measurements were made.[7] The levels associated with this absorption must be included in the sum over intermediate states in evaluating the cross section; because of possible interference effects, the result of including these states in the theory is not immediately evident. Further study is necessary to resolve this point.

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Rotationally Invariant Theory of Spin-Phonon Interactions in Paramagnets

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We propose a theory of spin-phonon interactions in paramagnetic materials. The theory is based upon the conservation of total, i.e., spin plus lattice, angular momentum. Rotational invariance of the Hamiltonian of the coupled system leads to new contributions to the spin-phonon interaction. These new contributions are determined by the anisotropy of the crystal field acting on the spin system.

Previous treatments of the interaction between spins and phonons in paramagnetic crystals have assumed *a priori* that the spins are coupled to the lattice only via deformations of the latter which can be described by a symmetrical elastic strain tensor e_{ij}.[1] In this paper we require the total Hamiltonian of the coupled spin-lattice system to be consistent with conservation of total angular momentum. This requirement leads to additional contributions to the spin-phonon interaction which have been previously ignored and which contribute antisymmetrical components to the stress tensor.

Total angular momentum of a closed system is conserved if the Hamiltonian $\hat{\mathcal{H}}$ is invariant to arbitrary rigid rotations of the system. Consider a paramagnetic spin $\vec{S}$ in an otherwise diamagnetic host lattice in the presence of an external field $\vec{H}$. Angular-momentum conservation requires that the Hamiltonian of this system is invariant to rigid rotations of the spin, the lattice, and the field together. We assume that the Hamiltonian $\hat{\mathcal{H}}$ describing the potential or stored energy is a function of the following variables:

$$\hat{\mathcal{H}}=\hat{\mathcal{H}}(S_i, H_i, \partial x_i/\partial X_j). \tag{1}$$

Here, the spatial coordinate $\vec{x}$ is the instantaneous position of the ion and the material coordinate $\vec{X}$ is its position in the undeformed lattice. By assuming the lattice energy to be determined solely by the deformation gradients $\partial x_i/\partial X_j$ and hence independent of the displacements $\vec{u}=\vec{x}-\vec{X}$, $\hat{\mathcal{H}}$ automatically has translational invariance. As written in Eq. (1), $\hat{\mathcal{H}}$ is a function of the components of five vectors: $\vec{S}$, $\vec{H}$, and $\partial\vec{x}/\partial X_j$, $j=1,2,3$. Such functions have complete rotational invariance if they can be expressed as functions of scalar invariants.[2] We choose the following complete but not unique set of invariants:

$$S_k^*=S_iR_{ik}, \tag{2a}$$

$$H_k^*=H_iR_{ik}, \tag{2b}$$

$$E_{kl}=\tfrac{1}{2}[(\partial x_i/\partial X_k)\partial x_i/\partial X_l-\delta_{kl}]. \tag{2c}$$

Here, R_{ik} is the finite rotation tensor and E_{kl} the finite strain tensor of the classical theory of elasticity. The invariants S_k^* and H_k^* are the components of spin and field on having been rigidly rotated by R_{ik}.[3] The above set of scalar invariants is complete only to the extent that parity is conserved, i.e., that $\hat{\mathcal{H}}$ is invariant to spatial inversion, $\vec{x}\to-\vec{x}$.[2] The rotationally invariant

Hamiltonian takes the form

$$\hat{\mathcal{H}}(S_i, H_i, \partial x_i/\partial X_j)=\mathcal{H}(S_k^*, H_k^*, E_{kl}). \tag{3}$$

The Hamiltonian $\mathcal{H}$ can now be approximated by a polynomial in the quantities S_k^*, H_k^*, and E_{kl}. Under the assumption of time-reversal symmetry, this polynomial will contain only even powers of S_k^*, H_k^*, or combinations of these. If we retain terms to second power in the invariant spin operators, the Hamiltonian can be written

$$\mathcal{H}=\beta g_{ij}S_i^*H_j^*+D_{ij}S_i^*S_j^*+\tfrac{1}{2}c_{ijkl}E_{ij}E_{kl}+F_{ijkl}S_i^*H_j^*E_{kl}+G_{ijkl}S_i^*S_j^*E_{kl}. \tag{4}$$

The tensor coefficients have their usual interpretation as the anisotropic "g"-factor tensor g_{ij}, the quadratic crystal field tensor D_{ij}, the magnetoelastic coupling constants F_{ijkl} and G_{ijkl}, and the elastic tensor c_{ijkl}. These material tensors must be invariant to the transformations of the point group which describes the site symmetry of the spin $\vec{S}$.

It is useful to rewrite Eq. (4) using the more common spin and field variables $\vec{S}$ and $\vec{H}$ given in Eqs. (2a) and (2b). We make the approximation that nonmagnetic terms in $\mathcal{H}$ should be correct to second order in the displacement gradients $u_{ij}=\partial u_i/\partial X_j=\partial x_i/\partial X_j-\delta_{ij}$. Terms of magnetic and magnetoelastic origin should be correct to first order in u_{ij}.[4] Therefore the finite elastic strain E_{ij} and rotation R_{ij} tensors can be replaced by these infinitesimal approximations:

$$E_{ij}\simeq e_{ij}=\tfrac{1}{2}(u_{ij}+u_{ji}), \quad R_{ij}\simeq \delta_{ij}+\omega_{ij}=\delta_{ij}+\tfrac{1}{2}(u_{ij}-u_{ji}). \tag{5}$$

The Hamiltonian can now be written

$$\mathcal{H}=\beta g_{ij}S_iH_j+D_{ij}S_iS_j+\tfrac{1}{2}c_{ijkl}e_{ij}e_{kl}+F_{ijkl}S_iH_je_{kl}+G_{ijkl}S_iS_je_{kl}+\beta g_{ij}(S_iH_k\omega_{kj}+S_kH_j\omega_{ki}) +D_{ij}(S_iS_k\omega_{kj}+S_kS_j\omega_{ki}). \tag{6}$$

The first five terms of this Hamiltonian are precisely those obtained in the usual treatment of this subject! However, the final two terms are a direct consequence of the requirement that $\mathcal{H}$ be invariant to arbitrary rigid rotations of the entire system. These new contributions to the spin-phonon interaction correspond to the interaction of the spin $\vec{S}$ with the rotational motion ω_{ij} associated with a transverse elastic wave. As is well known, and can be easily verified with the aid of Eqs. (5), a transverse elastic deformation u_{ij} can be decomposed into a pure strain e_{ij} and a pure rotation ω_{ij}, $u_{ij}=e_{ij}+\omega_{ij}$. Previous theories of spin-phonon interactions have ignored the possibility that the rotational part of this deformation ω_{ij} can contribute to the coupling. The coupling constants for these new contributions to the interaction are just the quantities measuring the anisotropy of the crystal field acting on the spin $\vec{S}$. No new unknown parameters are introduced by requiring rotational invariance.

A very simple rule can be formulated for determining whether rotational interaction terms such as the last two terms in Eq. (6) exist for a spin at a site of given symmetry. Rotational interactions of the above type will occur if and only if the rotation operator ω_{ij} corresponds to an elastic rotation about an axis perpendicular to a unique axis of the site symmetry of the spin. For the case of isotropic or cubic site symmetry there is no unique axis and these terms are required by symmetry to vanish. For uniaxial site symmetry $g_{ij}=0$ for all i and j except g_{33} and $g_{11}=g_{22}$. Also, all $D_{ij}=0$, except D_{33}. Therefore the rotational interaction terms for uniaxial symmetry are

$$\beta(g_{33}-g_{11})[(S_1H_3+S_3H_1)\omega_{13}+(S_2H_3+S_3H_2)\omega_{23}]+D_{33}[(S_1S_3+S_3S_1)\omega_{13}+(S_2S_3+S_3S_2)\omega_{23}]. \tag{7}$$

In agreement with the general rule stated above, ω_{13} and ω_{23} correspond to rotations about the "2" and "1" axes, respectively, both of which are perpendicular to the unique "3" axis. In fact, by explicit calculation or by considering the transformation properties of the strain e_{ij} and rotation ω_{ij} under the symmetry operations of the applicable point group, it is simple to verify the above general rule for all symmetries.

Three points concerning the present theory should be emphasized: (1) The new contributions of the spin-phonon interaction arise as a direct consequence of the requirement of rotational invariance which is itself equivalent to the conservation of total angular momentum. One can show explicitly that only a rotationally invariant theory is consistent with conservation of total angular momentum.[5] (2) The new contributions to the spin-phonon interaction are of the same "order" as the usual spin-phonon interaction which involves only the elastic strain. Therefore, a proper linear or "small-strain" approximation does not eliminate these added terms. (3) The rotational interaction is determined by the anisotropy of the crystal field acting on the spin. The effective coupling constants are simple combinations of the crystal field constants. A microscopic theory of the spin-phonon interaction based on any definite model must therefore be consistent with this relation between the crystal field parameters and the rotational coupling constants.[5]

In order to estimate the significance of the rotational contribution to the spin-phonon interaction consider the case of emerald [Cr^{3+} in $Be_3Al_2(SiO_3)_6$]. On substitutionally replacing Al, the Cr ions are located at trigonal (uniaxial) sites. The correct rotational contribution to the spin-phonon interaction is given by Eq. (7). The parameters g_{11}, g_{33}, and D_{33} have been determined from paramagnetic resonance spectra to be $g_{11}=1.97\pm0.01$, $g_{33}=1.973\pm0.002$, and D_{33} -0.895 cm^{-1}.[6] Since $g_{11}\simeq g_{33}$, the first term in Eq. (7) can be neglected. However, the second term must be compared with the corresponding term in the usual strain spin-phonon interaction:

$$2G_{44}[(S_1S_3+S_3S_1)e_{13}+(S_2S_3+S_3S_2)e_{23}]. \qquad (8)$$

Assuming the coupling constant G_{44} in emerald to be approximately equal to that in ruby (Cr^{3+} in Al_2O_3) we estimate $2G_{44}\simeq+1.8$ cm^{-1}.[7] Therefore the magnitude of the rotational coupling can be comparable to that of the usual strain coupling.

Should the expansion of the crystal-field interaction to terms quadratic in the spin of the orbital ground state not be adequate, certain new, although rather insignificant, features of the theory arise. Suppose quartic terms of the form

$$K_{ijkl}S_i{}^*S_j{}^*S_k{}^*S_l{}^* \qquad (9)$$

are necessary additions to the Hamiltonian given by Eq. (4). Rewriting $\mathcal{H}$ in terms of the more usual spin measure $\vec{S}$ leads to additional spin-phonon interaction terms linear in the rotation ω_{ij} and quartic in the spin S_k. The coefficients K_{ijkl} are usually quite small and in addition are nonzero only for spins $S\geqslant2$. For these reasons we have not treated these terms in detail although in principle they exist. Note that inclusion of terms of this type invalidates the general rule stated above regarding the existence of rotational spin-phonon coupling terms in the Hamiltonian.

In spite of our having considered a single paramagnetic spin in an essentially diamagnetic host lattice, the conclusions reached above are quite general. They apply equally well to a concentrated paramagnetic spin system such as a nuclear spin system in an otherwise diamagnetic crystal. Note that in such systems anisotropic spin-spin interactions (e.g., magnetic dipole) will contribute in principle to the total spin-phonon interaction. The present general formulation of spin-phonon interactions should be of interest in the fields of acoustic paramagnetic resonance, acoustic nuclear magnetic resonance, spin-lattice relaxation, and thermal conductivity in paramagnetic materials.

In conclusion we note that the concept of rotational invariance has been previously applied to magnetoelastic coupling in magnetically ordered materials.[8] Both the spin system and the lattice were treated as classical continua. The role of anisotropic magnetic interactions in determining rotational magnetoelastic coupling in an antiferromagnet was recently demonstrated experimentally.[9] In the present work we have imposed rotational invariance on the microscopic Hamiltonian describing a single paramagnetic ion in a diamagnetic host lattice. We have correctly included effects arising from an anisotropic interaction of the spin $\vec{S}$ with the external field $\vec{H}$ for the first time. Finally, we have shown that the existence of spontaneous magnetic order is in no way fundamental to the basic conclusions of a rotationally invariant theory.

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[4] This is more restrictive than the usual linear approximation. The present approximation neglects all terms in the Hamiltonian which are quadratic in both the spin operators S_i and the displacement gradients u_{ij}. Such terms can be divided into two categories. (1) Those terms for which $S_z{}^2$ is the quadratic spin operator do not result in spin transitions. They do, however, lead to field- and frequency-independent antisymmetrical contributions to the elastic constants. Being the order of g_{ij}, D_{ij}, F_{ijkl}, or G_{ijkl} compared to c_{ijkl}, these contributions are negligible in a paramagnetic system.

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Direct Verification of the Third-Derivative Nature of Electroreflectance Spectra

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The electric-field–induced change in the linear dielectric function for the E_1 and $E_1+\Delta_1$ transitions of Ge, determined from low-field electroreflectance measurements, is shown to be in quantitative agreement with the third derivative of the linear dielectric function measured by high-resolution ellipsometry techniques. This result relates electroreflectance spectra to other types of modulation spectra and provides the first direct verification of the nonlinear optical interpretation of electroreflectance.

We report quantitative experimental verification of the relation between low-field electroreflectance (ER) spectra and the third derivative of the linear dielectric function, predicted by a recent theory[1,2] which identifies low-field ER as a resonant third-order nonlinear optical susceptibility. This result is obtained by comparing the field-induced change in the linear dielectric function of the E_1 and $E_1+\Delta_1$ transitions of Ge, as determined from its low-field ER spectrum, with the third derivative of the linear dielectric function, calculated from data taken on the same crystal by high-resolution ellipsometric techniques.[3] In addition to being a stringent test of the above theory, this result defines the relationship of ER spectra[4] to those obtained by first-derivative modulation techniques such as piezoreflectance,[5] thermoreflectance,[6] and wavelength-derivative spectroscopy,[7] and provides a simple qualitative explanation of the fact that ER spectra are sharper and more richly structured than those measured by other modulation techniques.[8] These results also show that improved ellipsometric methods[3] enable the dielectric function to be measured directly with sufficient accuracy to allow the calculation of numerically differentiated spectra whose experimental uncertainties are not significantly larger than those obtained by modulation spectroscopy.

The nonlinear optical approach to ER[1] relates the complex one-electron dielectric function ϵ_0 to its complex field-induced change $\Delta\epsilon_0$ by the expression

$$\Delta\epsilon_0 = \frac{(\hbar\Omega)^3}{3E^2}\frac{d^3}{dE^3}(E^2\epsilon_0), \tag{1}$$

where E is the energy variable, and $\hbar\Omega$ is the characteristic energy given in terms of the interband energy $E_{cv}(\vec{k})$, or interband reduced mass μ, by

$$(\hbar\Omega)^3 = \tfrac{1}{8}e^2(\vec{\mathcal{E}}\cdot\nabla_{\vec{k}})^2E_{cv}(\vec{k}) = e^2\hbar^2\mathcal{E}^2/8\mu, \tag{2}$$

where $\vec{\mathcal{E}}$ is the uniform applied electric field. Equation (1) is expected to be valid if $\hbar\Omega$ is nearly independent of E (critical-point transitions between nearly parabolic bands), and if $\mathcal{E}$ is sufficiently small so that $|\hbar\Omega| < \frac{1}{3}\Gamma$, where Γ is the phenomenological broadening parameter. However, correlation effects are not included, and Γ is assumed to be energy independent. Correlation effects can be incorporated to lowest order by simply replacing $\Delta\epsilon_0$ and ϵ_0 in Eq. (1) with their experimentally measured equivalents $\Delta\epsilon$ and ϵ, respectively. This can be proven either from the results of Rees[9] or from the explicit equations approximating the dominant correlation effect, the electron-hole Coulomb interaction, by a contact potential.[10,11] Since phenomenological broadening is described by extending the energy E into the complex plane as $E+i\Gamma$, energy dependence of Γ appears after differentiation as a complex prefactor $1+id\Gamma/dE$, which can be removed (made equivalent to $d\Gamma/dE=0$) by explicit divi-