PHYSICAL REVIEW B VOLUME 14, NUMBER 3 1 AUGUST 1976

Rotational invariance, finite strain theory, and spin-lattice interactions in paramagnets; application to the rare-earth vanadates

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(Received 8 March 1976)

The propagation of transverse elastic waves in paramagnetic crystals in the presence of an applied magnetic field is investigated both theoretically and experimentally. A theory is developed which is based upon finite-deformation elasticity theory and a description of the paramagnetic ions as pseudospins. Although the spatial rotational properties of the pseudospin operators are not known, the theory correctly includes in the thermodynamic (i.e., quasistatic) limit the spin-lattice coupling arising from the rotational motion associated with a transverse elastic wave. Explicit calculations of the changes in the elastic constant c_{44} resulting from the spin-lattice coupling are presented for several systems in the thermodynamic limit. The lattice distortions involved correspond to transverse elastic waves propagating in the z and polarized in the x directions (u_{xz} distortion) and propagating in the x and polarized in the z directions (u_{zx} distortion). The infinitesimal strains e_{xz} associated with these waves are identical; the rotation ω_{xz} is of opposite sign for the two waves; the second-order lattice compression is along the respective propagation directions. The latter two contributions are not included in the usual small-strain theory but do make significant contributions to the elastic properties of the paramagnetic system. Because of these contributions, the shift in c_{44} due to the spin-lattice coupling is different for the two types of waves. In addition the shift can be either positive or negative depending on the relative magnitude and sign of the several coupling coefficients involved. Measurements of the shift in c_{44} in the presence of a magnetic field have been performed in the tetragonal phases of the four rare-earth vanadates: $TmVO_4$, $NdVO_4$, $TbVO_4$, and $DyVO_4$. These measurements confirm the predictions of the theory presented here and are in clear contradiction with the predictions of an infinitesimal-strain magnetoelastic theory. In all four cases the measured shifts in the elastic constant c_{44} are different for the u_{xz} and u_{zx} distortions. In the case of $TmVO_4$ the one is positive and the other negative.

I. INTRODUCTION

Toupin's[1] work on the "elastic dielectric" has stimulated considerable interest in the concept of "rotational invariance" and "finite-deformation theory" not only in dielectric materials but also in magnetoelastic systems. Tiersten,[2] Brown,[3] and Eastman[4] first applied these ideas to magnetoelastic phenomena in ferromagnetic crystals. Their work showed that a consistent treatment of magnetoelastic phenomena necessarily requires the use of finite-deformation theory even in magnetically isotropic systems. The consequences of the requirement of rotational invariance in magnetically anisotropic media were explicitly considered by Melcher[5,6] for the case of transverse-elastic-wave propagation in the uniaxial antiferromagnet MnF_2. For that case it was shown that the rotational motion of a transverse elastic wave couples to the antiferromagnetic spin system in precisely the same order as does the strain associated with the transverse elastic wave. Measurements of the shift in the sound velocity with magnetic field revealed that the magnitudes of the strain and rotational coupling terms in MnF_2 were equal to within the experimental error.[5,6] Magnetoelastic interactions in uniaxial rare-earth ferromagnets were treated with a rotationally invariant formalism by Southern and Goodings.[7] Their results are similar in many ways to those found for the uniaxial antiferromagnet.[5,6]

The first explicit discussion of contributions to the spin-lattice coupling in paramagnetic systems was apparently that of Kumar *et al.*[8] Their treatment of the rotational contributions to the spin-phonon Hamiltonian is based upon the early work of van Vleck[9] and involves the expansion of the crystal field acting on an ion in terms of the normal vibrational modes of the lattice. They point out that there is no basic reason to ignore the purely rotational modes. Independently, Melcher[10] applied the rotationally invariant formalism developed previously for magnetically ordered systems to the problem of a paramagnetic spin system. In this way it was possible to point out that the coefficients of the terms in the spin-phonon Hamiltonian which involve elastic rotations are simple combinations of the crystal-field parameters and that no new parameters are introduced by the inclusion of the rotational terms. This treatment is applicable only if the rotational properties of the spin operators are known. Taking the spin $\vec{J}$ to represent the true angular momentum of the system, its rotational properties are those of a simple vector and the explicit results obtained apply.[10] In many cases, however, the spin system is described

by pseudospin operators whose rotational properties in real space are not those of simple vectors and may in fact be unknown. Abragam *et al.*[11] have treated such a situation, i.e., a pseudospin $\frac{1}{2}$ system with cubic symmetry including rotational terms in the spin-phonon Hamiltonian. Their results are difficult to apply in general and, as pointed out below, are inconsistent in the appropriate limit with the conclusions of the present work. A preliminary description of the main results of the present paper has been presented previously.[12] Independently, Dohm and Fulde[13] have recently completed a theoretical study of rotational contributions to the spin-phonon interaction in rare-earth paramagnets. Their approach, which is consistent with Ref. 10, makes use of the known rotational properties of the total angular momentum operator $\vec{J}$. Dohm[14] has recently extended this work. For large J, explicit calculations become formidable and it is highly desirable to develop a valid formalism in which only a limited number of spin states need be considered even though these states are described by pseudospin operators whose spatial rotational properties may be unknown.

In this paper we discuss a means of circumventing our lack of knowledge of the rotational properties of pseudospins and thereby obtain useful results for describing a certain class of experiments which involve rotational spin-phonon interactions. In particular, by restricting our treatment to apply only to situations in which the frequency of the elastic deformations is much less than any spin-resonance frequency or spin-relaxation rate, we are able to express the Hamiltonian of the system in a coordinate system which is fixed with respect to the principal axes of the crystal. In this "crystal coordinate system" we are able to construct the thermodynamic free energy and thereby calculate the changes in the elastic properties of the lattice due to the spin-phonon interaction, including rotational contributions. In this way it is never necessary to know the rotational properties of the pseudospin operators. Measurements of magnetic-field-induced changes in the elastic constant c_{44}, corresponding to transverse-elastic-wave propagation in a series of rare-earth vanadates, are compared to predictions of the theory. Not only do these experiments demonstrate the necessity of including the rotational and finite-strain contributions to the spin-phonon Hamiltonian in order to obtain even qualitative agreement with experiment, but they also confirm the validity of the present approach to quasistatic magnetoelastic problems.

In Sec. II the experimental measurements are described. They represent the only (known to us) direct measurements of rotational spin-lattice coupling in paramagnetic systems. The general method of treating quasistatic spin-lattice interactions is described in Sec. III. Section IV is devoted to detailed calculations of the spin-phonon contributions to the elastic constant c_{44} for pseudospin systems describing a non-Kramers doublet ($TmVO_4$), a Kramers doublet ($NdVO_4$), and two systems ($DyVO_4$ and $TbVO_4$) the description of each of which requires the use of four pseudospin states. These calculations are compared to experiment in each case. In Sec. V we summarize and discuss the main theoretical and experimental results of the paper.

II. EXPERIMENTAL MEASUREMENTS

The measurements reported here were carried out using the continuous-wave transmission technique at a frequency of 30 MHz.[15] AC-cut quartz plates bonded to the samples with Non-aq stopcock grease were used as transducers. Each sample was a single crystal of $TmVO_4$, $NdVO_4$, $TbVO_4$, or $DyVO_4$ with two pairs of faces (normal to both the z and x axes) ground flat and parallel. A typical linear dimension of a prepared sample was 4 mm. Simultaneous measurements were made of the two velocities corresponding to transverse-elastic-wave propagation parallel to the z axis, polarized in the z plane and propagating parallel to the x axis, polarized along the z axis as a function of a magnetic field applied along the z axis. Fields up to 95 kOe were provided by a superconducting solenoid with the sample immersed either in liquid helium or liquid nitrogen.

The distortions associated with the two types of elastic waves are depicted in Fig. 1. Since the infinitesimal strain e_{xz}, associated with each wave, is the same, any theory based entirely on infinitesimal-strain coupling will predict identical results for the two experiments. On the other hand, the rotations $\pm\omega_{xz}$ associated with the two waves have different algebraic signs. Therefore a theory which includes rotational motion will in general predict different results for the two measurements. In addition, the two transverse waves produce second-order compressions, respectively, along the z and x axes. The origin of these compressions in the finite strain is discussed in Sec. III. Inclusion of these compressions leads to additional contributions to the magnetoelastic interaction. Note that the geometry of the present measurements is identical to that employed in the original verification of rotational magnetoelastic interactions in antiferromagnetic MnF_2.[5,6]

The elastic constant c_{44} corresponds to e_{xz} strains of the tetragonal crystals of interest here. In

Sec. IV, the experimental results are presented as the relative change in c_{44} as a function of the applied field strength, $[c_{44}(H)-c_{44}(0)]/c_{44}(0)$. In all cases the field is oriented along the z axis of the crystal.

III. GENERAL THEORY

The theoretical discussion of this section is divided into two parts. In Sec. III A we outline a general approach to a rotationally invariant theory of spin-lattice interactions valid for rare-earth ions for which the total angular momentum is conserved. A rotationally invariant Hamiltonian is constructed as a function of the components of the total angular momentum operator $\vec{J}$ of the rare-earth ion. This approach, which is equivalent to that used in Refs. 7, 10, 13, and 14, is generally valid for all static and/or dynamic phenomena associated with spin-lattice interactions. However, the calculational effort required to use this Hamiltonian to describe physical phenomena can be formidable. In Sec. III B we consider quasistatic phenomena for which the elastic wave (or phonon) frequency is restricted to be less than any spin-resonance frequency or spin-relaxation rate. By describing the spin system with a pseudospin formalism, simple but meaningful calculations can be performed. Even though the rotational properties of the pseudospin operators may not be known, we demonstrate how to correctly include the effects of crystal rotations and finite strains.

A. Hamiltonian based on angular momentum operators

The Hamiltonian of a rare-earth ion can be expressed as

$$\mathcal{H}^c = g_J \mu_B \vec{H}^c \cdot \vec{J}^c + \mathcal{H}^c_{CF}(J_i^c) + \mathcal{H}^c_{SL}(J_i^c, E_{ij}). \quad (1)$$

The three terms correspond, respectively, to the Zeeman interaction with applied magnetic field $\vec{H}^c$, the crystal-field Hamiltonian, and the spin-lattice interaction. The superscript c denotes that the operators and fields are referred to the "crystal coordinate system" which coincides with and is rigidly fixed to the principal axes of the crystal. Here g_J is the Landé g factor, μ_B the Bohr magneton, and E_{ij} denotes the finite-strain tensor given by

$$E_{ij} = \frac{1}{2}\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} + \sum_\alpha \frac{\partial u_\alpha}{\partial x_i}\frac{\partial u_\alpha}{\partial x_j}\right), \quad (2)$$

where $\vec{u}(x,t)$ is the elastic displacement field. The second-order contributions to E_{zz} and E_{xx} arising, respectively, from the $\partial u_x/\partial z$ and $\partial u_z/\partial x$ displacement gradients are indicated in Fig. 1. Note that in the crystal coordinate system (often referred to as the "material coordinate system," see Refs. 1–4) the crystal rotations do not appear explicitly. The purely elastic contributions to the Hamiltonian of the system have been omitted in Eq. (1).

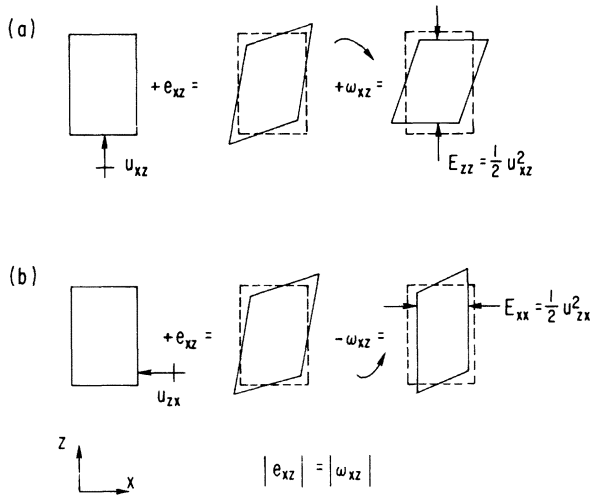

FIG. 1. Schematic diagram of the distortions associated with two transverse elastic waves corresponding to u_{xz} and u_{zx} displacement gradients, respectively. In (a) a u_{xz} distortion is seen to consist of an infinitesimal strain e_{xz}, a clockwise rotation ω_{xz}, and a quadratic contribution to the compression along the z axis given by $E_{zz} = \frac{1}{2}u_{xz}^2$ [see Eq. (2)]. In (b) a u_{zx} distortion consists of the same infinitesimal strain e_{xz}, a counterclockwise rotation $-\omega_{xz}$, and a compression along the x axis given by $E_{xx} = \frac{1}{2}u_{zx}^2$.

Each term in Eq. (1) must transform as the totally symmetric representation Γ_1 of the point group describing the symmetry of the site of the rare-earth ion. In addition, the Hamiltonian must possess time-reversal symmetry. This latter condition restricts the last two terms of Eq. (1) to contain only even-order polynomials of the components J_i^c of the angular momentum operators. The $4f$ configuration ($l=3$) of the rare-earth ions further restricts the polynomials to order six or less.

The Hamiltonian $\mathcal{H}^L$ of this system, expressed in the "laboratory coordinate system," which is rigidly fixed with respect to the measuring apparatus (applied magnetic field), is obtained by a simple rotation of $\mathcal{H}^c$:

$$\mathcal{H}^L = R\mathcal{H}^c R^{-1} = \mathcal{H}^L(\vec{H}^L, J_i^L, E_{ij}), \quad (3)$$

where

$$\vec{J}^L = R\vec{J}^c R^{-1}, \quad (4)$$

and $\vec{H}^L$ is related to $\vec{H}^c$ by the rotational properties of axial vectors. The relative orientation of the two sets of coordinate systems can be described by the vector $\vec{\theta}$. The rotational operator is given by

$$R = e^{-i\vec{J}^c \cdot \vec{\theta}} . \tag{5a}$$

The laboratory coordinate system is often referred to as the "spatial" reference frame (see Refs. 1–4).

The rotation tensor of continuum elasticity theory is given in terms of the finite strain E_{ij} and the displacement gradients $\partial u_i/\partial x_j \equiv u_{ij}$ by

$$R_{ij} = (\delta_{im} + u_{im})\left[(\underline{1} + 2\underline{E})^{-1/2}\right]_{mj} . \tag{5b}$$

To second order in the displacement gradients u_{ij}, this may be written[6]

$$R_{ij} \simeq \delta_{ij} + \omega_{ij} - \tfrac{1}{2}\omega_{mi}\omega_{mj} + \tfrac{1}{4}(u_{mi}u_{jm} - u_{im}u_{mj}) , \tag{5c}$$

where ω_{ij} is the antisymmetrical strain tensor defined by Eq. (9) below and a sign error occurring in Eq. (5–20) of Ref. 6 has been corrected here. To first order in displacement gradients this expression is identical to the usual rotation operator if ω_{ij} is interpreted as the infinitesimal angle of rotation. Because of the last term on the right-hand side of Eq. (5c) this interpretation of ω_{ij} cannot, in general, be made to second order in u_{ij}. However, for the experimentally interesting case of shear wave propagation in a plane, the last term in Eq. (5c) vanishes and ω_{ij} can be equated with the rotation angle to second order. For example, shear wave propagation in the xz plane corresponds to all $u_{ij} = 0$ except u_{xz} and u_{zx}. In this case the last term in Eq. (5c) is easily seen to be zero and, to second order, $\omega_{xz} = \frac{1}{2}(u_{xz} - u_{zx})$ is identical to the angle of rotation. The analysis in the remainder of this paper is primarily concerned with this special case although generalization to other cases is straightforward.

Take $\vec{\theta} = (0, \omega_{xz}, 0)$ which corresponds to a rotation about the y axis through the angle ω_{xz} (see Fig. 2). The Hamiltonian takes the form

$$\mathcal{H}^L = g_J \mu_B \vec{J}^L \cdot \vec{H}^L + \mathcal{H}^L_{CF}(J_i^L, \omega_{xz}) + \mathcal{H}^L_{SL}(J_i^L, E_{ij}, \omega_{xz}) . \tag{6}$$

In the laboratory coordinate system the Hamiltonian $\mathcal{H}^L$ explicitly contains the angular orientation ω_{xz} of the crystal with respect to the laboratory. This rotation corresponds either to a rigid static rotation of the entire crystal or to the local rotation associated with a transverse elastic wave (see Fig. 1).

In general the last two terms in Eq. (6) can be written

$$\begin{aligned}\mathcal{H}^L_{CF}(J_i^L, \omega_{xz}) + \mathcal{H}^L_{SL}(J_i^L, E_{ij}, \omega_{xz}) \\ = \mathcal{H}^L_{CF0}(J_i^L) + \mathcal{H}^L_{SL0}(J_i^L, E_{ij}) + \mathcal{H}^L_{CF\omega}(J_i^L, \omega_{xz}) \\ + \mathcal{H}^L_{SL\omega}(J_i^L, E_{ij}, \omega_{xz}) ,\end{aligned} \tag{7}$$

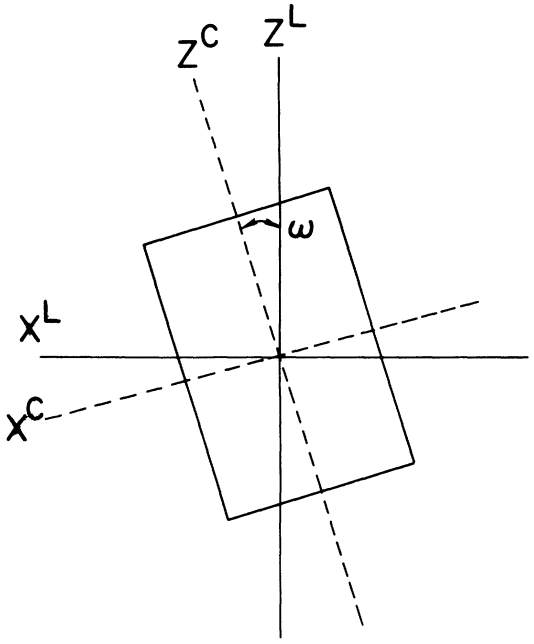

FIG. 2. Schematic diagram of the relative orientations of the crystal and laboratory coordinate systems. They are assumed to coincide at equilibrium and differ only by the rotation about the y axis, ω_{xz}, associated with a transverse elastic wave.

where the first two terms on the right-hand side are identical to the last two terms on the right-hand side of Eq. (1) with J_i^c replaced by J_i^L. The remaining two terms in Eq. (7) represent the changes occurring in the crystal field and spin-lattice Hamiltonians when they are expressed in the laboratory rather than the crystal coordinate system. Note that the finite strain E_{ij} is a rotational invariant and hence is identical in the two coordinate systems.[1–4]

The Hamiltonian given by Eq. (6) is rotationally invariant. It can be used in calculations of all phenomena associated with spin-lattice interactions. The total spin-lattice interaction [the last three terms of Eq. (7)] includes not only the effects due to lattice strains E_{ij} but also of rigid and/or local crystal rotations ω_{xz}. Since the rotational terms arise from the rotation of $\mathcal{H}^c$, their inclusion does not introduce any new magnetoelastic coupling constants or other parameters into the theory.

Although the above procedure is correct and relatively straightforward, actual calculations can be rather tedious because of the large number $(2J+1)$ of eigenstates of an ion with angular momentum J. Often it is convenient to consider only the lowest-lying manifold of the full J multiplet. This manifold is then described with a pseudospin formalism.[16] However, the pseudospin operators acting within this restricted manifold of states do not

possess simple rotational properties. Therefore it is difficult to deduce a correct rotationally invariant Hamiltonian.

B. Pseudospin Hamiltonian and the quasistatic limit

The crystal field interaction $\mathcal{H}^c_{CF}$ [Eq. (1)] lifts the $(2J+1)$-fold degeneracy of the free rare-earth ion into a series of manifolds. The eigenstates of each manifold transform as the basis functions of an irreducible representation of the point group describing the site symmetry of the ion. Often the ground manifold is sufficiently separated from the excited manifolds so that the thermal population of the latter can be neglected. In this case it is useful to define pseudospin operators S_i which operate only within the ground manifold. By projecting the total Hamiltonian onto the ground manifold, a pseudospin Hamiltonian can be constructed which describes the energy levels of this manifold. In the crystal coordinate system this pseudospin-phonon Hamiltonian takes the form

$$\mathcal{H}^c = g_{ij}\mu_B S^c_i H^c_j + \mathcal{H}^c_{CF}(S^c_i) + \mathcal{H}^c_{SL}(S^c_i, H^c_i, E_{ij}). \quad (8)$$

Here g_{ij} is the tensor spectroscopic splitting factor of the manifold. If the ground manifold is degenerate the crystal-field term $\mathcal{H}^c_{CF}(S^c_i)$ is a constant which can be taken to be zero.

In order to express the Hamiltonian of Eq. (8) in the laboratory coordinate system the transformation properties of the pseudospin operators S_i under spatial rotations must be known. The subscript i on the pseudospin operator S_i refers to pseudospin space and has in general no direct relationship to "real" space. Therefore the spatial rotational properties of the pseudospin are not in general known and the transformation of Eq. (8) to the laboratory coordinates cannot be carried out. However, if one is willing to restrict the calculation to the quasistatic or thermodynamic limit in which the frequency is much less than spin-relaxation rates or resonance frequencies, the calculation can be performed in the crystal coordinate system. The validity of this restriction and its extension to frequencies higher than the relaxation rates has been considered by Fedders and Melcher.[17]

Restricting ourselves to the quasistatic limit, the Hamiltonian of Eq. (8) can be used to calculate modifications of the elastic properties of a crystal due to interactions with the pseudospins. The components of the magnetic field $\vec{H}^c$ in the crystal are related to the field $\vec{H}^L$ applied in the laboratory by a simple rotation. Transverse elastic waves rotate the crystal with respect to the laboratory. Therefore the expression for $\vec{H}^c$ in terms of $\vec{H}^L$ involves the elastic rotation, i.e., the antisymmetric strain defined by

$$\omega_{ij} \equiv \frac{1}{2}\left(\frac{\partial u_i}{\partial x_j} - \frac{\partial u_j}{\partial x_i}\right). \quad (9)$$

In this way the Hamiltonian $\mathcal{H}^c$ [Eq. (8)] contains terms which couple the pseudospin operators to both the elastic strain E_{ij} and the elastic rotation ω_{ij}. The quasistatic changes in the elastic constants of the material arising from both the strain and rotational contributions to the magnetoelastic interaction can be calculated according to the following procedure. From the eigenvalues of $\mathcal{H}^c(S^c_i, H^L_i, E_{ij}, \omega_{ij})$ the partition function Z and the free energy F can be constructed. The effective elastic constant c_{ij} can be expressed as the second derivative of F with respect to the appropriate displacement gradient $u_{ij} \equiv \partial u_i/\partial x_j$. In the absence of magnetoelastic interactions this definition of c_{ij} is equivalent to the usual definition that c_{ij} is equal to the second derivative of F with respect to the strain E_{ij}. However, in the presence of magnetoelastic coupling this definition is no longer adequate because of the contributions of the elastic rotations. Furthermore, as discussed by Dohm[14] and in detail below, the quadratic displacement gradient contributions to the finite strain [Eq. (2)] can contribute independently to c_{ij} in magnetoelastic media.[18] In describing the second-order elasticity of nonmagnetic media the finite strain E_{ij} can be replaced by the infinitesimal strain e_{ij} defined by

$$e_{ij} = \frac{1}{2}\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right). \quad (10)$$

This is not, in general, valid in magnetoelastic media.

In order to make the above discussion more concrete we examine here a simple but nontrivial example which illustrates the points of interest in this paper. Consider an ion at a site of cubic symmetry whose ground manifold consists of a Kramers doublet separated from the first excited manifold by $\Delta \gg kT$. We assume that the crystal coordinate system and the laboratory system coincide at equilibrium, i.e., in the absence of crystal rotations. Referring to the character table for the cubic group, O,[19] the eigenstates of the Kramers doublet necessarily transform as the basis functions of the Γ_6 (or Γ_7) irreducible representation of the point group, O. The pseudospin operators S^c_i transforming as Γ_4 are given by

$$S^c_x = \frac{1}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}; \quad S^c_y = \frac{1}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}; \quad S^c_z = \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \quad (11)$$

The components of the applied field H^c_i also transform as Γ_4. The symmetrized strains E_1, $\{E_{E_1}, E_{E_2}\}$, and $\{E_{T_1}, E_{T_2}, E_{T_3}\}$ transform, respectively,

as Γ_1, Γ_3, and Γ_5 where

$$E_1 \equiv E_{xx}+E_{yy}+E_{zz},$$
$$E_{E_1}=E_{xx}-E_{yy};\quad E_{E_2}=(2E_{zz}-E_{xx}-E_{yy}), \tag{12}$$
$$E_{T_1}=E_{xy};\quad E_{T_2}=E_{xz};\quad E_{T_3}=E_{yz}.$$

Requiring that each term in the Hamiltonian transform as the totally symmetric representation Γ_1, the spin-phonon Hamiltonian to first order in the finite strain has the form

$$\mathcal{H}^c = g\mu_B(\vec{S}^c\circ\vec{H}^c)+F_{\Gamma_1}(\vec{S}^c\cdot\vec{H}^c)E_1+F_{\Gamma_3}[(2H_z^cS_z^c-H_x^cS_x^c-H_y^cS_y^c)E_{E_2}+(S_x^cH_x^c-S_y^cH_y^c)E_{E_1}]$$
$$+F_{\Gamma_5}[(S_x^cH_y^c+S_y^cH_x^c)E_{T_1}+(S_x^cH_z^c+S_z^cH_x^c)E_{T_2}+(S_y^cH_z^c+S_z^cH_y^c)E_{T_3}]. \tag{13}$$

In the static limit, additional terms quadratic in the finite strain are required for consistency and are included in the specific example below. In this equation, g is the spectroscopic splitting factor, μ_B the Bohr magneton, and F_{Γ_1}, F_{Γ_3}, and F_{Γ_5} are the magnetoelastic coupling constants. The method for constructing the pseudospin Hamiltonian is discussed in greater detail in Sec. IV.

We take the applied field to lie along the z axis in the laboratory. Thus $\vec{H}^L=(0,0,H_z^L)$. We restrict the discussion to distortions in the xz plane corresponding to the displacement gradients u_{xz} and u_{zx}. Thus the orientation of the crystal with respect to the laboratory is determined by the angle ω_{xz}:

$$H_x^c = H_z^L\sin\omega_{xz}\simeq H_z^L\omega_{xz},$$
$$H_z^c = H_z^L\cos\omega_{xz}\simeq H_z^L(1-\tfrac{1}{2}\omega_{xz}^2), \tag{14}$$

where we have assumed $\omega_{xz}\ll 1$. Using Eqs. (2), (12), and (14) to rewrite Eq. (13) correct to second order in the displacement gradients u_{xz} and u_{zx}, we obtain

$$\mathcal{H}^c = g\mu_BH_z^L\{S_x^c(\omega_{xz}+F_{\Gamma_5}e_{xz})$$
$$+S_z^c[1-\tfrac{1}{2}\omega_{xz}^2+\tfrac{1}{2}F_{\Gamma_1}(u_{xz}^2+u_{zx}^2)$$
$$+F_{\Gamma_3}(2u_{xz}^2-u_{zx}^2)$$
$$+F_{\Gamma_5}e_{xz}\omega_{xz}+Fe_{xz}^2]\}, \tag{15}$$

where the term in F arises from the quadratic strain contribution to the Hamiltonian. Of all the magnetoelastic terms in $\mathcal{H}^c$ only the term linear in e_{xz} would be included in an infinitesimal-strain nonrotationally invariant theory. The terms explicitly containing the rotation ω_{xz} arise directly from Eq. (14) for the field $\vec{H}^c$. The terms containing u_{xz} and u_{zx} explicitly arise from the quadratic contributions of these displacement gradients to E_{xx} and E_{zz}. Since e_{xz} and ω_{xz} are related to u_{xz} and u_{zx} by Eqs. (9) and (10) the effects of these two types of contributions are similar.

The eigenvalues of $\mathcal{H}^c$ correct to second order in u_{xz} and u_{zx} are

$$\lambda_\pm=\pm\lambda=\pm\tfrac{1}{2}g\mu_BH_z^L[1+2F_{\Gamma_5}e_{xz}\omega_{xz}$$
$$+\tfrac{1}{2}F_{\Gamma_5}^2e_{xz}^2+\tfrac{1}{2}F_{\Gamma_1}(u_{xz}^2+u_{zx}^2)$$
$$+F_{\Gamma_3}(2u_{xz}^2-u_{zx}^2+Fe_{xz}^2)]. \tag{16}$$

The free-energy density is given by

$$F=-(N_s/\beta)\ln Z=-(N_s/\beta)\ln(2\cosh\beta\lambda), \tag{17}$$

where N_s is the number density of spins and $\beta=(kT)^{-1}$.

The shifts in the elastic constant for transverse waves propagating in the z direction and polarized along x (u_{xz}) and waves propagating in the x direction and polarized along z (u_{zx}) are given, respectively, by

$$\Delta c_{xz}=\left(\frac{\partial^2F}{\partial u_{xz}^2}\right)_{\lim u_{xz}\to 0},$$
$$\Delta c_{zx}=\left(\frac{\partial^2F}{\partial u_{zx}^2}\right)_{\lim u_{zx}\to 0}. \tag{18}$$

These definitions for the shifts in the elastic constants are equivalent to those deduced from the shifts in the phase velocities. The latter can be determined from the relevant displacements using the free energy defined in Eq. (17).[2] From Eqs. (16) and (17) we obtain

$$\Delta c_{xz}=-N_s(\tfrac{1}{2}g\mu_BH_z^L)\tanh(\tfrac{1}{2}\beta g\mu_BH_z^L)$$
$$\times(\tfrac{1}{4}F_{\Gamma_5}^2+F_{\Gamma_1}+2F+F_{\Gamma_5}+4F_{\Gamma_3}) \tag{19a}$$

and

$$\Delta c_{zx}=-N_s(\tfrac{1}{2}g\mu_BH_z^L)\tanh(\tfrac{1}{2}\beta g\mu_BH_z^L)$$
$$\times(\tfrac{1}{4}F_{\Gamma_5}^2+F_{\Gamma_1}+2F-F_{\Gamma_5}-2F_{\Gamma_3}). \tag{19b}$$

The terms proportional to $F_{\Gamma_5}^2$ arise from the infinitesimal-strain contributions to Eq. (15); the terms in F_{Γ_1} and F_{Γ_3} arise from the quadratic displacement gradients in Eq. (15); the term in F arise from the e_{xz}^2 term in Eq. (15); and the term linear in F_{Γ_5} comes from the term in Eq. (15) in $e_{xz}\omega_{xz}$. Note that the pure rotational terms in Eq. (15) do not contribute.

Had both the rotations and the quadratic displacement gradient contributions to the finite strain been

ignored, the only term appearing on the right-hand side of Eqs. (19) would have been that proportional to $F_{\Gamma_5}^2$. Thus such a theory would predict not only that measurements of Δc_{xz} and Δc_{zx} would be identical, but also that they would necessarily be negative. On the other hand the present theory predicts that $\Delta c_{xz} \neq \Delta C_{zx}$ and says nothing regarding the sign of Δc_{xz} or Δc_{zx}.

Application of the Hamiltonian derived by Abragam *et al.*[11] for the Kramers doublet in cubic symmetry to the quasistatic limit leads to results which are different from those described by Eqs. (19). Their spin-lattice Hamiltonian is written only to first order in the displacement gradients. In addition, however, the coefficient of their linear term in ω_{xz} differs from ours. No comparison between the two Hamiltonians in the dynamic limit (explicitly considered in Ref. 11) can be made, since the present approach is restricted to the quasistatic limit.

In Sec. IV the quasistatic method described here is applied explicitly to the tetragonal rare-earth vanadates and compared to experiment. Good agreement is found.

IV. APPLICATION TO THE RARE-EARTH VANADATES AND COMPARISON WITH EXPERIMENT

The rare-earth vanadates $R\,VO_4$, $R = Tm^{3+}$, Nd^{3+}, Tb^{3+}, Dy^{3+}, etc., crystallize with the tetragonal zircon structure with space group D_{4h}^{19}. The site symmetry of the rare-earth ion is D_{2d}. These systems (with the exception of $NdVO_4$) have been exhaustively studied for the past several years largely because they exhibit cooperative Jahn-Teller behavior.[20] The coupling of the rare-earth Jahn-Teller ion to elastic shear modes in the basal plane E_{xy} or $E_{xx} - E_{yy}$ causes the crystals to become unstable at low temperature. They therefore undergo a uniform distortion to orthorhombic symmetry with an associated soft acoustic mode.[21] Our interest in this paper is unrelated to this cooperative behavior. Rather we are interested in the anisotropic magnetic properties in the undistorted high-temperature, tetragonal phase of these materials. This anisotropy, which arises from the tetragonal crystal field, causes significant contributions to the spin-lattice couplings from the rotational motion associated with transverse elastic waves and from quadratic displacement gradient contributions to the finite strains.

In the following sections we consider explicitly $TmVO_4$, $NdVO_4$, $TbVO_4$, and $DyVO_4$. In each case the treatment is restricted to the case of a dc magnetic field applied along the tetragonal z axis and only distortions in the xz plane corresponding to the displacement gradients u_{xz} and u_{zx} are considered. The results are ostensibly restricted to the quasistatic limit $\omega\tau \ll 1$, although in a separate paper it is shown[17] that for the present geometry the results are actually more generally valid.

In describing the symmetry properties of the states and operators we use the notation of Koster *et al.*[19] The character table for the D_{2d} point group is reproduced in Table I together with the transformation properties of some relevant functions.

The complete spin-lattice Hamiltonian to first order in the strain for the vanadates may be written

$$\begin{aligned}\mathcal{H}_{SL}^{c} = {} & G_{\Gamma_{1\alpha}} O_{\Gamma_{1\alpha}} E_{zz} + G_{\Gamma_{1\beta}} O_{\Gamma_{1\beta}} (E_{xx} + E_{yy}) \\ & + G_{\Gamma_3} O_{\Gamma_3} (E_{xx} - E_{yy}) + G_{\Gamma_4} O_{\Gamma_4} E_{xy} \\ & + G_{\Gamma_5} (O_{\Gamma_{5\alpha}} E_{xz} + O_{\Gamma_{5\beta}} E_{yz}) , \end{aligned} \tag{20}$$

where the G's are coupling constants and $O_{\Gamma_{i\alpha}}$ represents an operator transforming as the αth basis function of the ith irreducible representation of the D_{2d} point group. Typical examples of these operators are

$$\begin{aligned} & O_{\Gamma_{1\alpha}} = J_z^2; \quad O_{\Gamma_{1\beta}} = J_x^2 + J_y^2; \quad O_{\Gamma_3} = J_x^2 - J_y^2; \\ & O_{\Gamma_4} = (J_x J_y + J_y J_x); \quad O_{\Gamma_{5\alpha}} = (J_x J_z + J_z J_x); \\ & O_{\Gamma_{5\beta}} = (J_y J_z + J_z J_y) . \end{aligned} \tag{21}$$

TABLE I. Character table for the point group D_{2d} [see Ref. (19)].

D_{2d}	E	$\bar{E}$	$2S_4$	$2\bar{S}_4$	C_2 / $\bar{C}_2$	$2C_2'$ / $2\bar{C}_2'$	$2\sigma_d$ / $2\bar{\sigma}_d$	Basis functions
Γ_1	1	1	1	1	1	1	1	$J_x^2 + J_y^2$, J_z^2, $E_{xx} + E_{yy}$, E_{zz}
Γ_2	1	1	1	1	1	−1	−1	J_z, H_z
Γ_3	1	1	−1	−1	1	1	−1	$J_x^2 - J_y^2$, $E_{xx} - E_{yy}$
Γ_4	1	1	−1	−1	1	−1	1	$J_x J_y + J_y J_x$, E_{xy}
Γ_5	2	2	0	0	−2	0	0	$\{J_x, J_y\}$, $\{H_x, H_y\}$, $\{J_x J_z + J_z J_x, J_y J_z + J_z J_y\}$, $\{E_{xz}, E_{yz}\}$
Γ_6	2	−2	$\sqrt{2}$	$-\sqrt{2}$	0	0	0	$\{\phi(\frac{1}{2}, -\frac{1}{2}), \phi(\frac{1}{2}, \frac{1}{2})\}$
Γ_7	2	−2	$-\sqrt{2}$	$\sqrt{2}$	0	0	0	$\Gamma_6 \times \Gamma_3$

Spin-lattice coupling terms quadratic in the strains will be introduced as needed in the following paragraphs.

a. $TmVO_4$. The $(2J+1)$-fold degenerate ground state of the trivalent Tm ion ($J=6$) is lifted by the D_{2d} crystal field in $TmVO_4$ into three doublets and seven singlets. The ground manifold is a non-Kramers-doublet transforming as the Γ_5 irreducible representation of D_{2d} and is separated from the nearest excited state, a singlet, by $\sim 54\ \mathrm{cm}^{-1}$.[22,23] Therefore at temperatures such that the excited states are not thermally populated we are justified in describing the ground doublet with a pseudospin $\frac{1}{2}$ formalism. The transformation properties of the components of the magnetic field, the elastic strains and the total angular momentum operators are presented in Table I. The multiplication table for the group D_{2d} is given in Table II. Any operators with matrix elements within the ground doublet must be contained within the direct product decomposition

$$\Gamma_5 \times \Gamma_5 = \Gamma_1^S + \Gamma_2^A + \Gamma_3^S + \Gamma_4^S, \tag{22}$$

where the superscripts S and A denote the symmetric and antisymmetric decompositions, respectively.

Since the operators J_x^c and J_y^c transform as Γ_5 and hence do not appear in the decomposition in Eq. (22), the projection of the Zeeman Hamiltonian onto the doublet is given by

$$\mathcal{H}_z^c = g_{\parallel}\mu_B S_z^c H_z^c, \tag{23}$$

where the pseudospin operator S_z^c [Eq. (11)] transforms as Γ_2. The perpendicular spectroscopic splitting factor $g_\perp$, is zero by symmetry.[24] The crystal-field Hamiltonian $\mathcal{H}_{CF}^c$, when projected onto the degenerate ground doublet, is a constant which we take to be zero.

The projection of the spin-lattice interaction, Eq. (20), onto the ground doublet is

$$\begin{aligned}\mathcal{H}_{SL}^c = {} & G'_{\Gamma_{1\alpha}} \underline{1} E_{zz} + G'_{\Gamma_{1\beta}} \underline{1} (E_{xx}+E_{yy}) \\ & + G'_{\Gamma_3} S_x^c (E_{xx}-E_{yy}) + G'_{\Gamma_4} S_y^c E_{xy},\end{aligned} \tag{24}$$

where $G'_{\Gamma_{1\alpha}}$, $G'_{\Gamma_{1\beta}}$, G'_{Γ_3}, and G'_{Γ_4} are new coupling constants and S_x^c and S_y^c are, respectively, proportional to the projections of O_{Γ_3} and O_{Γ_4} onto the doublet. The projections of $O_{\Gamma_{1\alpha}}$ and $O_{\Gamma_{1\beta}}$ onto the doublet are proportional to the unit matrix $\underline{1}$. The first two terms in Eq. (24), being proportional to $\underline{1}$, cannot contribute to the magnetic field dependence of the elastic constant and will henceforth be dropped. The second two terms are responsible for the cooperative Jahn-Teller behavior exhibited by $TmVO_4$. However, since they are off-diagonal, the quadratic u_{xz} and u_{zx} parts of $E_{xx}-E_{yy}$ and E_{xy} do not contribute to the second-order elastic constants corresponding to the u_{xz} and u_{zx} displacement gradients. Thus the projection of Eq. (20) onto the degenerate ground doublet of $TmVO_4$ does not lead to any field-dependent contributions to the c_{44} elastic constant.

In the presence of an applied magnetic field the degeneracy of the doublet is lifted and the eigenstates are perturbed admixtures of higher-lying states of the multiplet. The projection of the spin-lattice Hamiltonian, Eq. (20), onto the ground doublet as perturbed by the applied field leads to the following contributions to the pseudospin-lattice interaction:

$$g_{\parallel}\mu_B S_z^c [F_{44} H_x^c E_{xz} + F_{31} H_z^c (E_{xx}+E_{yy}) + F_{33} H_z^c E_{zz}]. \tag{25}$$

By considering the transformation properties of the operators, fields, and strains (Table I), each term of Eq. (25) can be shown to transform as Γ_1. Note that contrary to common assumption,[25] there is no justification for including in Eq. (25) a term of the form $S_x^c H_z^c E_{xz}$. Since S_x^c transforms as the quadrupole operator O_{Γ_3}, i.e., as Γ_3, and hence is a time symmetric operator, $S_x^c H_z^c$ is therefore time antisymmetric and cannot appear in the pseudospin Hamiltonian.

For completeness we must include the quadratic strain interaction:

$$g_{\parallel}\mu_B F_{344} S_z^c H_z^c E_{xz}^2. \tag{26}$$

In a two-level system, terms of the form

TABLE II. Multiplication table for the group D_{2d}.

Γ_1	Γ_2	Γ_3	Γ_4	Γ_5	Γ_6	Γ_7	
Γ_1	Γ_2	Γ_3	Γ_4	Γ_5	Γ_6	Γ_7	Γ_1
	Γ_1	Γ_4	Γ_3	Γ_5	Γ_6	Γ_7	Γ_2
		Γ_1	Γ_2	Γ_5	Γ_7	Γ_6	Γ_3
			Γ_1	Γ_5	Γ_7	Γ_6	Γ_4
				$\Gamma_1+\Gamma_2+\Gamma_3+\Gamma_4$	$\Gamma_6+\Gamma_7$	$\Gamma_6+\Gamma_7$	Γ_5
					$\Gamma_1+\Gamma_2+\Gamma_5$	$\Gamma_3+\Gamma_4+\Gamma_5$	Γ_6
						$\Gamma_1+\Gamma_2+\Gamma_5$	Γ_7

$g_{\parallel}\mu_B F'_{344} S_z^{c2} E_{xz}^2$ do not contribute to the magnetic-field-dependent change in the elastic constant. Therefore such terms are omitted here.

Combining Eqs. (23), (25), and (26) the pseudospin Hamiltonian for the ground doublet of $TmVO_4$ may be written

$$\mathcal{H}^c = g_{\parallel}\mu_B S_z^c (H_z^c + F_{44} H_x^c e_{xz} + \tfrac{1}{2} F_{31} H_z^c u_{zx}^2 + \tfrac{1}{2} F_{33} H_z^c u_{xz}^2 + F_{344} H_z^c e_{xz}^2). \quad (27)$$

Here, consistent with the requirement that $\mathcal{H}^c$ be correct to second order in u_{xz} and u_{zx}, we have replaced E_{xz} by e_{xz}, E_{xx} by $\frac{1}{2}u_{zx}^2$, and E_{zz} by $\frac{1}{2}u_{xz}^2$. Using Eq. (14), $\mathcal{H}^c$ may be rewritten as

$$\mathcal{H}^c = g_{\parallel}\mu_B H_z^L S_z^c (1 - \tfrac{1}{2}\omega_{xz}^2 + F_{44}\omega_{xz} e_{xz} + \tfrac{1}{2} F_{31} u_{zx}^2 + \tfrac{1}{2} F_{33} u_{xz}^2 + F_{344} e_{xz}^2). \quad (28)$$

The eigenvalues of this Hamiltonian are easily found. The calculation of the change in the elastic constant c_{44} follows that of the example given in Sec. III B. The result is

$$\Delta c_{xz} = \tfrac{1}{4} N_s (\tfrac{1}{2} g_{\parallel}\mu_B H_z^L) \tanh(\tfrac{1}{2}\beta g_{\parallel}\mu_B H_z^L) \times (1 - 2F_{44} - 4F_{33} - 2F_{344}). \quad (29)$$

For waves propagating in the x direction and polarized along z, the corresponding shift in the elastic constant ($\Delta c_{zx} = \partial^2 F/\partial u_{zx}^2$) is given by Eq. (29) with F_{44} and F_{33} replaced by $-F_{44}$ and F_{31}, respectively.

The only term in Eq. (29) which would have been included in a theory in which only infinitesimal strains are considered is the F_{344} term.

In Fig. 3 we show experimental measurements of $\Delta c_{44}/c_{44}$ vs $(H_z^L)^2$ for both u_{xz} and u_{zx} distortions at 4.2 and 77.4 K. The most striking feature of the data is the difference in the sign of Δc_{44} for the two types of distortions. This feature cannot be explained on the basis of a theory which includes only infinitesimal strains. Since the infinitesimal strains e_{xz} associated with u_{xz} and u_{zx} distortions are identical, any theory based on infinitesimal strains will predict identical results for the two measurements. The proper inclusion of the elastic rotations and/or the finite strains are required to even qualitatively understand the behavior shown in Fig. 3.

The solid curves in Fig. 3 were plotted using Eq. (29) with $g_{\parallel} = 10$ and the following sets of parameters:
for $T = 4.2$ K

$$1 - 2F_{44} - 4F_{33} - 2F_{344} = 36.62, \quad 1 + 2F_{44} - 4F_{31} - 2F_{344} = -25.80; \quad (30)$$

for $T = 77.4$ K

$$1 - 2F_{44} - 4F_{33} - 2F_{344} = 26.44, \quad 1 + 2F_{44} - 4F_{31} - 2F_{344} = -9.68. \quad (31)$$

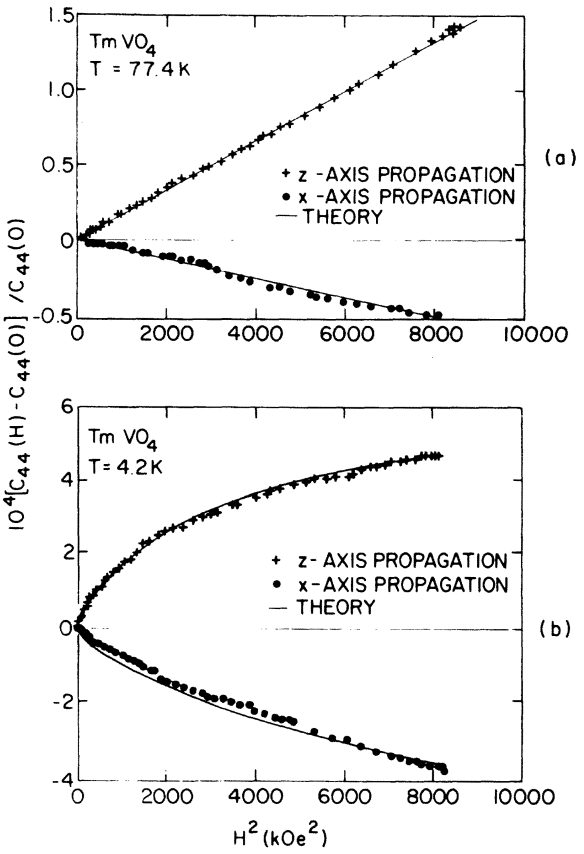

FIG. 3. Relative shift in the elastic constant c_{44} versus the square of the magnetic field in $TmVO_4$ at 4.2 and 77.4 K. The field is aligned along the z ($\langle 001 \rangle$) axis. The two sets of data at each temperature correspond to u_{xz} and u_{zx} distortions, respectively.

The difference in the parameters obtained from the data at the two temperatures is presumed to be a reflection of the increased thermal population of excited states of the multiplet at 77.4 K. These states have not been included in the present analysis. Note that in order to obtain values of the four independent coupling constants appearing in the Hamiltonian, Eq. (27), two additional independent measurements are required.

b. $NdVO_4$. Nd^{3+} is a Kramers ion whose ground multiplet has an angular momentum $J = \frac{9}{2}$. The $2J+1$ tenfold degeneracy of the free ion is lifted by the D_{2d} crystal field of $NdVO_4$ into five Kramers doublets. The lowest of these doublets lies some 100 cm^{-1} below the first excited doublet.[26,27] Therefore at low temperatures the ground doublet can be described as a pseudospin $\frac{1}{2}$ system.

The states describing the Kramers doublet transform as the Γ_7 irreducible representation of the D_{2d} double group.[27] However, the arguments of this section do not depend upon whether the Γ_6

or Γ_7 representation is used. The direct product (see Table II)

$$\Gamma_6\times\Gamma_6=\Gamma_7\times\Gamma_7=\Gamma_1+\Gamma_2+\Gamma_5 \tag{32}$$

determines the symmetry of operators which are capable of having nonzero matrix elements within the ground doublet. The projection of the Zeeman interaction onto the doublet may be written

$$\mathcal{H}^c_z=g_{\parallel}\mu_B S^c_z H^c_z+g_{\perp}\mu_B (S^c_x H^c_x+S^c_y H^c_y). \tag{33}$$

In contrast to the non-Kramers doublet [Eq. (23)] there is no reason based upon symmetry for the Kramers ion to have $g_{\perp}=0$. The values of the spectroscopic splitting factors as determined by EPR are $g_{\parallel}=\pm 0.915$ and $g_{\perp}=2.348$.[26,27] The pseudospin operators S^c_i, for the Kramers doublet transform as

$$S^c_z\rightarrow\Gamma_2,\quad \{S^c_x,S^c_y\}\rightarrow\Gamma_5. \tag{34}$$

In accordance with Kramers theorem the projection of the spin-lattice Hamiltonian, Eq. (20), onto the degenerate doublet is a constant which can be taken to be zero. In the presence of an applied field the projection onto the perturbed states is nonzero. The resulting pseudospin-lattice Hamiltonian for u_{xz} and u_{zx} distortions takes the form

$$\begin{aligned}\mathcal{H}^c_{SL}=&g_{\parallel}\mu_B F_{44} S^c_z H^c_x E_{xz}+g_{\perp}\mu_B F'_{44} S^c_x H^c_z E_{xz}\\&+g_{\parallel}\mu_B F_{33} S^c_z H^c_z E_{zz}+g_{\parallel}\mu_B F_{31} S^c_z H^c_z (E_{xx}+E_{yy})\\&+g_{\parallel}\mu_B F_{344} S^c_z H^c_z E^2_{xz}.\end{aligned} \tag{35}$$

From the transformation properties of the strain and field (see Table I) and the pseudospin operators [Eq. (34)], each term in Eq. (35) is seen to transform as Γ_1.

Combining Eqs. (35) and (33), expressing $\vec{H}^c$ in terms of the laboratory field $\vec{H}^L=(0,0,H^L_z)$, and constructing the free energy, the calculation of the shift in the elastic constant c_{44} yields

$$\begin{aligned}\Delta c_{xz}=&\tfrac{1}{4}N_s(\tfrac{1}{2}g_{\parallel}\mu_B H^L_z)\tanh(\tfrac{1}{2}\beta g_{\parallel}\mu_B H^L_z)\\&\times[1-2F_{44}-4F_{33}-2F_{344}-(g_{\perp}/g_{\parallel})^2(1+F'_{44})^2].\end{aligned} \tag{36}$$

For waves propagating in the x direction and polarized along z, the corresponding shift in the elastic constant Δc_{zx} is given by Eq. (36) with F_{44}, F_{33}, and F'_{44} replaced by $-F_{44}$, F_{31}, and $-F'_{44}$, respectively. This result differs from that for the non-Kramers doublet [Eq. (29)] only through the necessarily negative term in $(g_{\perp}/g_{\parallel})^2$. Had only infinitesimal strains been included in the theory the square brackets in Eq. (36) would be replaced by

$$[-2F_{344}-(g_{\perp}/g_{\parallel})^2F'^2_{44}]. \tag{37}$$

In Fig. 4 is shown the behavior of $\Delta c_{44}/c_{44}$ for $NdVO_4$ at 4.2 and 77.4 K for the u_{xz} and u_{zx} distortions, respectively. The solid curves are plotted using Eq. (36) with the following values of the parameters: for $T=4.2$ K

$$\begin{aligned}&1-2F_{44}-4F_{33}-2F_{344}-(g_{\perp}/g_{\parallel})^2(1+F'_{44})^2=-240,\\&1+2F_{44}-4F_{31}-2F_{344}-(g_{\perp}/g_{\parallel})^2(1-F'_{44})^2=-800;\end{aligned} \tag{38}$$

for $T=77.4$ K

$$\begin{aligned}&1-2F_{44}-4F_{33}-2F_{344}-(g_{\perp}/g_{\parallel})^2(1+F'_{44})^2=-328,\\&1+2F_{44}-4F_{31}-2F_{344}-(g_{\perp}/g_{\parallel})^2(1-F'_{44})^2=-1104.\end{aligned} \tag{39}$$

c. $TbVO_4$. The ground multiplet of the trivalent Tb ion has angular momentum $J=6$. The D_{2d} crystal field of $TbVO_4$ lifts the 13-fold degeneracy of the free ion into seven singlets and three doublets. The lowest-lying states of the multiplet consist of a singlet ground state, a non-Kramers doublet which lies at $\Delta\simeq 11.5$ cm^{-1} above the singlet, and a second singlet at $\Delta\simeq 11.5$ cm^{-1} above the doublet.[28] The other states of the multiplet are sufficiently far removed from these states that they can be neglected. In the presence of a magnetic field along the z axis the D_{2d} symmetry is reduced

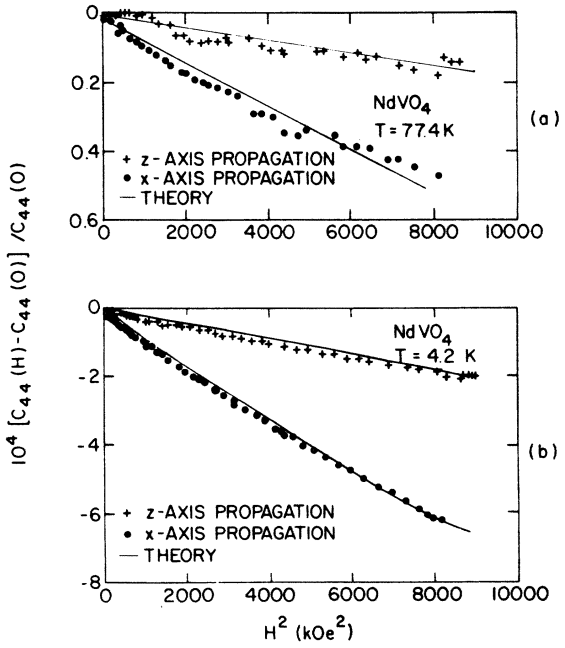

FIG. 4. Relative shift in the elastic constant c_{44} versus the square of the magnetic field in $NdVO_4$ at 4.2 and 77.4 K. The field is aligned along the z ($\langle 001\rangle$) axis. The two sets of data at each temperature correspond to u_{xz} and u_{zx} distortions, respectively.

to the point group S_4.[19] Labeling the four states according to the irreducible representations of S_4 we find that the singlets transform, respectively, as Γ_1 and Γ_2 and the components of the doublet as Γ_3 and Γ_4.

Projecting the Zeeman, the crystal field, and the spin-lattice Hamiltonians onto the four low-lying states leads to a pseudospin Hamiltonian which may be written

$$\mathcal{H}^c = \begin{array}{c} \\ \psi_{\Gamma_2} \\ \psi_{\Gamma_4} \\ \psi_{\Gamma_3} \\ \psi_{\Gamma_1} \end{array} \begin{array}{c} \begin{array}{cccc} \psi_{\Gamma_2} & \psi_{\Gamma_4} & \psi_{\Gamma_3} & \psi_{\Gamma_1} \end{array} \\ \begin{pmatrix} \lambda_{02}+M_{11} & M_{12} & M_{13} & 0 \\ M_{12} & \lambda_{04}+M_{22} & 0 & M_{24} \\ M_{13} & 0 & \lambda_{03}+M_{33} & M_{34} \\ 0 & M_{24} & M_{34} & \lambda_{01}+M_{44} \end{pmatrix} \end{array} . \tag{40}$$

Here, λ_{0i} are the eigenvalues of $\mathcal{H}_z^c+\mathcal{H}_{CF}^c$ for a z-axis magnetic field:

$$\begin{aligned} \lambda_{02} &= \Delta , \\ \lambda_{04} &= \tfrac{1}{2} g_{\parallel} \mu_B H_z^c , \\ \lambda_{03} &= -\tfrac{1}{2} g_{\parallel} \mu_B H_z^c , \\ \lambda_{01} &= -\Delta , \end{aligned} \tag{41}$$

where $g_{\parallel}$ is the parallel g factor for the $\Gamma_{3,4}$ doublet. The M_{ij} are matrix elements of the spin-lattice interaction between the eigenstates of $\mathcal{H}_z^c+\mathcal{H}_{CF}^c$. They are determined from the symmetry properties of the linearly perturbed eigenstates in the presence of a magnetic field and the symmetry of the angular momentum operators. They are given by

$$\begin{aligned} M_{11} &= G_{11} E_{xz}^2 , \\ M_{22} &= G_{22} E_{xz}^2 + \tfrac{1}{2} g_{\parallel} \mu_B [F_{44} H_x^c E_{xz} \\ &\quad + H_z^c (F_{33} E_{zz} + F_{31} E_{xx} + F_{344} E_{xz}^2)] , \\ M_{33} &= G_{22} E_{xz}^2 - \tfrac{1}{2} g_{\parallel} \mu_B [F_{44} H_x^c E_{xz} \\ &\quad + H_z^c (F_{33} E_{zz} + F_{31} E_{xx} + F_{344} E_{xz}^2)] , \\ M_{44} &= G_{44} E_{xz}^2 ; \end{aligned} \tag{42}$$

and

$$\begin{aligned} M_{12} &= G_{12} E_{xz} + \tfrac{1}{2} g_{12} \mu_B (G'_{12} E_{xz} H_z^c + G''_2 H_x^c) , \\ M_{13} &= -G_{12} E_{xz} + \tfrac{1}{2} g_{12} \mu_B (G'_{12} E_{xz} H_z^c + G''_2 H_x^c) , \\ M_{24} &= G_{24} E_{xz} + \tfrac{1}{2} g_{24} \mu_B (G'_{24} E_{xz} H_z^c + G''_4 H_x^c) , \\ M_{34} &= -G_{24} E_{xz} + \tfrac{1}{2} g_{24} \mu_B (G'_{24} E_{xz} H_z^c + G''_4 H_x^c) , \end{aligned} \tag{43}$$

where g_{12} and g_{24} are the perpendicular spectroscopic splitting factors. Note that the diagonal spin-lattice matrix elements M_{ii} are correct to second order in the u_{xz} and u_{zx} displacement gradients, whereas the off-diagonal matrix elements $M_{ij}, i \neq j$, are correct only to first order. Using Eq. (14), H_x^c is seen to be first order in ω_{xz} for the laboratory field $\vec{H}^L = (0, 0, H_z^L)$, assumed here.

From Eq. (40) the shift in the elastic constant is given by

$$\Delta c_{44} = \frac{N_s}{Z_0} \sum_{i=1}^{4} e^{-\beta \lambda_{0i}} \lambda_i'' , \tag{44}$$

where

$$Z_0 = \sum_{i=1}^{4} e^{-\beta \lambda_{0i}} , \tag{45}$$

and λ_i'' denotes the second derivative with respect to either u_{xz} or u_{zx} of the eigenvalues of Eq. (40). These eigenvalues are given by

$$\begin{aligned} \lambda_2 &= \lambda_{02} + M_{11} + \frac{M_{12}^2}{\lambda_{02}-\lambda_{04}} + \frac{M_{13}^2}{\lambda_{02}-\lambda_{03}} , \\ \lambda_4 &= \lambda_{04} + M_{22} + \frac{M_{12}^2}{\lambda_{04}-\lambda_{02}} + \frac{M_{24}^2}{\lambda_{04}-\lambda_{01}} , \\ \lambda_3 &= \lambda_{03} + M_{33} + \frac{M_{34}^2}{\lambda_{03}-\lambda_{01}} + \frac{M_{13}^2}{\lambda_{03}-\lambda_{02}} , \\ \lambda_1 &= \lambda_{01} + M_{44} + \frac{M_{34}^2}{\lambda_{01}-\lambda_{03}} + \frac{M_{24}^2}{\lambda_{01}-\lambda_{04}} . \end{aligned} \tag{46}$$

We substitute Eq. (46) into Eq. (44) and obtain the following results in the high-temperature limit ($\beta \lambda_{0i} \ll 1$):

$$\Delta c_{xz} = \tfrac{1}{8} N_s \beta (\tfrac{1}{2} g_{\parallel} \mu_B H_z^L)^2 [1 - 2F_{44} - 4F_{33} - 2F_{344} - 2(g_{12}/g_{\parallel})^2 (1+G'_{12})^2 - 2(g_{24}/g_{\parallel})^2 (1+G'_{24})^2] + O(\beta^2) , \tag{47}$$

where $O(\beta^2)$ indicates that we have taken $\beta G_{ij} \ll 1$. The elastic constant shift Δc_{zx}, corresponding to a u_{zx} displacement gradient, is obtained by replacing F_{44}, F_{33}, G'_{12}, and G'_{24} by $-F_{44}$, F_{31}, $-G'_{12}$, and $-G'_{24}$, respectively.

Δc_{xz} and Δc_{zx} are quadratic in H_z^L which is in agreement with the experimental results shown in Fig. 5. The difference in the slopes of the data for u_{xz} and u_{zx} distortions is entirely a consequence of the inclusion of the rotational motion and the use of finite strains. As in the case of $TmVO_4$ and $NdVO_4$, the use of infinitesimal strains results in Δc_{44} being the same for both u_{xz} and u_{zx} distortions.

d. $DyVO_4$. The ground multiplet of the Kramers ion Dy^{3+} has an angular momentum $J = \frac{15}{2}$. The lowest-lying states of the multiplet in the presence of the D_{2d} crystal field in $DyVO_4$ consist of two Kramers doublets separated by $2\Delta = 9\ \mathrm{cm}^{-1}$. We

label the eigenstates by their symmetries according to the point group S_4 (corresponding to a z-axis field) and obtain the Hamiltonian in the form

$$\mathcal{H}^c = \begin{array}{c} \\ \psi_{\Gamma_5} \\ \psi_{\Gamma_6} \\ \psi_{\Gamma_8} \\ \psi_{\Gamma_7} \end{array} \begin{array}{c} \begin{array}{cccc} \psi_{\Gamma_5} & \psi_{\Gamma_6} & \psi_{\Gamma_8} & \psi_{\Gamma_7} \end{array} \\ \begin{bmatrix} \lambda_{05}+M_{11} & M_{12} & M_{13} & 0 \\ M_{12} & \lambda_{06}+M_{22} & 0 & M_{24} \\ M_{13} & 0 & \lambda_{08}+M_{33} & M_{34} \\ 0 & M_{24} & M_{34} & \lambda_{07}+M_{44} \end{bmatrix} \end{array}, \tag{48}$$

where the eigenvalues of $\mathcal{H}_z^c + \mathcal{H}_{CF}^c$ are given by

$$\begin{aligned} \lambda_{05} &= -\Delta - \tfrac{1}{2} g_{\parallel} \mu_B H_z^c, \\ \lambda_{06} &= -\Delta + \tfrac{1}{2} g_{\parallel} \mu_B H_z^c, \\ \lambda_{07} &= +\Delta + \tfrac{1}{2} g'_{\parallel} \mu_B H_z^c, \\ \lambda_{08} &= +\Delta - \tfrac{1}{2} g'_{\parallel} \mu_B H_z^c. \end{aligned} \tag{49}$$

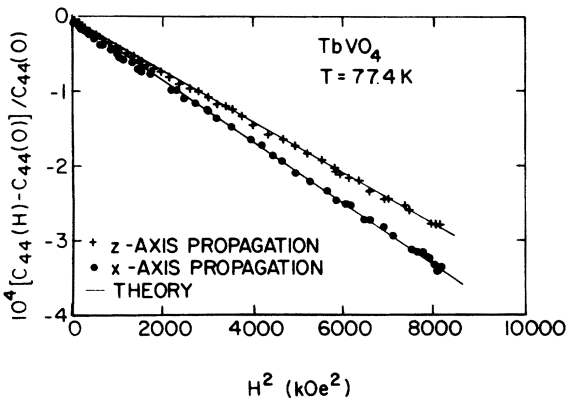

FIG. 5. Relative shift in the elastic constant c_{44} versus the square of the magnetic field in $TbVO_4$ at 77.4 K. The field is aligned nominally along the z ($\langle 001 \rangle$) axis. The two sets of data correspond to the u_{xz} and u_{zx} distortions, respectively.

Here, $g_{\parallel}$ and $g'_{\parallel}$ are, respectively, the parallel g factors for the two doublets. The matrix elements of the spin-lattice interaction between the eigenstates of $\mathcal{H}_z^c + \mathcal{H}_{CF}^c$ are given by

$$\begin{aligned} M_{11} &= G_{11} E_{xz}^2 - \tfrac{1}{2} g_{\parallel} \mu_B F_{44} H_x^c E_{xz} - \tfrac{1}{2} g_{\parallel} \mu_B H_z^c (F_{33} E_{zz} + F_{31} E_{xx} + F_{344} E_{xz}^2), \\ M_{22} &= G_{11} E_{xz}^2 + \tfrac{1}{2} g_{\parallel} \mu_B F_{44} H_x^c E_{xz} + \tfrac{1}{2} g_{\parallel} \mu_B H_z^c (F_{33} E_{zz} + F_{31} E_{xx} + F_{344} E_{xz}^2), \\ M_{33} &= G_{33} E_{xz}^2 - \tfrac{1}{2} g'_{\parallel} \mu_B F'_{44} H_x^c E_{xz} - \tfrac{1}{2} g'_{\parallel} \mu_B H_z^c (F'_{33} E_{zz} + F'_{31} E_{xx} + F'_{344} E_{xz}^2), \\ M_{44} &= G_{33} E_{xz}^2 + \tfrac{1}{2} g'_{\parallel} \mu_B F'_{44} H_x^c E_{xz} + \tfrac{1}{2} g'_{\parallel} \mu_B H_z^c (F'_{33} E_{zz} + F'_{31} E_{xx} + F'_{344} E_{xz}^2); \end{aligned} \tag{50}$$

and

$$\begin{aligned} M_{12} &= \tfrac{1}{2} g_{\perp} \mu_B (G'_{12} H_z^c E_{xz} + G''_{12} H_x^c), \\ M_{13} &= -G_{13} E_{xz} + \tfrac{1}{2} g'_{\perp} \mu_B (G'_{13} H_z^c E_{xz} + H_x^c), \\ M_{24} &= G_{13} E_{xz} + \tfrac{1}{2} g'_{\perp} \mu_B (G'_{13} H_z^c E_{xz} + H_x^c), \\ M_{34} &= \tfrac{1}{2} g''_{\perp} \mu_B (G'_{34} H_z^c E_{xz} + H_x^c). \end{aligned} \tag{51}$$

The eigenvalues of Eq. (48) can be expressed formally as in Eq. (46) and the shift in the elastic constant can then be expressed as in Eq. (44). The results are given in the high-temperature limit by

$$\begin{aligned} \Delta c_{xz} = {} & \tfrac{1}{8} N_s \beta (\tfrac{1}{2} g_{\parallel} \mu_B H_z^L)^2 (1 - 2F_{44} - 4F_{33} - 2F_{344}) - \frac{N_s \beta}{8} \left(\frac{g_{\perp} \mu_B H_z^L}{2} \right)^2 (G'_{12} + 1)^2 \\ & + \tfrac{1}{8} N_s \beta (\tfrac{1}{2} g'_{\parallel} \mu_B H_z^L)^2 (1 - 2F'_{44} - 4F'_{33} - 2F'_{344}) - \frac{N_s \beta}{8} \left(\frac{g''_{\perp} \mu_B H_z^L}{2} \right)^2 (G'_{34} + 1)^2 - \frac{N_s \beta}{4} \left(\frac{g'_{\perp} \mu_B H_z^L}{2} \right)^2 (G'_{13} + 1)^2. \end{aligned} \tag{52}$$

The elastic constant shift Δc_{zx}, corresponding to a u_{zx} displacement gradient, is obtained from Eq. (52) by replacing F_{44}, F_{33}, G'_{12}, F'_{44}, F'_{33}, G'_{34}, and G'_{13} with $-F_{44}$, F_{31}, $-G'_{12}$, $-F'_{44}$, F'_{31}, $-G'_{34}$, and $-G'_{13}$.

The behavior of Δc_{44} vs $(H_z^L)^2$ in the high-temperature limit in $DyVO_4$ is shown in Fig. 6 at 77.4 K for both u_{xz} and u_{zx} distortions. The proportionality to $(H_z^L)^2$ in the high-temperature limit is clearly seen as is the difference in the slopes for the two distortions arising from the contributions of the rotations and the finite strains.

V. SUMMARY

The main conclusions of the present investigation are (i) the elastic rotations associated with transverse elastic waves, together with finite-strain effects, make significant contributions to the magnetoelastic properties of paramagnetic

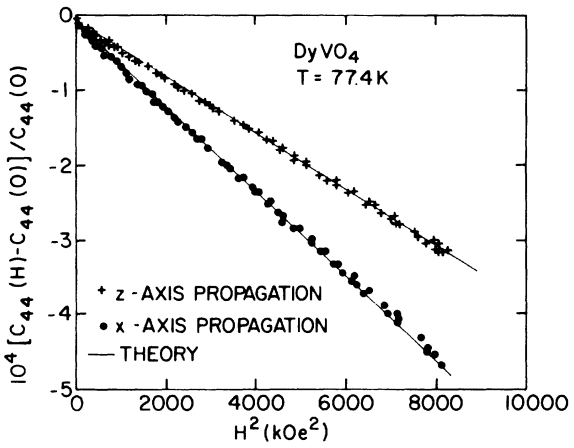

FIG. 6. Relative shift in the elastic constant c_{44} versus the square of the magnetic field in $DyVO_4$ at 77.4 K. The field is aligned nominally along the z ($\langle 001 \rangle$) axis. The two sets of data correspond to the u_{xz} and u_{zx} distortions, respectively.

materials. These effects are not included in the usual infinitesimal-strain theory. (ii) We have developed a calculational technique, valid in the quasistatic limit, which enables us to correctly calculate the changes in the elastic properties associated with the magnetoelastic coupling. This technique can be used even when the magnetic system is described by pseudospin operators whose rotational properties are not known. (iii) Experimental data on four paramagnetic materials, $TmVO_4$, $NdVO_4$, $TbVO_4$, and $DyVO_4$, have been presented. These data clearly exhibit significant deviations from infinitesimal-strain theory and confirm the theory presented here. These data are the first to clearly demonstrate these effects in paramagnetic materials.

ACKNOWLEDGMENTS

We have benefited from useful discussions with Professor P. A. Fedders. We are grateful to F. Dacol for making measurements presented here, to P. M. Marcus for carefully reading the manuscript, and to B. A. Scott for providing the vanadate crystals used in this investigation.

[1]R. A. Toupin, J. Ration. Mech. Anal. 5, 849 (1956).
[2]H. F. Tiersten, J. Math. Phys. 5, 1298 (1964).
[3]W. F. Brown, Jr., J. Appl. Phys. 36, 994 (1965).
[4]D. E. Eastman, Phys. Rev. 148, 530 (1966).
[5]R. L. Melcher, Phys. Rev. Lett. 25, 1201 (1970).
[6]R. L. Melcher, in *Proceedings of the International School of Physics "Enrico Fermi," Varenna, Course LII,* edited by E. Burstein (Academic, New York, 1971).
[7]B. W. Southern and D. A. Goodings, Phys. Rev. B 7, 534 (1973); B. W. Southern, Can. J. Phys. 51, 1646 (1973).
[8]S. Kumar, T. Ray, and D. K. Ray, Phys. Status Solidi 37, K65 (1970).
[9]J. H. van Vleck, J. Chem. Phys. 7, 72 (1939).
[10]R. L. Melcher, Phys. Rev. Lett. 28, 165 (1972).
[11]A. Abragam, J. F. Jacquinot, M. Chapelier, and M. Goldman, J. Phys. C 5, 2629 (1972).
[12]Lynn Bonsall and R. L. Melcher, Bull. Am. Phys. Soc. 20, 349 (1975).
[13]V. Dohm and P. Fulde, Z. Phys. B 21, 369 (1975).
[14]V. Dohm, Z. Phys. B 23, 153 (1976).
[15]R. L. Melcher, J. B. Merry, and D. I. Bolef, Rev. Sci. Instrum. 39, 1618 (1968).
[16]A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Oxford U.P., London, 1970).
[17]P. A. Fedders and R. L. Melcher, following paper, Phys. Rev. B 14, 1142 (1976).
[18]Note, however, that Dohm's (Ref. 14) comments are misleading concerning the original experimental evidence for the rotational contribution to the magnetoelastic properties of an antiferromagnet (Refs. 5 and 6). In the case of a uniaxial antiferromagnet in the presence of an axial dc magnetic field at low temperature, magnetoelastic terms such as $G_{11}M_{\alpha x}^2$ contribute to the free energy only in third or higher order in the displacement gradients and consequently do not contribute to the second-order elastic constants. (Here, $M_{\alpha i}$ denotes the ith component of the αth sublattice magnetization.) Similarly, terms such as $G_{33}M_{\alpha z}^2E_{zz}$ do not contribute to the magnetic field dependence of the second-order elastic constants since the parallel susceptibility of the antiferromagnet is zero. Neither of these two types of terms contributes to the experiments reported in Refs. 5 and 6. Therefore, the conclusions in that work (Refs. 5 and 6) and in particular that the departures from infinitesimal-strain theory arise from the rotational motion are correct and unambiguous.
[19]G. F. Koster, J. O. Dimmock, R. G. Wheeler, and H. Statz, *Properties of the Thirty-Two Point Groups* (MIT, Cambridge, Mass., 1963).
[20]G. A. Gehring and K. A. Gehring, Rep. Prog. Phys. 38, 1 (1975).
[21]R. L. Melcher and B. A. Scott, Phys. Rev. Lett. 28, 607 (1972); J. R. Sandercock, S. B. Palmer, R. J. Elliott, W. Hayes, S. R. P. Smith, and A. P. Young, J. Phys. C 5, 3126 (1972); R. L. Melcher, E. Pytte, and B. A. Scott, Phys. Rev. Lett. 31, 307 (1973); R. L. Melcher, in *Physical Acoustics,* edited by W. P. Mason and R. N. Thurston (Academic, New York, to be published), Vol. 12.
[22]K. D. Knoll, Phys. Status Solidi B 45, 553 (1971).
[23]D. E. Wortman, R. P. Leavitt, and C. A. Morrison, J. Phys. Chem. Solids 35, 591 (1974).
[24]J. M. Baker and B. Bleaney, Proc. R. Soc. A 245,

156 (1958).
[25]E. B. Tucker, in *Physical Acoustics*, edited by W. P. Mason (Academic, New York, 1966), Vol. 4A.
[26]U. Ranon, Phys. Lett. A 28, 228 (1968).
[27]N. Karayianas, C. A. Morrison, and D. E. Wortman, J. Chem. Phys. 62, 4125 (1965).
[28]R. J. Elliott, R. T. Harley, W. Hayes, and S. R. P. Smith, Proc. R. Soc. A 328, 217 (1972).