PHYSICAL REVIEW VOLUME 134, NUMBER 3A 4 MAY 1964

Selection Rules and Angular Dependence in Paramagnetic Acoustic Resonance*

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(Received 28 October 1963; revised manuscript received 2 January 1964)

The problem of spin transitions between magnetic sublevels under ultrasonic excitation is treated by considering perturbation terms $\beta\mathbf{H}_0\cdot\boldsymbol{h}\cdot\mathbf{S}$ (dipolar) and $\mathbf{S}\cdot\boldsymbol{d}\cdot\mathbf{S}$ (quadrupolar). When the tensors $\boldsymbol{h}$ and $\boldsymbol{d}$ are expanded in acoustic strains, the resulting expansion coefficients form a magnetoelastic matrix which describes the spin-phonon coupling. For the quadrupolar term which is dominant for $S>\frac{1}{2}$, the magnetoelastic matrices are obtained for all crystal classes with the assumption that they are not necessarily symmetric. By using the transformation of spin operators, which includes the case of anisotropic g factors, general expressions for acoustic transition probabilities in dipolar and quadrupolar cases are derived in terms of h_i and d_i. It is shown, on the basis of these expressions with magnetoelastic matrices and strain transformations to crystalline axes, how the acoustic absorption coefficients are obtained for any direction of polarization and wave propagation, for arbitrary direction of the external magnetic field, and for all crystal classes. It turns out that the explicit angular dependence of absorption coefficients is different in the dipolar and quadrupolar cases for anisotropic g factors, but often for isotropic g factors the forms of angular dependences are similar. This treatment is valid for iron group and S state ions and also is formally applicable to nuclear quadrupole transitions under acoustic excitation. The theory is compared to the results of our experiments, in which absorption coefficients at magnetic resonance were measured for 10 kMc/sec acoustic waves. The essential points of the theory are borne out by experimentally measured angular dependences of acoustic absorption.

I. INTRODUCTION

THE investigation of spin-phonon interactions by paramagnetic acoustic resonance has been stimulated by the close relationship of this problem to that of spin-lattice relaxation. The experimental methods[1–6] which have emerged during the last few years were preceded and accompanied by general theoretical treatments[7–9] based mainly on the assumption of the Van Vleck[10] spin-phonon interaction mechanism, although other mechanisms have also been considered.[7]

The acoustic-resonance methods involve propagation of coherent acoustic waves (often at microwave frequencies) in single crystals containing paramagnetic ions, usually at low temperatures. When the frequency of the acoustic waves corresponds to the separation of magnetic sublevels of the ion, transitions are induced and an absorption of the acoustic waves is observed. Certain sets of selection rules, which depend on the dominant coupling mechanism, effectively describe these transitions. The exact form of these rules for different acoustic modes in various physical systems determines what types of experiments can be performed. Interpretation of observations involving the propagation of acoustic waves at magnetic resonance is contingent on a knowledge of the form of the angular and polarization dependence of the spin-phonon transition probabilities. To experiments of this kind belong paramagnetic acoustic absorption,[3–6] certain maser experiments[11] (acoustic or electromagnetic-acoustic maser), saturation effects of ultrasonics on ordinary spin resonance,[1,2] and nuclear polarization by acoustic means.[12]

In this paper we calculate paramagnetic-acoustic absorption coefficients applicable to iron group and S-state ions for arbitrary direction of wave propagation and polarization and for any external magnetic-field direction. The derivations are given for both dipolar- and quadrupolar-selection rules and for all crystal field symmetries. A few representative cases are compared with experiments.

II. CALCULATION OF ACOUSTIC TRANSITION PROBABILITIES

A. Phenomenological Spin-Phonon Interaction

Detailed investigations of the paramagnetic-resonance spectra of iron-group ions have established

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[12] C. D. Jeffries, Progr. Cryog. 3, 149 (1961).

that, to a good approximation, the energy levels of the lowest state may be described by an effective spin Hamiltonian:

$$\mathcal{H}=\beta\mathbf{H}_0\cdot\boldsymbol{g}\cdot\mathbf{S}+\mathbf{S}\cdot\boldsymbol{D}\cdot\mathbf{S}. \qquad (1)$$

The first term is the Zeeman interaction of the effective magnetic moment of the ion with the external field $\mathbf{H}_0$; the second term is the electrostatic interaction of the effective quadrupole moment of the ion with the crystalline electric field. In some cases, e.g., S-state ions Mn^{2+} and Fe^{3+} in cubic fields, it is necessary to add higher order crystal field terms of the form aS_x^4. The spin Hamiltonian, Eq. (1), has been of considerable utility in interpreting paramagnetic-resonance data, and in obtaining the values of the $\boldsymbol{g}$ tensor and the $\boldsymbol{D}$ tensor.

In the Van Vleck theory[10] of spin-lattice relaxation, the dominant spin-phonon interaction is assumed to be one in which the periodically modulated crystalline electric field affects the orbital motion of the electrons, which is coupled to the spin through spin-orbit coupling. The over-all effect of this modulation, due to lattice strains set up either by thermal vibration or by applied coherent acoustic waves, is to modulate the static interaction, Eq. (1), and to induce transitions between the magnetic levels. This time-dependent perturbation may be expressed in the form

$$\mathcal{H}_{\mathrm{sp}}=\beta\mathbf{H}_0\cdot\boldsymbol{h}\cdot\mathbf{S}+\mathbf{S}\cdot\boldsymbol{d}\cdot\mathbf{S}, \qquad (2)$$

where $\boldsymbol{h}$ is a tensor representing the modulation of the g tensor; similarly, $\boldsymbol{d}$ is a tensor representing the modulation of the $\boldsymbol{D}$ tensor. The use of the phenomenological spin-phonon Hamiltonian, Eq. (2), is justified by the fact that it is consistent with the detailed microscopic relaxation theory. In this theory[8] the crystalline field part of the total Hamiltonian of the paramagnetic ion is expanded in the displacements of the ion nearest neighbors, and these are further expanded in the normal modes of the lattice vibrations, thus leading to a term in which the coordinates of the lattice and the paramagnetic ion are mixed. This is the spin-phonon interaction operator and it is shown to be

$$\mathcal{H}_{\mathrm{sp}}=\sum_{f,i>j}[n(\omega)\hbar\omega/Mv^2]^{1/2}\cdot\sin\gamma\cdot R\cdot a_f\cdot[\lambda L_i{}^f\hbar\omega S_i$$
$$+2\beta\lambda L_{ij}{}^f(S_iH_j+S_jH_i)+\lambda^2L_{ij}{}^f(S_iS_j+S_jS_i)]; \qquad (3)$$

where $f=1, 2, \cdots, 6$; $i,j=1, 2, 3$ (or x, y, z), $M=$ crystal mass, $v=$ sound velocity (lattice is assumed dispersionless, all phonons having the same velocity), $n(\omega)=$ number of phonons of frequency ω, $\lambda=$ spin-orbit coupling constant, $R=$ equilibrium distance from the nucleus of the paramagnetic ion to the nearest neighbor. Here γ is a phase factor resulting from the expansion of the ionic displacement from equilibrium in normal lattice modes, a_f are coefficients determined by the direction cosines of the velocity and polarization, H_i are components of the magnetic field, $L_{ij}{}^f$ are tensor components representing sums of matrix elements of crystalline field and angular-momentum operators between the ground and excited orbital states. S_i are spin components; one should bear in mind that they are components of the real spin of the ion in the ground state and thus expressions involving them are not generally interpretable in terms of S_i, S_j in Eq. (2), where S is the effective spin. However, for iron-group ions in many cases the effective and the real spins are the same and then formal relationships between quantities in Eq. (3) and phenomenological parameters in Eq. (2) can be obtained.

Although it is possible that in some physical systems both terms of Eq. (2) would have to be taken into account, in most cases for $S>\frac{1}{2}$ at the field strength of several thousand oersteds, the second term predominates since it is larger by $\lambda/\beta H$ than the first term. On the other hand, for $S=\frac{1}{2}$ the matrix elements of the operator $S_iS_j+S_jS_i$ vanish, and thus we have to be concerned only with the first term.

Further validity of Eq. (2) was demonstrated by Shiren,[4] who has shown that Van Vleck calculations can be reduced explicitly to the form of the dominant second term for Cr^{3+} and Ni^{2+} in MgO. Blume and Orbach[13] have shown that even the S-state ion Mn^{2+} in MgO can be treated by this form of spin-phonon perturbation. Although MgO is cubic, and the static $\boldsymbol{D}$ tensor vanishes; nevertheless the modulation restores effectively the quadrupolar term as a dominant one for relaxation.

The utility of the effective spin-phonon Hamiltonian is that it enables us to calculate, as is done in this paper, the transition probabilities due to any specified lattice strains from the simple spin eigenfunctions of the spin Hamiltonian. Such expressions are very useful in analyzing the angular dependence and polarization dependence of the data from acoustic experiments and are necessary in order to determine experimentally the spin-phonon coupling constants, defined by Eq. (5). In this sense this phenomenological approach is an extension of the widespread use of the spin Hamiltonian in the analysis of energy levels.

B. Transition Probabilities for Quadrupolar Term ($\mathbf{S}\cdot\boldsymbol{d}\cdot\mathbf{S}$; $S>\frac{1}{2}$)

Most experimental work so far has been done on ions with effective spin $S>\frac{1}{2}$ or S-state ions. Since tensor $\boldsymbol{D}$ in Eq. (1) is symmetric and, furthermore, since expressions L_{ij} in Eq. (3) are symmetric in i and j, we expect the tensor $\boldsymbol{d}$ to be also symmetric; then the second term of Eq. (2) becomes

$$\mathcal{H}_q=d_{xx}S_x^2+d_{yy}S_y^2+d_{zz}S_z^2+d_{yz}(S_zS_y+S_yS_z)$$
$$+d_{xz}(S_zS_x+S_xS_z)+d_{xy}(S_yS_x+S_xS_y), \qquad (4)$$

where x, y, z are principal axes of the local crystalline electric field.

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[13] M. Blume and R. Orbach, Phys. Rev. **127**, 1587 (1962).

Linear expansion of d_{ij} in strains defines the magnetoelastic matrix G:

$$d_{ij}=\sum_{k,l} G_{ijkl}\epsilon_{kl}\,, \tag{5}$$

$\epsilon_{kl}=$ strains; $k,\ l=x,\ y,\ z$.

For a given wave mode and crystalline field symmetry, a particular combination of coefficients G_{ijkl} describes the paramagnetic-acoustic-resonance effects. The pertinent combinations can be obtained from the form of magnetoelastic matrices and from the strains associated with elastic waves. The most general matrix (triclinic symmetry) contains 36 independent constants (30 if the trace of $\boldsymbol{d}$ is set equal to zero) and for a general strain does lead to rather complex expressions for transition probabilities. The situation is simpler for higher symmetries, particularly if one takes the trace of the tensor $\boldsymbol{d}$ equal to zero.[14]

The assumption of zero trace and the effect it has on the form of G amounts to a special definition of the magnetoelastic matrix, but the number of independent matrix components which can be obtained from experiment is not affected by this assumption.[15] The number of independent elements depends in part on whether the G matrix is a symmetric or a nonsymmetric one. It seems that no physical reason (such as exists in the case of the elastic tensor) can be given for *intrinsic* symmetry of the G matrix. Thus, we shall assume it to be nonsymmetric and in those special cases when symmetry or near-symmetry exists, suitable changes can be easily introduced. The number of independent components of the G matrix is determined by the local symmetry, since Eq. (5) must be invariant to a coordinate transformation included in the symmetry elements of the local crystalline field. Applying these arguments to magnetoelastic matrices, somewhat in analogy to the photoelastic case, and $\sum_{i=1}^{3} d_i=0$, we obtain results which are given below in the Voigt notation.

Monoclinic, classes C_2, C_{2h}, C_{1h}:

$$G=\left[\begin{array}{cccccc} G_{11} & G_{12} & G_{13} & 0 & 0 & G_{16} \\ G_{21} & G_{22} & G_{23} & 0 & 0 & G_{26} \\ -(G_{11}+G_{21}) & -(G_{12}+G_{22}) & -(G_{13}+G_{23}) & 0 & 0 & -(G_{16}+G_{26}) \\ 0 & 0 & 0 & G_{44} & G_{45} & 0 \\ 0 & 0 & 0 & G_{54} & G_{55} & 0 \\ G_{61} & G_{62} & G_{63} & 0 & 0 & G_{66} \end{array}\right]. \tag{6}$$

Here, and in all other cases, the rotation axis is taken along the Ox_3 (z direction) axis. From (6), the magnetoelastic matrix for orthorhombic symmetry, classes D_2, C_{2v} and D_{2h} can be obtained by setting $G_{16}=G_{26}=G_{45}=G_{54}=G_{61}=G_{62}=G_{63}=0$.

Trigonal, classes C_3, C_{3i}:

$$G=\left[\begin{array}{cccccc} G_{11} & G_{12} & -G_{33}/2 & G_{14} & G_{15} & G_{16} \\ G_{12} & G_{11} & -G_{33}/2 & -G_{14} & -G_{15} & -G_{16} \\ -(G_{11}+G_{12}) & -(G_{11}+G_{12}) & G_{33} & 0 & 0 & 0 \\ G_{41} & -G_{41} & 0 & G_{44} & G_{45} & G_{46} \\ -G_{46} & G_{46} & 0 & -G_{45} & G_{44} & G_{41} \\ -G_{16} & G_{16} & 0 & -G_{15} & G_{14} & (G_{11}-G_{12})/2 \end{array}\right]. \tag{7}$$

The following substitutions in (7) are required to obtain G matrices for: trigonal symmetry, classes C_{3v}, D_3, D_{3d}—set $G_{15}=G_{16}=G_{45}=G_{46}=0$; tetragonal symmetry, classes C_{4v}, D_2, D_4, D_{4h}—set $G_{14}=G_{15}=G_{16}=G_{41}=G_{45}=G_{46}=0$, substitute G_{66} for $(G_{11}-G_{12}/2)$, tetragonal symmetry, classes C_4, S_4, C_{4h}—set $G_{14}=G_{15}=G_{41}=G_{46}=0$, substitute G_{66} for $(G_{11}-G_{12}/2)$, $-G_{61}$ for G_{16} in the last row only; hexagonal symmetry, classes C_6, C_{3h}, C_{6h}—set $G_{14}=G_{15}=G_{41}=G_{46}=0$; hexagonal symmetry, classes D_{3h}, C_{6v}, D_6, D_{6h}—set $G_{14}=G_{15}=G_{16}=G_{41}=G_{45}=G_{46}=0$.

Cubic, classes T, T_h:

$$G=\left[\begin{array}{cccccc} G_{11} & G_{12} & -(G_{11}+G_{12}) & 0 & 0 & 0 \\ -(G_{11}+G_{12}) & G_{11} & G_{12} & 0 & 0 & 0 \\ G_{12} & -(G_{11}+G_{12}) & G_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & G_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & G_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & G_{44} \end{array}\right]. \tag{8}$$

By substituting $-G_{11}/2$ for G_{12} in (8) we obtain the magnetoelastic matrix for cubic symmetry classes T_d, O, O_h. In this case we have a symmetric matrix with only two independent constants.

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[14] R. B. Shulman, B. J. Wylunda, and P. W. Anderson, Phys. Rev. **107**, 953 (1957).

[15] R. J. Harrison and P. L. Sagalyn, Phys. Rev. **128**, 1630 (1962).

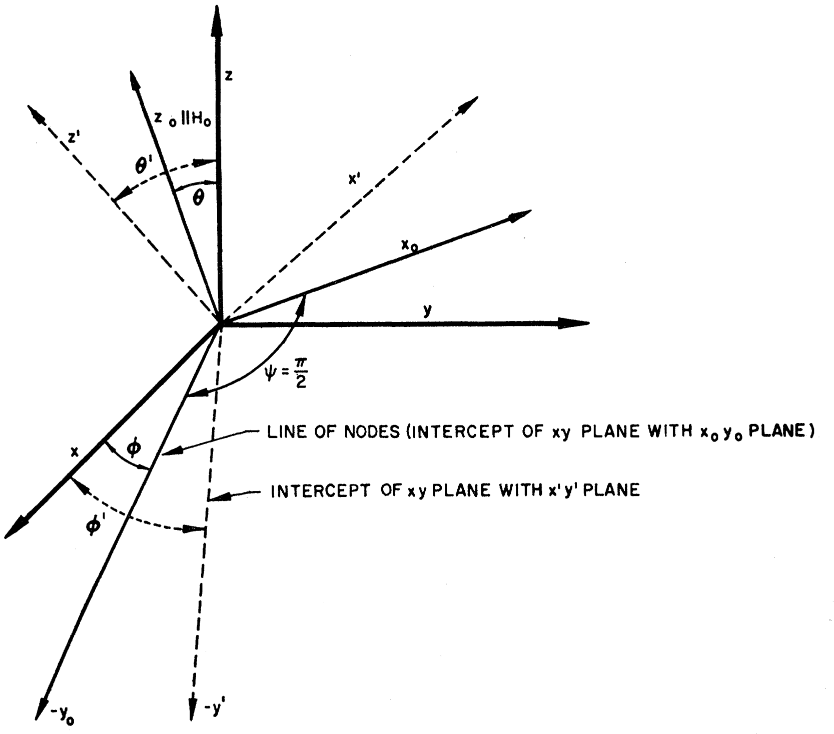

FIG. 1. x, y, z—crystalline coordinate system. x_0, y_0, z_0—laboratory coordinate system. x', y', z'—diagonal coordinate system. $\theta' = \sin^{-1}[(g_\perp/g)\sin\theta]$, $\varphi' = \sin^{-1}[(g_x/g_\perp)\sin\varphi]$. Direction of H_0 in the xyz system is specified by the Eulerian angles θ, φ; since the choice of x_0, y_0 is arbitrary, the third Eulerian angle is taken as $\psi = \pi/2$ without loss of generality.

If a wave can be described by one strain component $\epsilon_i \cos\omega t$ $(i = 1, 2 \cdots 6)$ in the crystalline-field coordinate system, the elements of the G matrix entering in the transition probabilities can be obtained from the above given expressions (6)–(8), by taking only the column which corresponds to this strain. In the more complicated cases these matrices are to be used upon performing strain transformation to crystalline coordinate system on the basis of the known polarization and direction of wave propagation. Thus, a pure longitudinal wave[15a] of strain $\epsilon_{x''x''} = \epsilon$, propagating in l, m, n direction with respect to crystalline axes (x,y,z) is equivalent to strains referred to those axes:

$$\begin{aligned} \epsilon_{xx} &= l^2\epsilon & \epsilon_{yz} &= 2nm\epsilon \\ \epsilon_{yy} &= m^2\epsilon & \epsilon_{zx} &= 2nl\epsilon \\ \epsilon_{zz} &= n^2\epsilon & \epsilon_{xy} &= 2lm\epsilon , \end{aligned} \tag{9}$$

The combination of nonvanishing components of the G matrix and strains will determine then which components of the $\boldsymbol{d}$ tensor are to be included and thus which matrix elements of the spin operators would have to be evaluated in order to find the acoustic transition probabilities. Therefore these matrix elements will depend explicitly on the direction of the magnetic field H_0, the direction and polarization of the acoustic wave, and the local crystal-field symmetry. Taking ψ_m and ψ_m' as eigenfunctions of the static Hamiltonian in Eq. (1), we can write the acoustic transition probability as

$$W = [g(\nu)/(2\hbar)^2] |\langle\psi_m|\mathcal{H}_{qa}|\psi_m'\rangle^2 \text{ sec}^{-1}. \tag{10}$$

Here $\mathcal{H}_{qa}$ is the amplitude of the time-dependent perturbation $\mathcal{H}_q(t) = \mathcal{H}_{qa}\cos\omega t$, and $g(\nu)$ is the normalized line shape of the acoustic-resonance line.

If the D term is appreciable, ψ_m and ψ_m' can be obtained exactly by diagonalizing the spin Hamiltonian. On the other hand, if the D term is negligible (or H_0 is parallel to the c axis) to a good approximation we can get useful formulas by transforming the spin operators in the crystal xyz axes to a new coordinate system $x'y'z'$ in which the Zeeman term alone is diagonal, i.e., the transformation must be such that the coefficients of $S_{x'} \pm iS_{y'}$ vanish. We define $x'y'z'$ by the Eulerian angles θ', φ', ψ' in Goldstein's notation[16] and may furthermore take $\psi' = \pi/2$ without loss of generality (see Fig. 1). The same figure also shows a laboratory coordinate system $x_0y_0z_0$ defined by Eulerian angles θ, φ, and $\psi = \pi/2$, with the field H_0 along z_0.

In the general case the spin components transform

[15a] Usually of interest are directions of propagation near the pure mode axes. Such directions include axes of twofold or higher rotational symmetry, directions perpendicular to a sixfold axis or to a reflection plane, as well as other directions which depend on relations between elastic constants and, in some special cases of cubic and tetragonal symmetry, can include any direction in the crystal. [See F. E. Borgnis, Phys. Rev. **98**, 1000 (1955)]. If a pure mode cannot be propagated along a given direction, the wave can always be decomposed into nonindependent longitudinal and transverse components.

[16] H. Goldstein, *Classical Mechanics* (Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1951), p. 107.

as follows:

$$S_x=-\frac{g_{\parallel}g_x}{g_{\perp}g}\cos\theta\,\sin\varphi S_x'-\frac{g_y}{g_{\perp}}\cos\varphi S_y'+\frac{g_x}{g}\sin\theta\,\sin\varphi S_z',$$

$$S_y=\frac{g_{\parallel}g_y}{g_{\perp}g}\cos\theta\,\cos\varphi S_x'-\frac{g_x}{g}\sin\varphi S_y'-\frac{g_y}{g}\sin\theta\,\cos\varphi S_z',$$

$$S_z=\frac{g_{\perp}}{g}\sin\theta S_x'+\frac{g_{\parallel}}{g}\cos\theta S_z'. \tag{11}$$

Here

$$g_{\perp}=(g_x^2\sin^2\varphi+g_y^2\cos^2\varphi)^{1/2},$$
$$g=(g_{\parallel}^2\cos^2\theta+g_{\perp}^2\sin^2\theta)^{1/2}.$$

When the g factor is isotropic, it drops out of the transformation expressions and then the diagonal and laboratory systems coincide. Sometimes, when there is an appreciable mixing of wave functions by an axial field, they are computed and given in the laboratory coordinate system; in such cases Eq. (11) also can be used to obtain the matrix elements in (10). When the total spin Hamiltonian is numerically diagonalized in crystalline coordinates, matrix elements can be calculated directly using Eqs. (4) and (10).

With (10) we get acoustic absorption coefficients at paramagnetic resonance:

$$\alpha=\frac{\Delta nh\nu}{\frac{1}{2}\rho v^3\epsilon^2}W=\frac{\pi\Delta n\nu g(\nu)}{\rho v^3\epsilon^2\hbar}|\langle\psi_m|\mathcal{H}_{qa}|\psi_{m'}\rangle|^2, \tag{12}$$

ρ = density of crystal; Δn = spin-population excess per unit volume in the lower level; ϵ is the peak value of strain. Since it also enters into $\mathcal{H}_{qa}$, the strain cancels out, as it should for purely magnetic attenuation.

Now using Eqs. (4) through (12), the acoustic absorption coefficients for practically any case of interest can be obtained in terms of angular functions and spin-phonon coupling constants.

General expressions for paramagnetic acoustic absorption coefficients for cubic symmetry (T_d,0,O_h) thus derived are:

1. Longitudinal Wave; Strain in (l,m,n) Direction with Respect to Cubic Axes (x,y,z), M → M−1

$$\begin{aligned}\alpha=C_1\{[&-(\sin2\theta/4)(3G_{11}l^2\sin^2\varphi\\&+3G_{11}m^2\cos^2\varphi-3G_{11}n^2-4G_{44}lm\sin2\varphi)\\&+2G_{14}\cos2\theta(mn\cos\varphi-ln\sin\varphi)]^2\\&+[(\sin\theta/4)(-3G_{11}l^2\sin2\varphi\\&+3G_{11}m^2\sin2\varphi+8G_{44}lm\cos2\varphi)\\&\quad-2G_{44}\cos\theta(mn\sin\varphi+ln\cos\varphi)]^2\},\end{aligned}$$

$$C_1=\frac{\pi\Delta n\nu g(\nu)}{\rho v^3\hbar}\frac{[(S+M)(S-M+1)(2M-1)^2]}{4}. \tag{13}$$

2. Longitudinal Wave; Strain in (l,m,n) Direction, M → M−2

$$\begin{aligned}\alpha=C_2\{&\tfrac{1}{2}G_{11}[(l^2-1)\cos^2\theta\sin^2\varphi\\&+(m^2-1)\cos^2\theta\cos^2\varphi+n^2+(3n^2-1)\sin^2\theta\\&+\cos^2\varphi(m^2-2l^2)+\sin^2\varphi(l^2-2m^2)\\&+2\cos^2\theta(m^2\cos^2\varphi+l^2\sin^2\varphi)]\\&+2G_{44}(mn\cos\varphi\sin2\theta-ln\sin\varphi\sin2\theta)\\&-2G_{44}lm\sin2\varphi(\cos^2\theta+1)\}^2\\&+16C_2[\tfrac{3}{8}G_{11}(l^2-m^2)\sin2\varphi\cos\theta\\&-G_{44}(mn\sin\theta\sin\varphi+nl\sin\theta\cos\varphi\\&\qquad+lm\cos\theta\cos2\varphi)]^2,\end{aligned}$$

$$\begin{aligned}C_2=[\pi\Delta n\nu g(\nu)/16\rho v^3\hbar][&(S+M)(S-M+1)\\&\times(S+M-1)(S-M+2)].\end{aligned} \tag{14}$$

A strain $\epsilon_{x''y''}$ associated with a transverse wave can be related to the crystalline-axes strains by expressions similar to Eq. (9). With l_1, m_1, n_1—direction cosines of x''; l_2, m_2, n_2—direction cosines of y''; and substitutions: $l_1\cdot l_2\rightarrow l^2$, $m_1\cdot m_2\rightarrow m^2$, $n_1\cdot n_2\rightarrow n^2$, $(m_1n_2+m_2n_1)\rightarrow 2mn$, $(n_1l_2+n_2l_1)\rightarrow 2nl$, $(l_1m_2+l_2m_1)\rightarrow 2lm$ in equations of the type of Eqs. (13) and (14) we get expressions for absorption coefficients of any desired transverse mode for any direction of H_0.

By expanding the electric-field-gradient components in a Taylor series of the strain components and treating the acoustic wave as time-dependent perturbation on the nucleus, Bolef and Menes[17] calculated the coefficients of acoustic absorption due to the nuclear spins for longitudinal waves propagated along the cube axis. It should be pointed out that the method described in this section may be formally applied to nuclear quadrupole systems, where instead of Eq. (1) we have

$$\mathcal{H}=\beta_n g_n\mathbf{H}_0\cdot\mathbf{I}+\mathbf{I}\cdot\boldsymbol{P}\cdot\mathbf{I}, \tag{15}$$

and the nuclear spin-phonon perturbation is of the form $\mathcal{H}_q=\mathbf{I}\cdot\boldsymbol{d}_n\cdot\mathbf{I}$. Within the above mentioned restrictions on the wave functions, our results can be used to calculate acoustic absorption coefficients in nuclear quadrupole systems in terms of nuclear spin-lattice coupling constants.

C. Dipolar Selection Rules ($\beta\mathbf{H}_0\cdot\boldsymbol{h}\cdot\boldsymbol{S}$)

We now evaluate Eq. (10) using instead of H_q the dipolar spin-phonon perturbation,

$$\mathcal{H}_d=\beta\sum_{i,k=1}^{3}S_ih_{ik}H_k, \tag{16}$$

i, $k=x$, y, z. By comparing the terms in Eq. (3) which we have respectively absorbed into h_{ik} and d_{ik}, we expect the properties of the tensor $\boldsymbol{h}$ to be similar to those of the tensor $\boldsymbol{d}$. Furthermore, for small wave amplitudes we can make a linear expansion of $\boldsymbol{h}$ in

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[17] D. I. Bolef and M. Menes, Phys. Rev. **114**, 1441 (1959).

strains, as it was done for $\boldsymbol{d}$ in Eq. (5), and the matrix of coefficients defined by this expansion will then be of the form similar to that of the G matrix. With Eq. (11), (12), (16) and the following transformation of the components of the magnetic field (Fig. 1):

$$\begin{aligned} H_x &= H_0 \sin\varphi \sin\theta \\ H_y &= -H_0 \cos\varphi \sin\theta \\ H_z &= H_0 \cos\theta\,, \end{aligned} \tag{17}$$

we can now easily derive a general expression for the absorption coefficient in terms of h_i ($i=1, 2\cdots 6$ in Voigt notation). For the isotropic g factor in Eq. (1), the absorption coefficient for the transition $M \rightarrow M-1$ becomes

$$\begin{aligned} \alpha_d = C_3(H_0^2/\epsilon^2)\{&[-\tfrac{1}{2}(\sin 2\theta) \\ &\times(h_1 \sin^2\varphi + h_2 \cos^2\varphi - h_3 - h_6 \sin 2\varphi) \\ &+\cos 2\theta (h_4 \cos\varphi - h_5 \sin\varphi)]^2 \\ &+[\tfrac{1}{2}(\sin\theta)(-h_1 \sin 2\varphi + h_2 \sin 2\varphi + 2h_6 \cos 2\varphi) \\ &\qquad -\cos\theta (h_4 \sin\varphi + h_5 \cos\varphi)]^2\}\,, \\ C_3 = (\pi\Delta n\nu g(\nu)&\beta^2/\rho v^3 h)(S+M)(S-M+1)\,. \end{aligned} \tag{18}$$

But substitution $d_i \rightarrow h_i$ makes the expression in curly brackets identical to the one which can be derived quite generally for the isotropic case on the basis of the quadrupolar term of the previous section with Eqs. (4) and (11). Thus, in cubic crystals where wave functions are only slightly perturbed by the crystal field at H_0 values of several kiloersteds, the angular dependence of absorption coefficients (transition probabilities) in certain directions is essentially the same in dipolar and quadrupolar cases. In particular, for longitudinal waves propagating along the cube axis, except for variations (usually small) of H_0 with θ for some lines, the transition probabilities are proportional to $\sin^2\theta \cos^2\theta$ for both cases.

If the Zeeman wave functions are substantially perturbed by the crystalline field, then even for isotropic g's we would have different angular dependences of transition probabilities. This arises from the fact that in the quadrupolar case we would now have nonvanishing matrix elements of S_x^2, S_z^2, and $(S_xS_y+S_yS_x)$ for transitions between adjacent levels. When the g factors are anisotropic the explicit angular dependence in the two cases is of different form.

Thus, for H_0 in the x, z plane ($\varphi=-\pi/2$) we get with Eq. (11) in the quadrupolar case, $M \rightarrow M-1$:

$$\begin{aligned} \alpha_q = \frac{C_1}{\epsilon^2}\Bigg[&(d_3-d_1)g_{\parallel}g_{\perp}\frac{\cos\theta \sin\theta}{g_{\parallel}^2 \cos^2\theta + g_{\perp}^2 \sin^2\theta} \\ &+d_5\frac{g_{\parallel}^2 \cos^2\theta - g_{\perp}^2 \sin^2\theta}{g_{\parallel}^2 \cos^2\theta + g_{\perp}^2 \sin^2\theta}\Bigg]^2 \\ &+\frac{C_1}{\epsilon^2}\,\frac{(d_4 g_{\parallel} \cos\theta - d_6 g_{\perp} \sin\theta)^2}{g_{\parallel}^2 \cos^2\theta + g_{\perp}^2 \sin^2\theta}\,, \end{aligned} \tag{19}$$

and in the dipolar case:

$$\begin{aligned} \alpha_d = \frac{C_3 H_0^2}{\epsilon^2}\Bigg[&(h_3 g_{\perp} - h_1 g_{\parallel})\frac{\cos\theta \sin\theta}{(g_{\parallel}^2 \cos^2\theta + g_{\perp}^2 \sin^2\theta)^{1/2}} \\ &+h_5\frac{(g_{\parallel} \cos^2\theta - g_{\perp} \sin^2\theta)}{(g_{\parallel}^2 \cos^2\theta + g_{\perp} \sin^2\theta)^{1/2}}\Bigg]^2 \\ &+\frac{C_3 H_0^2}{\epsilon^2}(h_4 \cos\theta - h_6 \sin\theta)^2\,. \end{aligned}$$

Hence, in some cases the observation of the angular dependence of the transition probabilities does provide a means of distinguishing between the quadrupolar and dipolar rules, but in other cases it does not give a clear-cut proof for dominance of one or the other term. The dominance of the quadrupolar term in the experimentally studied cases has been established, however, by the relatively weak intensity of the $\frac{1}{2}\leftrightarrow-\frac{1}{2}$ transition.

In the formulas for $M \rightarrow M-1$ transitions, C_1 in Eq. (13) and C_3 in Eq. (18) contain expressions $(S+M)\times(S-M+1)(2M-1)^2$ and $(S+M)(S-M+1)$, which are characteristics of the quadrupolar and dipolar selection rules, respectively. On the basis of these expressions one expects the $\frac{1}{2}\leftrightarrow-\frac{1}{2}$ transition to be forbidden in the quadrupolar, but not in the dipolar case.

III. COMPARISON WITH EXPERIMENT

We have constructed an experimental apparatus (shown in Fig. 2), which is an adaptation of Jacobsen's[18] and Bommel-Dransfeld's[19] microwave phonon-generation technique to paramagnetic-acoustic-resonance absorption. Microwave acoustic pulses at frequency 10^{10} cps and of 1 μsec duration are generated in a quartz rod or plate which is inserted in one cavity, then transmitted through a paramagnetic sample and detected in the other cavity. All echoes are detected by the microwave receiver but only a particular one is integrated by a gated box-car integrator which puts out a dc voltage proportional to the acoustic pulse power. Waveguides and cavities are in a liquid-helium Dewar which is placed between the pole pieces of a Varian 12-in. magnet. When the magnetic field is varied through resonance, acoustic absorption lines due to spin transitions are displayed on the recorder which is connected to the box-car integrator. A system of waveguide and ferrite switches (to protect the receiver) allows studies of transmitted and reflected signals from both ends.

The problem of interest to experimentalists at these

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[18] E. H. Jacobsen, Phys. Rev. Letters **2**, 249 (1959); E. H. Jacobsen in *Quantum Electronics*, edited by C. H. Townes (Columbia University Press, New York, 1960); E. H. Jacobsen, J. Acoust. Soc. Am. **32**, 949 (1960).

[19] H. E. Bommel and K. Dransfeld, Phys. Rev. Letters **1**, 234 (1958); H. E. Bommel and K. Dransfeld, *ibid.* **3**, 83 (1959).

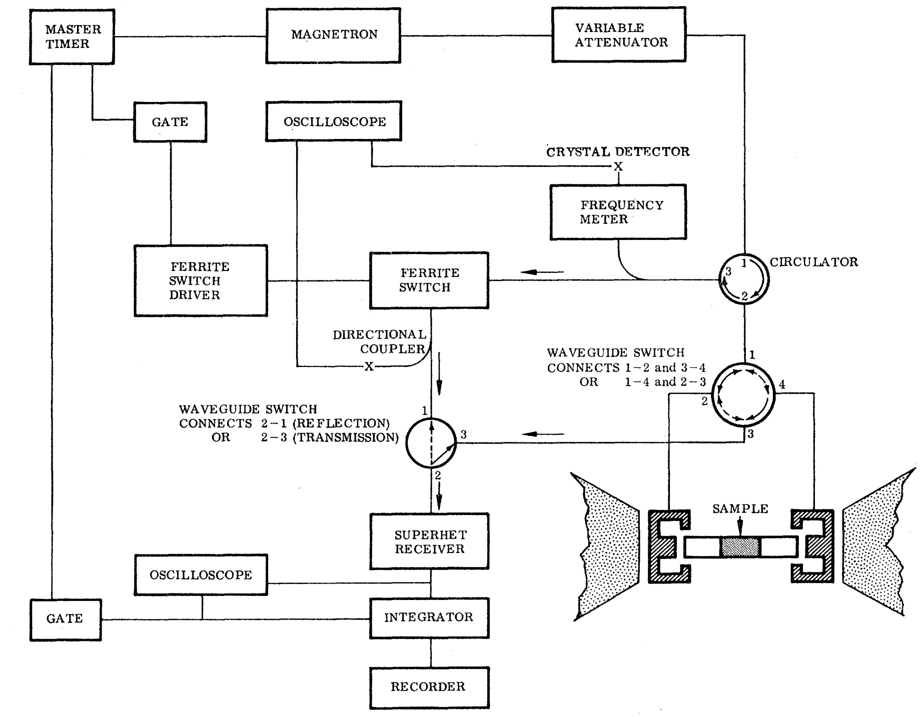

FIG. 2. Block diagram of experimental apparatus.

frequencies is how to achieve a satisfactory bond between the transducers and specimen. In our experiments the paramagnetic crystals are clamped between two quartz rods ($\frac{1}{8}$-in. diam), each of which has a circular brass collar ($\frac{7}{32}$-in. o.d.) glued to it with strong epoxy resin. One of the collars is threaded and fits inside of a cylindrical brass clamp, the other end of which fastens to the plain collar on the other quartz rod. The sample, both ends of which are wetted with nonaq stopcock grease (made by Fisher Company), is thus placed inside of a brass clamp under slight pressure from the transducers. Since it is essential to achieve a reasonably good parallelism of this combination as well as a good bond, the whole thing is tested and corrected until transmission of pulses of acoustic power at 500 Mc is maximized. The 500-Mc phonons can be easily transmitted at room temperature and for this reason are used as a test indicator for actual experiments at 10 kMc. The advantages of this technique are good mechanical strength and prevention of bending of the sample, something of importance here, because even a slight amount of bending may cause sufficient deviation from parallelism to destroy the signal. Another good feature is that samples put together in this way can be warmed up to room temperature and cooled down repeatedly without appreciable deterioration of transmission.

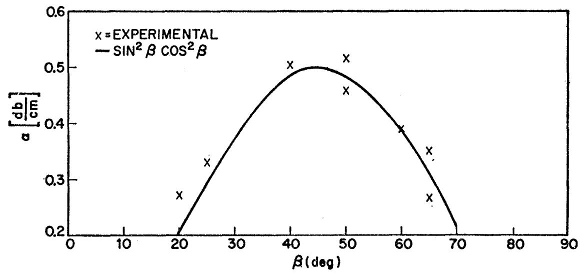

FIG. 3. Acoustic absorption coefficient of Eu^{2+} in CaF_2 at resonance versus angle β between H_0 and propagation direction of 9.3 kMc longitudinal waves.

In some experiments transverse waves were generated by exciting ferromagnetic resonance[19] in thin cobalt films. Cobalt films were chosen because they can be used to excite coherent phonons continuously over a range of several thousands oersteds and such magnetically broad excitation makes possible overlap and observation of relatively narrow paramagnetic acoustic absorption lines produced by spin transitions in the film substrate.

The angular variation of the acoustic absorption coefficient (lines $\frac{3}{2}\leftrightarrow\frac{1}{2}$ and $-\frac{3}{2}\leftrightarrow-\frac{5}{2}$) of Eu^{2+} ions in a CaF_2 crystal observed with our apparatus is shown in Fig. 3.

Divalent Eu has a $^4f^7$, $^8S_{7/2}$ configuration and in cubic CaF_2 is described by[20]

$$\mathcal{H}=\beta g\mathbf{H}\cdot\mathbf{S}+B_4(P_4^0+5P_4^4)+B_6(P_6^0-21P_6^6)+A\mathbf{S}\cdot\mathbf{I}, \quad (21)$$

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[20] J. M. Baker, B. Bleany, and W. Hayes, Proc. Roy. Soc. (London) **A247**, 141 (1958).

where the effective spin $S=7/2$, and $P_n{}^m$ are operators which transform like spherical harmonics $Y_n{}^m$ (e.g., $P_4{}^0 \propto S_z{}^4, S_z{}^2$; $P_4{}^4 \propto S_\pm{}^4$, etc.).

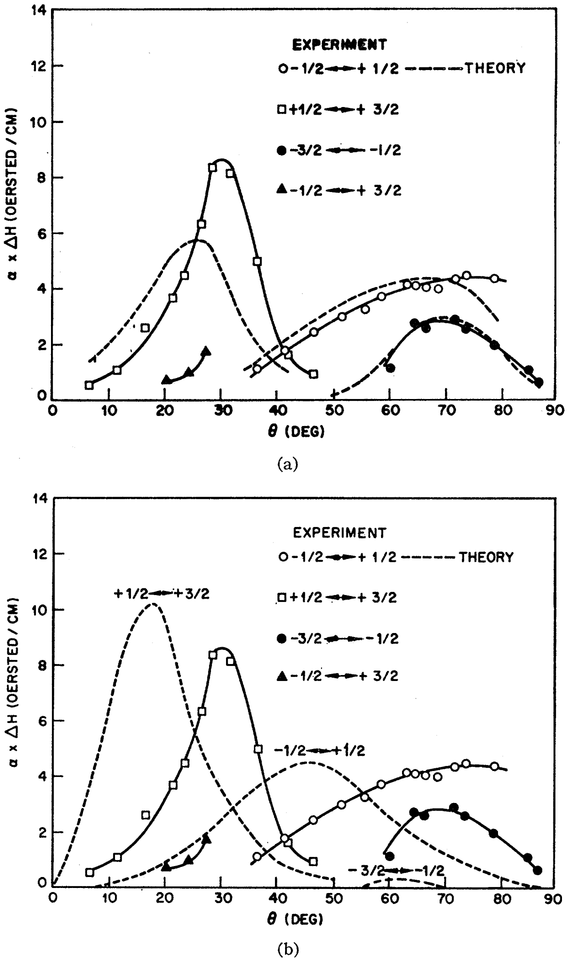
Since CaF_2 is cubic, Eq. (21) does not contain terms like $P_2{}^m$ which correspond to the quadrupolar term $S\cdot \boldsymbol{D}\cdot S$ in (1). However, the acoustic strain effectively restores a term $\mathbf{S}\cdot \boldsymbol{d}\cdot \mathbf{S}$ to the spin-phonon interaction, which may exceed the higher order terms. This occurs for Fe^{3+} in MgO[2], as demonstrated by the disappearance of the $+\frac{1}{2}\leftrightarrow-\frac{1}{2}$ line. We did not observe the $+\frac{1}{2}\leftrightarrow-\frac{1}{2}$ line in the acoustic spectrum of Eu^{2+} either, although it was quite strong in the ordinary spin-resonance spectrum. Actually, only the $\pm\frac{3}{2}\leftrightarrow\pm\frac{5}{2}$ and $\pm\frac{3}{2}\leftrightarrow\pm\frac{1}{2}$ acoustic resonance lines were observed. Probably the $\pm\frac{5}{2}\leftrightarrow\pm\frac{7}{2}$ lines were too weak to be seen; in the spin-resonance spectrum they were rather broad and weaker than expected.

In the experiment longitudinal waves were propagated along the [111] crystalline direction; β is the angle between H_0 and [111] in an arbitrary plane. It is easily shown that the angles θ and φ in Eq. (13) can be transformed to express the angular dependence of the absorption coefficient for longitudinal waves as $\sin^2\beta\cos^2\beta$ regardless of the plane spanned by H_0 and the [111] axis. When this is done it turns out that although we are dealing with longitudinal waves, the coefficient G_{11} disappears from the expression for α (since $d_1=d_2=d_3=0$) and we get:

$$\alpha_{[111]}=\frac{\pi\Delta n\nu g(\nu)}{\rho v^3\hbar}[(S+M)(S-M+1)] \times(2M-1)^2G_{44}{}^2\sin^2\beta\cos^2\beta. \quad (22)$$

No charge compensation is required in order to substitute divalent europium ions for Ca^{2+}; the local field symmetry is practically undistorted cubic. The static terms B_4 and B_6 in (21) are small enough so that the Zeeman wave functions assumed in the derivation of (22) would need correction of only a few percent. Corrections to Eq. (22) thus would be less than the experimental error and would not influence the generally satisfactory comparison between the $\sin^2\beta\cos^2\beta$ curve and experimental points. From the measured values of α, sample length of 7 mm, and Eu concentration (0.3%), we get the spin-phonon coupling constant, $G_{44}=6\pm2\cdot10^{-17}$ ergs.

Figures 4(a) and 4(b) show comparison between our experimental measurements of $\alpha/g(\nu)$ in 0.08% ruby (c axis taken as z; longitudinal waves were propagated along the c axis) and theoretical curves based on dipolar and quadrupolar selection rules and corrected for variations in Δn versus θ. Here the transition probabilities were calculated using Eq. (10) and exact wave functions[21] for both cases. As we can see, the agreement in angular dependence with experiment is more satisfactory for quadrupolar interaction than for dipolar, although there seems to be some discrepancy between experimental results and theoretical quadrupolar curve for the $\frac{3}{2}\leftrightarrow\frac{1}{2}$ transition. The $\frac{3}{2}\leftrightarrow\frac{1}{2}$ transition occurs at relatively high fields for $\theta=0$ to 30°. The dipolar transition probabilities which depend on $H_0{}^2$ are relatively high for θ between 10 and 25°. But from the comparison of Fig. 4(a) and 4(b) it does not seem likely that the dipolar contribution can account for the measured α's being greater than one would expect on the basis of quadrupolar theory alone.



(a)

(b)

FIG. 4. Comparison of the quadrupolar [Fig. 4(a)] and dipolar [Fig. 4(b)] theories with the experimental angular dependence of the absorption coefficient multiplied by the linewidth in 0.08% ruby. To normalize the theoretical curves the computed point for $\frac{1}{2}\leftrightarrow-\frac{1}{2}$ transition was set equal to the experimental value for $\theta=70°$ in Fig. 4(a) and $\theta=55°$ in Fig. 4(b).

Some deviations of experimental data from theory can be attributed to variations in the direction of the c axis throughout the sample. Since line positions depend on the angle between H_0 and c axis, these variations tend to distort the lines, especially where they are strongly anisotropic. Variations of the c axis were

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[21] E. O. Schulz-Du Bois, Bell System Tech. J. 38, 271 (1959); W. S. Chang and A. E. Siegman, Stanford University Technical Report No. 1958 (unpublished).

observed in all 6 ruby samples and to some extent this reflects a limitation of the experimental technique, since we need relatively long samples in these measurements and consequently certain crystalline defects have greater effects on results than in experiments which could be done with shorter samples, such as, for example, ordinary spin resonance or observation of spin-resonance saturation by phonons. Experimental curves, which Tucker obtained by this latter technique,[3] are similar to those in Fig. 2, and they, too, seem to show a stronger spin-phonon interaction for the $\frac{3}{2}\leftrightarrow\frac{1}{2}$ line than theory predicts. The saturation technique is a more sensitive one for observation of relative transition probabilities, but cannot completely exclude the effects of other modes on spin transitions which are usually present together with the main mode. By direct observation of the phonon attenuation due to flipping spins, the absorption technique separates the effects of longitudinal and transverse modes, thus offering an advantage for angular-variation studies. Furthermore, it allows a direct observation of acoustic-interaction bandwidth and measurements of magnetoelastic coupling constants, from which spin-lattice relaxation times can be calculated.[3,4,6]

By transmitting transverse waves and also longitudinal waves perpendicular to the c axis of ruby we have measured $G_{14}=0.31\cdot10^{-15}$ ergs. From longitudinal-wave measurements along the c axis we obtained $G_{33}=1.16\pm0.08\cdot10^{-15}$ erg, in agreement with Tucker's measurements. The coupling constants do not show any dependence on Cr^{3+} concentration in the range 0.02–0.5% covered by our measurements. Thus the direct relaxation time, which can be inferred from the coupling constants, does not depend on the concentration in that particular range either. This conclusion is in agreement with Van Vleck's theory and in disagreement with the theory by Kochelaev[22] who predicted variations in direct relaxation times proportional to concentration to the $-4/3$ power.

IV. SUMMARY

A general treatment of paramagnetic acoustic resonance absorption with particular emphasis on its angular and polarization dependence has been developed. This was accomplished by introducing spin-lattice coupling matrices for all crystal classes and also by the introduction of general-strain and spin-operator transformations applicable to systems with isotropic and anisotropic g factors. It was shown that the acoustic-transition probabilities calculated from dipolar- and quadrupolar-selection rules have similar dependences on the angles between the crystalline axes and magnetic field, and on the angles between crystalline axes and directions of propagation and polarization, when g factors are isotropic. When g factors are anisotropic or when wavefunctions are significantly perturbed by crystalline fields, the angular functions are dissimilar for the two sets of rules. Some features of the theory are in satisfactory agreement with experiment, but others need further experimental verification. In particular, this applies to the form of the magnetoelastic matrices and to the observation of dipolar selection rules, detailed studies of which would require improvements in present experimental techniques.

ACKNOWLEDGMENTS

Professor C. D. Jeffries' participation and interest in this work are gratefully acknowledged. Gratitude is also due to M. E. Browne for his interest and encouragement.

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[22] B. I. Kochelaev, Dokl. Akad. Nauk. SSSR **131**, 1053 (1960).