, 681 (1953).

<sup>14</sup> W. G. Proctor and W. H. Tantilla, *Phys. Rev.* **101**, 1757 (1956).

<sup>15</sup> W. G. Proctor and W. A. Robinson, *Phys. Rev.* **104**, 1344 (1956).

<sup>16</sup> E. F. Taylor and N. Bloembergen, *Phys. Rev.* **113**, 431 (1959).

<sup>17</sup> E. H. Jacobsen, N. S. Shiren, and E. B. Tucker, *Phys. Rev. Letters* **3**, 81 (1959).

<sup>18</sup> R. D. Mattuck and M. W. P. Strandberg, *Phys. Rev. Letters* **3**, 550 (1959).

TABLE I. Order of magnitude of phonon attenuation ( $\sigma$ ) and saturation coefficient ( $\gamma$ ) for ruby.

Case \ $\nu_r$	10 <sup>7</sup> cps	10 <sup>10</sup> cps
$\sigma_{DM}, (S_A=0)$	$10^{-16} \text{ cm}^{-1}$	$10^{-4} \text{ cm}^{-1}$
$\sigma_{DM}, (S_A \approx 1)$	$10^{-5} \text{ cm}^{-1}$	$10 \text{ cm}^{-1}$
$\gamma_{DM}, (S_A=0)$	$5 \times 10^{-9}$	?
$\gamma_{DM}, (S_A \approx 1)$	60	?

be unobservably small for the low-frequency case with  $S_A=0$ , but quite large when  $S_A \sim 1$ . (For a discussion of minimum observable values of  $\sigma$  and  $\gamma$ , see Mattuck.<sup>19</sup>) Thus, two types of experiments could be done to verify the quadrupole selection rule: (i) A microwave phonon experiment in which  $\sigma$  is measured as a function of crystal orientation in the dc  $H$  field. When  $H$  is parallel to the ruby optic axis,  $\sigma$  should become very small for transitions between the  $\pm \frac{1}{2}$  or the  $\pm \frac{3}{2}$  levels, as described by Eq. (61). (ii) Two low-frequency saturation experiments—one between the  $\pm \frac{1}{2}$  low-field Kramers doublets to verify that  $\gamma$  is not observable in this case ( $S_A=0$ ), and the other between the  $+\frac{3}{2}$ ,  $-\frac{1}{2}$  levels at the field and orientation where these levels almost cross over, to show that, under these conditions (since  $S_A \sim 1$ ), acoustic saturation can be detected.

The cause of the very low value for  $\gamma_{DM}$  in ruby at low fields and frequencies is the large zero-field splitting that makes  $W_{eff}$  large and separates the Kramers doublets, with the result that  $W_{DM}$  becomes small, according to the quadrupole selection rule. If we have small zero-field splitting, this would no longer be true. Consider MgO doped with  $\text{Cr}^{+++}$ , for example. According to current investigations, this crystal contains a large number of  $\text{Cr}^{+++}$  ions on sites of nearly perfect cubic symmetry,<sup>20</sup> which implies negligible zero field splitting, and four almost equally spaced Zeeman levels. Spin-spin interaction will maintain these levels in equilibrium with each other, so that in considering interaction with phonons, we need take only those level pairs with  $S_A \sim 1$ . We find that  $W_{eff} = W_{RR}$  in this case, since  $W_{DR}$  is very small as a result of the  $\nu_r^2$  dependence [Eq. (70)]. Using Eq. (74), we find  $W_{eff} \sim 10^{-1} \text{ sec}^{-1}$ . From Eq. (81), we obtain  $W_{DM} \sim 10^{-6}$ ; this yields  $\gamma_{DM} = 10^7$ , which is a very large effect.

We might note here that, of the two types of acoustic experiment, the observation of  $\sigma$  possesses the advantage of providing very direct information about  $\mathcal{H}_{\text{interaction}}$ , in contrast to  $\gamma$ , which requires measurement of the auxiliary quantity,  $W_{eff}$ . ( $W_{eff}$  can be determined by an rf saturation experiment.) On the other hand,  $\sigma$  is detectable only in the microwave region, and the techniques for production of microwave phonons are not yet standard. For this reason, the experiments described in the following section were

all of the  $\gamma$  type, and were conducted at low frequencies ( $\sim 10^7$  cps), a region in which methods for generating phonons are well known.

#### 4. EXPERIMENTAL RESULTS

##### A. Apparatus

The paramagnetic resonance equipment consisted of a Pound-Watkins oscillator, followed by a narrow-band 50-cycle amplifier and a phase-sensitive detector. The dc magnetic field was provided by two pairs of Helmholtz coils, and could be swept from  $-20$  to  $+30$  gauss. Two auxiliary coils were used for the 50-cycle modulating field. The minimum measurable susceptibility was  $\sim 5 \times 10^{-9}$  at  $4.2^\circ \text{K}$ , which is the equivalent of  $10^{16}$  spins/gauss. The signal,  $S$ , is thus the slope of the imaginary part of the paramagnetic susceptibility.

The phonon generator is shown in Fig. 2. It consists of a 13-Mc/sec X-cut quartz vibrator, fine ground on both sides and coated on one side with an evaporated layer of chrome-silver, and driven by a signal generator. The uncoated side is in contact at a few points with a spring-loaded brass plate. It was found essential to keep the loading sufficiently large to maintain continuous electrical contact between the periphery of the silvered quartz surface and the brass head; otherwise, direct electrical pickup by the oscillator tank coil prevented the oscillator from operating. If this precaution was taken, pickup was confined to a small frequency region well within the tank bandwidth of

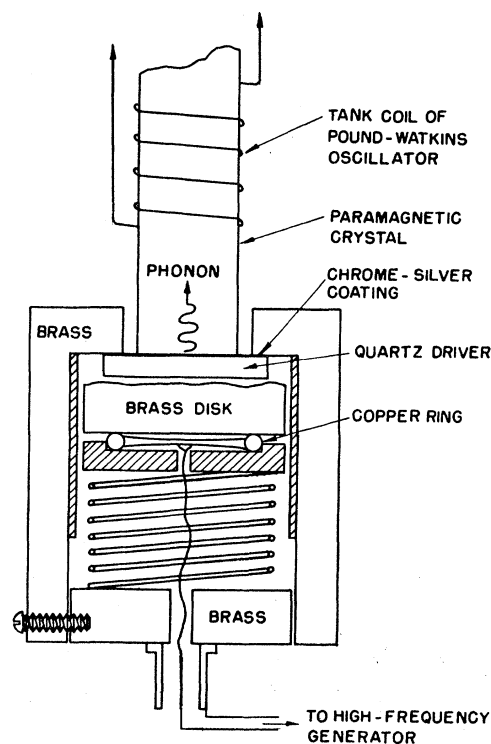


FIG. 2. Phonon generator.

<sup>19</sup> R. D. Mattuck, Ph.D. thesis, Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts, May, 1959 (unpublished).

<sup>20</sup> W. Low, Phys. Rev. **105**, 801 (1957).

approximately 0.05 Mc/sec. Sound waves were coupled into the paramagnet by cementing one end of it to the silvered face with No-nac vacuum grease. It was found that acoustical contact was always maintained at 4.2°K, provided that *neither* of the two surfaces so joined was highly polished.

The phonon energy density,  $\mathcal{E}$ , was determined from the usual equation

$$(d/dt)(\mathcal{E}V) = P_i - (\mathcal{E}V/\tau_p) = 0, \quad (\text{in steady state}) \quad (90)$$

where  $V$  = crystal volume,  $P_i$  = acoustic power input, and the phonon relaxation time  $\tau_p$  characterizes the rate at which phonons are lost by all mechanisms, including radiation into helium bath and collisions (phonon-phonon, phonon-boundary, phonon-dislocation, phonon-spin, etc.). The phonon-bath relaxation time for a crystal 1 cm long, with a density of 3 g/cm<sup>3</sup> is calculated to be  $\sim 3 \times 10^{-4}$  sec. There are no published data on the other relaxation processes at 4.2°K, but they are probably much longer than  $10^{-4}$  sec; Simons<sup>21</sup> calculated  $\tau_{(\text{phonon-phonon})}$  to be  $\sim 10$  sec for 10-Mc/sec phonons in a rod of solid argon at 3°K. From Table I,  $\tau_{(\text{phonon-spin})} \sim 1$  sec. Experiments at room temperature yield  $\tau_p \sim 5 \times 10^{-4}$  sec. For the relaxation time at 4.2°K, we shall take  $\tau_p \sim 10^{-4}$  sec as a reasonable guess.

Input resistance and reactance of the quartz circuit was measured in the vicinity of resonance with a General Radio impedance bridge. This was done with the quartz unloaded at room temperature, and with the quartz loaded at 4.2°K, thus providing enough

information to calculate the power input,  $P_i$ , in terms of the input voltage. Maximum power was  $\sim \frac{1}{2}$  watt, which is equivalent to  $\mathcal{E}_{\text{max}} \sim 100$  ergs/cm<sup>3</sup> for a 3-cm<sup>3</sup> crystal. We used  $\mathcal{E} \sim 10$  ergs/cm<sup>3</sup> in the calculations of the preceding section since the value of  $\tau_p$  is uncertain.

### B. Experiments on MgO Doped with Cr<sup>+++</sup>

A crystal of MgO,  $\frac{1}{4}$  by  $\frac{1}{4}$  by  $1\frac{1}{4}$  inches, containing approximately  $10^{19}$  Cr<sup>+++</sup> ions/cm<sup>3</sup> was employed in these experiments.<sup>22</sup> At  $\nu_r \sim 10$  Mc/sec, the resonance occurs at  $\sim 3$  gauss, and since the linewidth is  $\sim 3$  gauss, the line shape is considerably distorted by the "negative resonance" term in the transition probability formula. With the phonon frequency held at 13.1 Mc/sec, the frequency of the Pound-Watkins oscillator was changed in steps from  $\nu_r = 10$  Mc/sec to  $\nu_r = 20.5$  Mc/sec (the rf power level being kept constant). We defined signal saturation as the ratio of the signal with phonon power *on*,  $S$ , to the signal with phonon power *off*,  $S_0$ , and plots were made of  $S/S_0$  versus  $\nu_r$  for two different phonon power levels. These curves appear in Fig. 3. To make sure that the observed effect was due to phonons and not to electromagnetic radiation, the experiment was repeated with several layers of tissue paper at the bottom of the MgO crystal to act as a phonon barrier. A small dummy load was placed on the quartz to keep the voltage across the quartz approximately equal to its value in the saturation experiment. Under these circumstances, no saturation effect was detected.

The curves in Fig. 3 show two expected features: first, the saturation increases with increasing phonon power, and second, it is maximum when the phonon frequency,  $\nu_p$ , is equal to the spin resonance frequency,  $\nu_r$  [see Eq. (75)]. They are also anomalous in two respects: first, with  $S/S_0 = 1/(1+\gamma)$ , it is clear that  $\gamma$  here is  $\sim 1$ , whereas the predicted  $\gamma$  is  $\sim 10^7$ ; second, from Eq. (75), the bandwidth of the effect would be expected to be of the order of the spin linewidth ( $\sim 10$  Mc/sec), but clearly it is much broader.

To determine, if possible, an upper limit to the bandwidth, an experiment was performed (on a different spectrometer) at  $\nu_r = 195$  Mc/sec and  $\nu_p = 13.1$  Mc/sec to obtain  $S/S_0$  as a function of phonon input power. This produced the rather startling result shown by the dotted curve of Fig. 4. For comparison, saturation curves taken at two lower frequencies are shown in the same figure; they appear considerably more normal.

It seems likely that the explanation of some of the above anomalies lies in the fact that the Cr<sup>+++</sup> ion in MgO does not satisfy the assumption that it causes little lattice distortion (see Sec. 2-A). As Low<sup>20</sup> points out, the Cr<sup>+++</sup> ion is a "poor fit" in the lattice

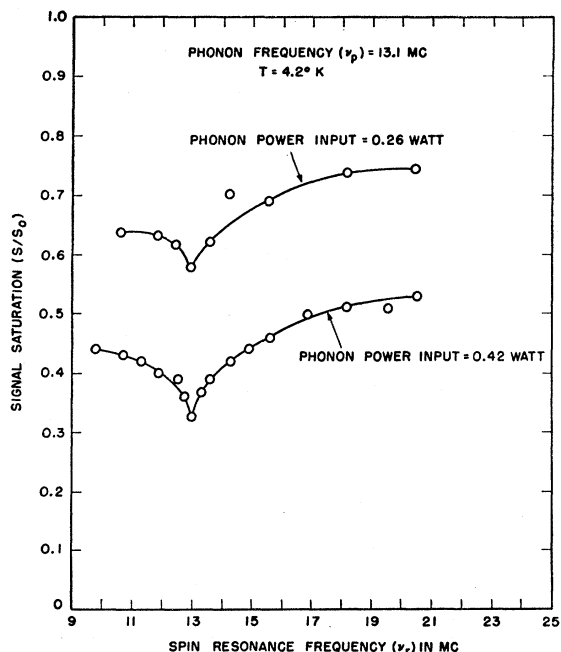


FIG. 3. Acoustic saturation vs spin resonance frequency in MgO doped with Cr<sup>+++</sup>.

<sup>21</sup> S. Simons, Proc. Cambridge Phil. Soc. 53, 702 (1957).

<sup>22</sup> We would like to acknowledge the cooperation of Joseph V. Fisher of Semi-elements, Inc., Saxonburg, Pennsylvania, in obtaining this crystal.

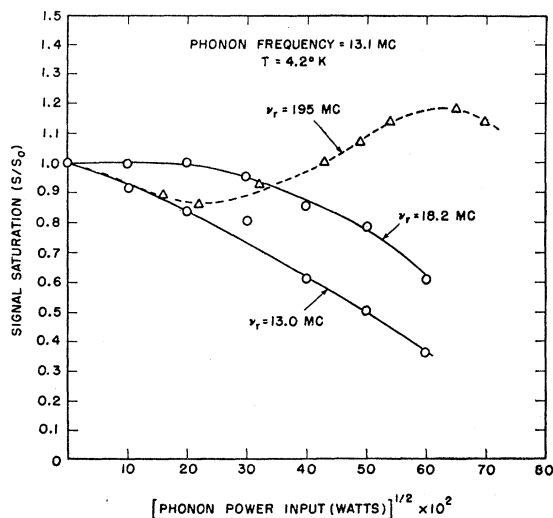


FIG. 4. Acoustic saturation vs square root of the phonon input power in MgO doped with  $\text{Cr}^{+++}$ .

because its uncompensated extra charge causes it to pull in the surrounding oxygen ions. If this effect is large enough, our theory no longer applies. Some evidence that this may be the case is found in the fact that, although our order-of-magnitude calculations predicted  $W_{\text{eff}} \sim 10^{-1}$  sec, that is,  $\tau_p(\text{relaxation}) \sim 10$  sec, crude observation indicated that the relaxation time was certainly less than 1 sec. If an accurate measurement of  $\tau$  yielded times considerably less than 1 sec, this would indicate the presence of a different type of spin-phonon interaction mechanism. (Such a measurement needs to be made.) Korringa<sup>4</sup> shows that in the case of  $F$  centers, the radial normal modes of the nearest neighbors (which contribute nothing in our theory) are the chief vehicle of the interaction, and can result in much shorter relaxation times than those predicted on the basis of the theory we have described.

The broad bandwidth of the interaction might possibly be interpreted as being the result of the contribution of a frequency-independent Raman mechanism. Such terms exist in our theory [see terms in Eq. (84) which have  $\nu_k^2 k = \nu_r$ ], but they are far too small to account for the observed effect. Conceivably, they might be considerably larger in a theory that included lattice distortion. Another possibility is that part of the saturation is due to heating of the crystal by the phonons, thus causing signal decrease, in accord with the Curie law. However, this seems unlikely in view of the fact that thermal heating would have an effect completely independent of frequency, which is evidently not true in this case if the results at 195 Mc/sec are taken into consideration.

The peculiar saturation curve obtained at 195 Mc/sec is difficult to interpret, especially the fact that  $S/S_0 > 1$ . Such an effect was also observed in fused quartz (see the following section). The line width was carefully

measured to see if any compensating decrease in width accompanied the increase in height, but the data were not quite good enough to determine this. Further work is required.

Experiments were also conducted on the low-field Kramers doublets in ruby and potassium chromicyanide, and, as predicted in Sec. 3-C, no acoustic saturation was observed. The experiment on the ruby crossover region is now being designed.

### C. Experiments on Irradiated Natural Quartz

An apparent saturation effect was observed in a crystal of Brazilian quartz that had been given a  $1.4 \times 10^7$  rad dose of 1-Mev  $\gamma$  rays in a  $\text{Co}^{60}$  source. Some of the data appear in Fig. 5. (The large error is the result of the fact that the  $F$ -center quartz contained only about  $10^{17}$  spins/cm<sup>3</sup>, and the signal-to-noise ratio, consequently, was poor. A control experiment showed that the saturation disappeared when a phonon barrier was used.) The effect here seems roughly independent of frequency. To determine the bandwidth, an experiment was performed at  $\nu_r = 189$  Mc/sec, and revealed  $S/S_0 \sim 0.6$  at a power input of 0.2 watt. (The  $S/S_0$  versus phonon power curve was normal.) Since our power determinations were quite crude, this observation is probably not inconsistent with the statement that the saturation is not a function of frequency.

Jacobsen, Shiren, and Tucker<sup>17</sup> also have reported a frequency-independent saturation effect in irradiated quartz, which they observed with microwave phonons. The bandwidth was greater than 500 Mc/sec in their case.

These observations point strongly to an assumption of thermal heating. To examine this possibility, let us approximate the crystal by a sphere of radius  $R$ , with thermal conductivity  $k$ , immersed in a bath that maintains the surface at temperature  $T_0$ . Assume that a quartz vibrator attached to the sphere introduces acoustic power  $P_{\text{in}}$  that is lost through radiation to the bath (relaxation time,  $\tau_r$ ) and by conversion into thermal phonons by phonon-phonon collisions, and so

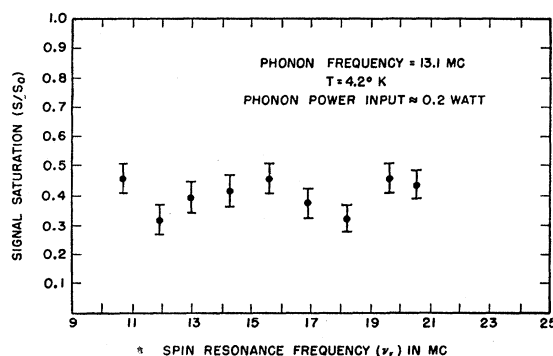


FIG. 5. Apparent acoustic saturation vs frequency in crystalline  $F$ -center quartz.

on (relaxation time,  $\tau_t$ ). Then, we have

$$\begin{aligned} P_{\text{in}} &= P_{\text{th}} + P_{\text{rad}} \\ &= \mathcal{E}V \left( \frac{1}{\tau_t} + \frac{1}{\tau_r} \right), \end{aligned} \quad (91)$$

from which

$$P_{\text{th}} = P_{\text{in}} (1 + \tau_t / \tau_r)^{-1}. \quad (92)$$

The heat diffusion equation for a sphere with a power source ( $P_{\text{th}}/V$ ) ergs/cm<sup>3</sup>-sec distributed uniformly throughout is

$$k \nabla^2 T + \frac{P_{\text{th}}}{V} = \rho c \frac{\partial T}{\partial t} = 0, \quad (93)$$

if a steady state is assumed. This is solved by using Gauss's theorem to obtain

$$T = (P_{\text{th}}/6kV)(R^2 - r^2) + T_0, \quad (94)$$

from which

$$T_{\text{max}} = (P_{\text{th}}/8\pi kR) + T_0. \quad (95)$$

Taking one half this as a rough average temperature rise, and using Eq. (92), we find

$$\frac{S}{S_0} = \frac{T_0}{T_{\text{av}}} = \frac{1}{1 + P_{\text{in}}/16\pi T_0 R k (1 + \tau_t/\tau_r)}. \quad (96)$$

Suppose we take  $P_{\text{in}} = \frac{1}{2}$  watt,  $T_0 = 4.2^\circ\text{K}$  and  $R \sim 1$  cm. The most favorable situation for the thermal effect is if  $\tau_t \ll \tau_r$  and  $k$  is very small. Experimental measure-

ments on thermal conductivity in neutron-irradiated crystalline quartz at  $T = 4.2^\circ\text{K}$  indicate that  $k$  decreases as the dose increases (owing to formation of lattice defects), and approaches the conductivity of quartz glass,  $k = 10^{-3}$  watt/cm-deg, as a limit. Taking  $\tau_t = 0$ , and  $k = 10^{-3}$ , we find  $S/S_0 = 0.3$ . In our experiment, we obtained  $S/S_0 \sim 0.4$ . Thus, in the most favorable case, the thermal heating effect is just large enough to be significant. Actually the situation is not so simple because, as we have indicated in connection with Eq. (90),  $\tau_t$  (which is  $\sim \tau_{\text{(phonon-phonon)}}$ ) should be  $10^5$  times greater than  $\tau_r$ , making thermal heating negligible.

If thermal heating is indeed the cause of the effect, an even greater saturation should be seen in irradiated fused quartz, since its thermal conductivity is reported to be lower than that of natural quartz. However, when the experiment was performed, it was found that, at a phonon power  $\sim 0.2$  watt,  $S/S_0 = 1.15 \pm 0.03$ , which is an increase in signal similar to that seen in MgO. There was some indication of a decrease  $\sim 5\%$  in linewidth accompanying the increase in line height. It should be noted that in a slope measurement the maximum slope is reciprocally proportional to the *square* of the linewidth. Hence these two effects tend to cancel each other.

#### ACKNOWLEDGMENT

The authors wish to thank B. V. Gokhale for some very illuminating discussions on the perturbation procedures used.