PHYSICAL REVIEW B VOLUME 4, NUMBER 10 15 NOVEMBER 1971

Linear and Nonlinear Electrodynamics in Elastic Anisotropic Dielectrics

M. Lax and D. F. Nelson
Bell Telephone Laboratories, Murray Hill, New Jersey 07974
(Received 6 May 1971)

We have constructed an *ab initio* macroscopic Lagrangian theory of linear and nonlinear electrodynamics for an anisotropic dielectric possessing acoustic, ionic, electronic, and other internal excitations. This theory can with modest effort predict the symmetry, frequency dispersion, and internal mechanisms for susceptibilities governing all orders of direct and indirect interactions between these excitations and the electromagnetic field. Application is made to optical harmonic generation, and the direct and indirect electro-optic and photoelastic effects. The theory starts with a Lorentzian microscopic formulation in terms of moving, massive point charges in a vacuum. It is converted to a long-wavelength macroscopic theory via a continuum limit. A Lagrangian is constructed from the vacuum electromagnetic Lagrangian, the usual interaction between the matter charge current and the electromagnetic field, a kinetic energy of the matter's internal motions and a matter stored-energy term. The stored energy must be invariant under arbitrary body rotations, displacements, and spatial reflections and is therefore a function of the basic invariants: the finite strain tensor and body components of the excitation fields. Parity-violating terms are also considered. The stored energy is expanded as a polynomial in these basic invariants with coefficients, called material descriptors (since they describe intrinsic properties of the crystal), which are restricted in form by the crystal space-group symmetry. Effective-local-field effects are shown to be included in the stored energy. Equations for the electromagnetic field, the acoustic field, and the internal excitations follow deductively from the Lagrangian. Elimination of the internal excitations leads to electromagnetic and acoustic equations with piezoelectric, photoelastic, electro-optic, frequency mixing, and other couplings. Among the linear results are a new eigenvector formulation of crystal optics, a generalized Lyddane-Sachs-Teller relation, and a dyadic Green's function for radiations in crystals of arbitrary anisotropy. Constitutive relations for linear and nonlinear susceptibilities in terms of the material descriptors indicate the mechanisms involved. All indirect contributions to any nonlinear interaction arise automatically, and their symmetry, which often differs from that of the direct interaction, is predicted. The nonlinear results include previously ignored rotational contributions to photoelastic interactions of all orders.

I. INTRODUCTION

Lasers have led to the discovery of a vast number of new nonlinear optical interactions—optical harmonic generation, two-photon absorption, self-focusing of light, self-induced transparency, etc. They have also led to a renewed interest in, and extensive studies of, a number of nonlinear optical interactions known for decades—the linear electro-optic (Pockels) effect, the quadratic electro-optic (Kerr) effect, acousto-optic diffraction, Brillouin scattering, and Raman scattering.

Based on the experimental results, many of these interactions have been given a phenomenological formulation in which a tensor of appropriate symmetry is assumed to lead to mixing of the input fields to give a nonlinear polarization which drives the wave equation. Theoretical justifications for such formulations have been given for many of the nonlinear interactions. However, formulations for some interactions, such as the photoelastic interaction which governs both acousto-optic diffraction and Brillouin scattering, have not been derived from a basic point of view. Such derivations have often been inhibited by the complexity of the task when a fully quantum-mechanical treatment was attempted. What we wish to show here is that a first-principles *classical* treatment can be carried through to yield a prediction of the form of the interaction.

The immediate motivation of this work was the desire to obtain deductively the form of the nonlinear polarization governing acoustically induced optical harmonic generation.[1] The experiment consisted of mixing an input optic wave with an input acoustic wave to yield an output optic wave at a frequency displaced from the optical harmonic by the much lower acoustic frequency. As such it is a *four*-wave acousto-optic interaction. Because it is a high-order interaction, a number of multistep indirect contributions to the effect exist besides the direct interaction which mixes the waves in one step. For this reason it is not apparent what form the nonlinear polarization should have when approached from a phenomenological point of view. A deductive derivation is needed.

Since we are interested in the interaction of visible light or longer-wavelength electromagnetic radiation with ultrasonic waves having frequencies as high as, say, 10^{10} Hz, the theory can be a long-wavelength, that is macroscopic, theory. Because the material velocities we are concerned with are acoustic velocities which are ~ 10^{-5} times the velocity of light, the theory can be nonrelativistic. Also we believe that a basic deductive-type theory at which we aim should begin from a microscopic point of view in order to account properly for the various material motions and resonances (electronic, ionic, excitonic, etc.). The fruitfulness of this approach is illustrated by the results we have obtained for the form of the photoelastic interaction[2] and of the acoustically induced optical harmonic generation interaction.[3] Our interest lies particularly in those phenomena which involve the anisotropy of crystalline solids and so the development will take a form applicable to materials of arbitrary anisotropy.

Our approach is to construct a microscopic Lagrangian consisting of a particle Lagrangian for all the material particles of the crystal, a field Lagrangian for the electromagnetic field in a vacuum, and a field-particle interaction Lagrangian. The field Lagrangian and the field-particle Lagrangian for nonrelativistic charged particles are both known from classical electromagnetic theory. The kinetic energy of nonrelativistic particles, which is part of the particle Lagrangian, is also well known. There is a potential energy of the particles, that is, the stored energy of the solid, which does not arise from classical electromagnetic forces, but rather from quantum-mechanical effects. The *explicit* form of this stored energy, thus, cannot be written down on the basis of this classical theory. The energy, however, must be expressible as a function of the configuration of the solid. This configuration is describable in terms of displacement gradients and of internal displacements that are generally, but not invariably, associated with contributions (ionic, excitonic, electronic) to the polarization. The energy will be expressed in terms of these variables and their first derivatives, since in the long-wave limit higher derivatives make progressively smaller contributions to the energy. In addition, the stored energy must be invariant against body rotations and displacements, and symmetry operations of the crystal space group. Thus the energy must be written in terms of an independent set of rotational and displacemental invariants constructed from the above-mentioned variables and their derivatives. We extend the treatment of Toupin's classic paper[4] by using the finite strain tensor and body components of several polarizationlike displacements as the relevant invariant variables. The stored energy can then be expanded as a power series in these independent variables with coefficients called "material descriptors," in Toupin's terminology.[4] These are here matrix-tensor quantities of known symmetry but of unknown numerical value. They characterize the solid under study and are not functions of any of the characteristics (e.g., frequency or wave vector) of any applied influence. Their numerical values can be calculated only from quantum mechanics; here, we will regard their numerical values to be determined by comparison with experiment. It is hoped that a consequence of this work will be to focus attention on, and to lead to a quantum-mechanical calculation of, those material descriptors which on the basis of this work are found to be responsible for particular interactions.

The choice of polarizationlike coordinates among the expansion variables of the stored energy is a logical procedure needing no further justification. Nevertheless, let us point out three important consequences of this choice which contrast sharply with the results that would be obtained if the electric field were used as an expansion variable, a procedure that occasionally is used in the literature.[5] First, it is apparent that the *several* polarizationlike coordinates can give a more detailed and hence more nearly correct expression for the stored energy when compared to the single electric field. Second, the eventual elimination of the polarizationlike coordinates in interaction tensor expressions in terms of the input electric field leads to the appearance of susceptibilitylike functions which contain all of the predicted frequency dependence (which arises naturally from the dynamical nature of the equations) of the material tensor being calculated. Third, since the elimination just spoken of can introduce an input or intermediate elastic field, as well as an input or intermediate electric field, all multistep indirect contributions to the over-all interaction arise automatically and in a way that none can be forgotten.

Once the microscopic Lagrangian has been constructed, the development becomes entirely deductive. The continuum limit, in which sums over energies of discrete particles are replaced by integrals over a material continuum, is first taken and then the Lagrange equations formed using the particle positions and the scalar and vector potentials of the electromagnetic field as the independent variables. This yields a set of electromagnetic field equations and a set of dynamical equations governing the modes of motion (including resonances) of the material medium. The equations are coupled by field-particle interaction terms. Widely applicable techniques are presented for the solution of nonlinear optical or acousto-optical problems. In the process, general expressions for the constitutive relations (explicit expressions for the polarization, current, and charge as functions of the field variables) are obtained. Constitutive expressions for linear and nonlinear acoustic properties are also obtained. Application of this theory to the photoelastic interaction[2] and to the acoustically induced optical harmonic generation[3] interaction have already been published.

It can be seen that the theory presented here has much in common conceptually with the Lorentz "electron theory" of matter[6] but represents a considerable generalization over it by inclusion of crystal symmetry, anisotropy, nonlinearity, elastic deformation, ionic mode polarization, etc. We believe that the present theory is as basic as a classical theory of wave interactions in dielectrics can be. Nevertheless, it is best described as an intermediate theory because, even though it is more basic than a phenomenological formulation based on experimental results and intuitive ideas, it is less basic than a completely quantum-mechanical theory.

We believe, however, that our classical approach will have a wide range of applicability in linear and nonlinear optics and acoustics. For nonlinear interactions of light and sound fields, whose energies are large compared to the quantum of energy, quantization of the electromagnetic and sound fields is unnecessary. When driven nonlinear processes are considered the ionic motions can also be treated classically. It is less obvious that the polarization associated with an excitonic transition can be treated classically. However, Hopfield[7] has shown that the transition polarization operator has approximately boson character and has used this to justify a highly successful classical analysis of optical absorption associated with excitons.[8]

Raman and Brillouin scattering differ from acousto-optic scattering in that one of the input fields is thermal rather than driven. A classical treatment with the thermal occupancy $\bar{n}(\omega) = (e^{\hbar\omega/kT} - 1)^{-1}$ is possible for the anti-Stokes line. The Stokes line can also be treated classically *á la* Einstein by introducing a thermal input larger than that for the anti-Stokes line in the ratio $(\bar{n}+1)/\bar{n} = e^{\hbar\omega/kT}$, where $\hbar\omega$ is the energy of the excitation (phonon, polariton, etc.) that is to be emitted. This procedure is equivalent to the use of Nyquist's theorem to estimate the thermal input (see, for example, Barker and Loudon[9]). This reasoning justifies the comparison between experiment and "classical theory" used in the past, and indicates that the major task of a quantum theory is not to reproduce the classical results with the *ad hoc* introduction of nonlinear energies but rather the calculation of the material descriptors describing the strength of the nonlinear interaction.

The theory we develop here can predict the following with modest effort: (i) the symmetry of any nonlinear, as well as linear, interaction of electromagnetic waves and various excitation modes of the crystal such as acoustic, ionic, electronic, and mixed character (e.g., polaritons) vibrations; (ii) the various multistep indirect contributions to the over-all interaction, their symmetry, and their relation to various linear and nonlinear interactions; (iii) the frequency dispersion of the susceptibility that governs any nonlinear interaction; (iv) the form of any nonlinear, as well as linear, interaction susceptibility in terms of the fundamental material descriptors. Since material descriptors can be associated with particular interactions, prediction (iv) indicates all the basic mechanisms that contribute to an observed susceptibility. A significant example of (i) is the prediction[2,10] that the symmetry of the photoelastic interaction is lower than that expected according to the Pockels[11] phenomenological formulation, the accepted formulation since 1889. Our theory predicted that the measure of elastic deformation relevant to the photoelastic interaction is the displacement gradient since *both* strains and rotations affect the light propagation in the crystal. This effect removes the symmetry of the Pockels photoelastic tensor upon interchange of its elastic indices. Experimental verification of this has recently been obtained.[12]

An example of (ii) above is the prediction[3] of five indirect processes of significant size that contribute to acoustically induced optical harmonic generation. Each was shown to have a distinct and lower symmetry compared to the direct interaction. Each had a different and explicit dependence on the wave vectors of the interacting waves. An example of (iii) and (iv) above is the prediction[2] of the form of the susceptibility governing the photoelastic interaction. Terms contributing to the susceptibility which had different symmetries because they arose from different internal mechanisms were shown to have different frequency dependences. The frequency dependence predicted is explicit because it results from the solution of the time-dependent dynamical equations and because the numerically unknown material descriptors are frequency independent quantities. The theory can be extended to predict the wave-vector dependence of various susceptibilities. In a long-wavelength theory such as this, wave-vector dispersion would result, for example, from the addition, when symmetry allows, of terms linear or quadratic in the wave vector of the optic or acoustic wave. Effects arising from these terms (optical activity, for example) are considerably smaller than frequency dispersion effects. For this reason we have omitted a derivation of wave-vector dispersion effects in this paper even though polarization gradient terms, from which the effects arise, have been included in the stored energy.

Besides wave-vector dispersion effects, we omit for simplicity a number of effects in this paper. We treat ideal dielectrics here, and so set the free charge equal to zero. The existence of electron spin is ignored, and hence ferromagnetic phenomena are excluded. Ferroelectric phenomena are also excluded in the present treatment. [The contributions to nonlinear susceptibilities calculated in this paper (for second-harmonic generation, photoelasticity, etc.) are all present in ferroelectrics, but some additional contributions may be necessary for some susceptibilities.] Neither will we include loss in the various vibration modes of the crystal. Last, we exclude all thermal phenomena. We surmise that all of these except the last involve relatively straightforward, though sometimes complex, extensions of the present treatment. The inclusion of thermal phenomena will require inclusion of statistical effects as well as the mechanical effects treated in this paper.

It would take far too much space to describe here all of the major advances in the subject that we are treating and so we will cite here mainly those papers that have had a direct impact on this work and a few others that deal with closely related topics. Of greatest importance to this work was the paper by Toupin[4] in which he developed a static theory of an elastic dielectric. In that paper he gave a rigorous discussion of the method of constructing a stored energy of the solid which possesses the four types of invariances mentioned above. Later he developed a dynamic theory of elastic dielectrics and applied it to a number of phenomena including the photoelastic interaction in isotropic media.[13] Our present theory contrasts to Toupin's dynamic theory in several ways. First, Toupin's treatment began from a macroscopic continuum point of view in which an elastic dielectric is assumed to be completely characterized by the deformation gradient and the polarization. He assumed that the polarization had an instantaneous response time, that is, he did not introduce separate ionic and electronic dynamic displacement variables which contribute to the total polarization with response times governed by the infrared and ultraviolet resonances of the medium. Toupin's procedure thus is equivalent to assuming that the dielectric tensor is independent of frequency. In Toupin's treatment, which begins from a set of conservation laws, it is necessary to make what he calls "special assumptions" concerning various physical quantities entering the conservation laws including the body force and the rate of work done by the electromagnetic field on the body. These assumptions are not independent, however, and must be chosen consistently. Toupin has done this. Toupin's theory yields a constitutive relation which contains terms of lowest (electric dipole) order. His treatment of the Faraday effect and magnetoelastic dragging, however, employs the *ad hoc* addition of a term of magnetic dipole order to the constitutive relation (and nowhere else). In contrast, our theory begins from a microscopic discrete-particle point of view, a procedure which we feel is an important aid in finding the proper form of various interactions. We introduce a complete set of coordinates to characterize all modes of vibration of the medium. This leads to a deductive prediction of the frequency dependence of the dielectric tensor as well as other measurable tensors characterizing the material. In our Lagrangian approach only the Lagrangian need be constructed; all other quantities such as body forces, work done on the body by the field, etc., are obtained deductively. We feel this method reduces the chances of error as compared to the conservation-law approach. Our constitutive relations are also obtained completely deductively from the Lagrangian including higher-order (magnetic dipole, electric quadrupole, etc.) effects. Thus when we include magnetic dipole effects in the Lagrangian, terms will appear in the center-of-mass force equation, the energy-conservation equation, and the equation of motion of the internal coordinates which are automatically consistent with one another.

Born and Huang's monograph on crystal lattices[5] gives a fine discussion from a general point of view of the linear elastic and electromagnetic properties of dielectric crystals.[14] They devote only a little space, however, to considering nonlinear interactions (Raman and Brillouin scattering) and their treatment of Brillouin scattering is not sufficiently fundamental to obtain the contribution from rotations to the light scattering.[2,10,12]

Penfield and Haus[15] have recently written a monograph on electrodynamics of moving media including effects from elastic deformation and thermal phenomena. Their major interest is in resolving the long-standing controversy concerning the form of the Maxwell stress tensor. Their emphasis thus is on relativistic correction terms. By including relativistic effects, ferromagnetism, and thermal effects their work relates to a wider class of phenomena than our present work does. However, except for a few special cases they make no attempt at deriving constitutive relations. This contrasts it to our work, one of whose major contributions is an *ab inito* classical derivation of the various constitutive relations. DeGroot's recent monograph[16] on the derivation of the Maxwell equations from electron theory contrasts to our work in a somewhat different manner. He considers the material properties that enter the Maxwell equations from a microscopic point of view but does not consider at all the dynamical equations which govern the various modes of vibration of the medium, as our work does. His interest was not in a derivation of the constitutive relations but in obtaining expressions for the material properties whose Lorentz invariance can be demonstrated. Like Penfield and Haus, De Groot's interest is in resolving the controversy over the relativistic $(\sim v^2/c^2)$ terms in the Maxwell stress tensor. It is interesting to note that Blount[17] has just proposed a resolution to this controversy based on the distinction between real and crystal momentum.

A classical nonlinear one-dimensional oscillator model introduced by Bloembergen[18] has been found to give a useful qualitative understanding of various nonlinear optical phenomena by Garrett and Robinson,[19] Garrett,[20] Robinson,[21] and Kurtz and Robinson.[22] Review works by Bloembergen,[18] Butcher,[23] Terhune and Maker,[24] and Kleinman[25] and papers by Armstrong *et al.*[26] and Pershan[27] treat the progress in understanding of nonlinear optical interactions from viewpoints quite different from that developed here.

The organization of this paper is as follows: In the last part of this introductory section, we write down Maxwell's equations with their source terms, which we shall see are consequences of our Lagrangian and are not being separately assumed. This is done because the resulting equations are immediately recognizable, and it becomes clear that the main task consists in deriving the constitutive relations for the various multipole contributions to the source terms by solving the matter equations of motion which are also consequences of our Lagrangian. In Sec. II we develop a microscopic Lagrangian and obtain a set of associated microscopic equations of motion. In Sec. III passage to the continuum limit is made. This leads in Sec. IV to a macroscopic Lagrangian, the corresponding macroscopic electromagnetic field, and matter equations. We turn in Sec. V to a study of the stored energy and the invariance requirements it must obey: rotational, displacemental, translational (homogeneity), and space-group invariance. In Appendices A and B we expand the charge and current densities in multipole form, i.e., into electric dipole, magnetic dipole, and electric quadrupole contributions. In Sec. VI we make the corresponding multipole expansion of the electric and magnetic forces. In Sec. VII we take up the question of local-field corrections and show that explicit corrections need not be made since the local fields are included in the parameters describing the internal energy. In order to obtain useful equations, we make an explicit separation into center-of-mass motion (elastic equations) and internal motion (equations governing the various degrees of internal polarization). This is done in Sec. VIII and Appendix D. In Sec. IX we consider explicitly the nonlinear interaction energy and the forces that arise from it. We can then make a separation of linear and nonlinear terms in both the matter equations and the Maxwell equations. The associated macroscopic equations for the electric field $\vec{E}$ and the displacement field $\vec{u}$ are presented in Sec. X. We then summarize the linear acoustic equations of motion in Sec. XI including the piezoelectric corrections to these equations. The linear optical equations of motion are presented in Sec. XII. In order to facilitate the solution of the nonlinear equations that will follow in Secs. XIII and XIV and later papers, we must invert the $\overleftrightarrow{\alpha}$ dyadic that appears on the left-hand side of Eq. (1.18). This inversion is accomplished in several ways in Appendix F. The most practical inversion procedure makes use of the eigenvectors of $\overleftrightarrow{\alpha}$. But these eigenvectors are merely the electric field directions of the modes of propagation of a free electromagnetic field in a crystal (the ordinary and extraordinary waves in a uniaxial crystal) and of the usually omitted longitudinal mode needed to describe the driven response. Section XII contains a discussion of crystal optics in the eigenvector terminology, a discussion of propagation in the region of exciton and phonon (polariton) dispersion, and an examination of the validity of the Lyddane-Sachs-Teller[28] theorem in anisotropic media. We prove that for special orientations the usual form of the Lyddane-Sachs-Teller theorem exists, but that for arbitrary directions of propagation a modified theorem must be used. Our modified theorem is slightly more explicit than the one introduced by Cochran and Cowley,[29] and is established in an *elementary* way using the zeros and poles of the longitudinal dielectric constant. Also in Sec. XII we examine the dielectric tensor of the medium above and below the piezoelectric resonance and evaluate the contribution to it from this resonance. Section XIII presents an iterative method of solving the nonlinear equations. As examples of the method we derive for a dielectric the form of the optical mixing tensor, the harmonic generation tensor, the clamped and unclamped electro-optic tensor, and the direct and indirect photoelastic effect. Section XIV presents a technique of solution using a new dyadic Green's function evaluated for materials of arbitrary anisotropy and useful when only a finite volume can radiate the output wave.

Since the primary probe in a nonlinear optical experiment is the light field, we summarize in this Introduction the Maxwell-Lorentz equations that we obtain in Sec. II from our Lagrangian for a dielectric. Our theory is indeed more in the spirit of Lorentz[6] than of Maxwell because we have electromagnetic fields that propagate in a vacuum which contains certain charges and currents. Thus the fundamental Maxwell-Lorentz equations take the form

$$\vec{\nabla}\times\frac{\vec{B}(\vec{z},t)}{\mu_0}-\epsilon_0\frac{\partial\vec{E}(\vec{z},t)}{\partial t}=\vec{j}(\vec{z},t)\,, \qquad (1.1)$$

$$\vec{\nabla}\times\vec{E}(\vec{z},t)+\frac{\partial\vec{B}(\vec{z},t)}{\partial t}=0\,, \tag{1.2}$$

$$\vec{\nabla}\cdot\vec{E}(\vec{z},t)=q(\vec{z},t)/\epsilon_0\,, \tag{1.3}$$

$$\vec{\nabla}\cdot\vec{B}(\vec{z},t)=0\,, \tag{1.4}$$

where the charge density is found to be

$$q(\vec{z},t)=q_{\text{free}}-\vec{\nabla}\cdot\vec{P}'(\vec{z},t)\,,\quad \vec{P}'\equiv\vec{P}-\tfrac{1}{2}\vec{\nabla}\cdot\overleftrightarrow{Q} \tag{1.5}$$

in terms of the polarization $\vec{P}$ and the quadrupole tensor $\overleftrightarrow{Q}$. The current density is found to take the form

$$\vec{j}=\vec{j}_{\text{free}}+\frac{\partial\vec{P}'}{\partial t}+\vec{\nabla}\times\vec{M}'\,, \tag{1.6}$$

$$\vec{M}'\equiv\vec{M}+\vec{P}\times\dot{\vec{x}}-\tfrac{1}{2}[(\vec{\nabla}\cdot\overleftrightarrow{Q})+\overleftrightarrow{Q}\cdot\vec{\nabla}]\times\dot{\vec{x}}\,, \tag{1.7}$$

where $\vec{M}$ is the magnetization associated with moving charges only since electron spin is not included in this paper.

The derivation of the results Eqs. (1.5)–(1.7) is given in Sec. IV and Appendices A and B. In these Appendices, we do not merely derive the form of the charge and current, but show that it has the above form with specific expressions for the polarization, quadrupolarization, and magnetization in terms of the variables characterizing the material medium. Without benefit of the specific expressions $\vec{P}$, $\overleftrightarrow{Q}$, and $\vec{M}$, it is possible to define $\vec{D}$ and $\vec{H}$ in the conventional manner:

$$\vec{D}=\epsilon_0\vec{E}+\vec{P}'\,, \tag{1.8}$$

$$\vec{H}=\vec{B}/\mu_0-\vec{M}'\,. \tag{1.9}$$

The Maxwell forms of the electromagnetic equations are then obtained:

$$\vec{\nabla}\cdot\vec{D}=q_{\text{free}}=0, \tag{1.10}$$

$$\vec{\nabla}\times\vec{H}-\frac{\partial\vec{D}}{\partial t}=\vec{j}_{\text{free}}=0\,. \tag{1.11}$$

The current of moving free charge in Eq. (1.11) is, of course, not necessarily zero, but this paper is restricted to nonconducting dielectric media. By the elimination of the magnetic field between Eqs. (1.1) and (1.2), we obtain an equation for the electric field in the form

$$\vec{\nabla}\times(\vec{\nabla}\times\vec{E})+\frac{1}{c^2}\frac{\partial^2\vec{E}}{\partial t^2}=-\mu_0\frac{\partial\vec{j}}{\partial t}\,. \tag{1.11$'$}$$

We can now separate Eq. (1.11′) into linear and nonlinear contributions by writing

$$\vec{j}=\vec{j}^{L}+\vec{j}^{\text{NL}}\,, \tag{1.12}$$

$$\vec{j}^{L}=\frac{\partial(\vec{P}')^{L}}{\partial t}+\vec{\nabla}\times(\vec{M}')^{L}\,, \tag{1.13}$$

$$(\vec{P}')^{L}=\epsilon_0(\overleftrightarrow{\kappa}-\overleftrightarrow{1})\cdot\vec{E}\,, \tag{1.14}$$

$$(\vec{M}')^{L}=(\overleftrightarrow{\kappa}_m-\overleftrightarrow{1})\cdot\vec{H}=(\overleftrightarrow{1}-\overleftrightarrow{\kappa}_m^{-1})\cdot\vec{B}/\mu_0\,, \tag{1.15}$$

where $\overleftrightarrow{\kappa}$ is the dielectric tensor and $\overleftrightarrow{\kappa}_m$ is the magnetic permeability tensor of the dielectric medium. In writing Eq. (1.14), we have discarded a possible permanent polarization (ferroelectricity). In Eq. (1.14), the frequency is assumed sufficiently high that the piezoelectric term that would ordinarily be present can be omitted. This term is discussed in detail in Sec. X of this paper. Inserting the above separation into linear and nonlinear terms into Eq. (1.11), we obtain

$$\vec{\nabla}\times[\overleftrightarrow{\kappa}_m^{-1}\cdot(\vec{\nabla}\times\vec{E})]+\frac{1}{c^2}\overleftrightarrow{\kappa}\cdot\frac{\partial^2\vec{E}}{\partial t^2}=-\mu_0\frac{\partial\vec{j}^{\text{NL}}}{\partial t}\,, \tag{1.16}$$

in which all linear properties of the electromagnetic medium are contained on the left-hand side and all nonlinear properties are displayed on the right-hand side. If we use the abbreviated notation

$$\vec{k}=-i\vec{\nabla}\,, \tag{1.17}$$

the contribution of each single frequency ω in $\vec{j}^{\text{NL}}$ to the output field $\vec{E}$ can be obtained by solving

$$\overleftrightarrow{\alpha}(\vec{k},\omega)\cdot\vec{E}=\vec{\mathcal{P}}/\epsilon_0\,, \tag{1.18}$$

where we define

$$\overleftrightarrow{\alpha}(\vec{k},\omega)\cdot\vec{E}\equiv-n^2\vec{s}\times[\overleftrightarrow{\kappa}_m^{-1}\cdot(\vec{s}\times\vec{E})]-\overleftrightarrow{\kappa}\cdot\vec{E}\,, \tag{1.19}$$

$$\vec{s}\equiv\vec{k}/k\,,\quad k\equiv|\vec{k}|\,,\quad n\equiv ck/\omega\,, \tag{1.20}$$

$$\begin{aligned}\vec{\mathcal{P}}\equiv\vec{P}^{\text{NL}}-\tfrac{1}{2}\vec{\nabla}\cdot\overleftrightarrow{Q}+(i/\omega)\{\vec{\nabla}\times[\vec{M}^{\text{NL}}\\ +(\vec{P}-\tfrac{1}{2}(\vec{\nabla}\cdot\overleftrightarrow{Q})-\tfrac{1}{2}\overleftrightarrow{Q}\cdot\vec{\nabla})\times\dot{\vec{x}}]\}\,.\end{aligned} \tag{1.21}$$

The form (1.18) is particularly suitable when the nonlinear polarization is decomposed into Fourier components in time and plane waves in space. When magnetic effects can be neglected, the tensor $\overleftrightarrow{\alpha}$ reduces to the particularly simple form

$$\overleftrightarrow{\alpha}(\vec{k},\omega)=n^2(\overleftrightarrow{1}-\vec{s}\,\vec{s})-\overleftrightarrow{\kappa}(\omega)\,. \tag{1.22}$$

II. MICROSCOPIC LAGRANGIAN AND EQUATIONS OF MOTION

We consider a crystal as a mechanical system consisting of a set of point particles of fixed charge e^{α} and fixed mass m^{α} at position $\vec{x}^{n\alpha}$. The index n has three integral components that name the primitive cell n (the smallest volume unit of structural repetition), and α is an index that labels the type of particle. The particles reside in a vacuum and are subject to mechanical forces (of quantum-mechanical origin) that can be obtained from a potential energy $V(\{\vec{x}^{n\alpha}\})$, where $\{\vec{x}^{n\alpha}\}$ denotes the set of positions $\vec{x}^{n\alpha}$ for all values of n and α. The particles are also subject to forces arising from electric and magnetic fields, either of external origin or produced by the charges themselves.

The total Lagrangian L of the system can be decomposed by

$$L = L_P + L_F + L_I \tag{2.1}$$

into a nonrelativistic particle Lagrangian of the form

$$L_P = \tfrac{1}{2}\sum_{n\alpha} m^\alpha(\dot{\vec{x}}^{n\alpha})^2 - V(\{\vec{x}^{n\beta}\}) , \tag{2.2}$$

a field Lagrangian[30] expressed in rationalized mks units of the form

$$L_F = \int \mathcal{L}_F\, d\vec{z} = \tfrac{1}{2}\epsilon_0 \int [\vec{E}^2(\vec{z},t) - c^2\vec{B}^2(\vec{z},t)]\, d\vec{z} , \tag{2.3}$$

and an electromagnetic field-particle interaction Lagrangian[30] of the form

$$L_I = \int \mathcal{L}_{FI}\, d\vec{z} = -\sum_{n\alpha} e^\alpha\, \Phi(\vec{x}^{n\alpha}(t)) + \sum_{n\alpha} e^\alpha\, \dot{\vec{x}}^{n\alpha}(t)\cdot \vec{A}(\vec{x}^{n\alpha}(t)) . \tag{2.4}$$

Here $d\vec{z} \equiv dz_1 dz_2 dz_3$ is the volume element in the laboratory coordinate system. The electric and magnetic field vectors $\vec{E}$ and $\vec{B}$ are understood to be expressed in terms of the scalar and vector potentials Φ and $\vec{A}$ by means of

$$\vec{E}(\vec{z},t) = -\vec{\nabla}\Phi(\vec{z},t) - \frac{\partial \vec{A}(\vec{z},t)}{\partial t} , \tag{2.5}$$

$$\vec{B}(\vec{z},t) = \vec{\nabla}\times\vec{A}(\vec{z},t) . \tag{2.6}$$

Equation (2.4) can also be used to define the interaction Lagrangian density

$$\mathcal{L}_{FI} = -q(\vec{z},t)\Phi(\vec{z},t) + \vec{j}(\vec{z},t)\cdot\vec{A}(\vec{z},t) , \tag{2.7}$$

where the charge density $q(\vec{z},t)$ and the current density $\vec{j}(\vec{z},t)$ are defined by

$$q(\vec{z},t) = \sum_{n\alpha} e^\alpha\, \delta(\vec{z} - \vec{x}^{n\alpha}(t)) , \tag{2.8}$$

$$\vec{j}(\vec{z},t) = \sum_{n\alpha} e^\alpha\, \dot{\vec{x}}^{n\alpha}(t)\, \delta(\vec{z} - \vec{x}^{n\alpha}(t)) , \tag{2.9}$$

where $\delta(\vec{z} - \vec{x}^{n\alpha})$ is a product of three Dirac δ functions, one for each component of the argument. The subscript F in Eq. (2.7) denotes that this interaction density is in a form suitable for obtaining the electromagnetic field equations. The Lagrangian equations of motion for the generalized coordinates Φ, $\vec{A}$ applied to the Lagrangian density $\mathcal{L}_F + \mathcal{L}_{FI}$ yield the electromagnetic equations[30]

$$\vec{\nabla}\cdot\vec{E}(\vec{z},t) = q(\vec{z},t)/\epsilon_0 , \tag{2.10}$$

$$\vec{\nabla}\times\frac{\vec{B}(\vec{z},t)}{\mu_0} - \frac{\partial[\epsilon_0\vec{E}(\vec{z},t)]}{\partial t} = \vec{j}(\vec{z},t) , \tag{2.11}$$

where the charge and current densities have been defined in Eqs. (2.8) and (2.9). The remaining Maxwell equations (1.2) and (1.4) follow automatically from the definitions (2.5) and (2.6).

The Lagrangian $L_P + L_I$ leads to the familiar equations of motion for the mass points

$$m^\alpha\, \ddot{\vec{x}}^{n\alpha}(t) = -\frac{\partial V}{\partial \vec{x}^{n\alpha}} + e^\alpha[\vec{E}(\vec{x}^{n\alpha}(t),t) + \dot{\vec{x}}^{n\alpha}(t)\times\vec{B}(\vec{x}^{n\alpha}(t),t)] , \tag{2.12}$$

with the expected electric and magnetic forces and a force arising from the gradient of the potential energy

$$\left(\frac{\partial V}{\partial \vec{x}^{n\alpha}}\right)_i \equiv \frac{\partial V}{\partial x_i^{n\alpha}} . \tag{2.13}$$

III. PASSAGE TO CONTINUUM LIMIT

When we replace the discrete lattice system by a continuum, the particle index α is retained as a sublattice index but the index n, which names the cell, is replaced by a continuous variable $\vec{X}$. In other words, the original names n which were uniformly and discretely spaced are now replaced by names $\vec{X}$ which are uniformly and continuously distributed. We shall refer to $\vec{X}$ as a material coordinate because it rides with a particular mass point. Thus we make the replacement

$$\vec{x}^{n\alpha}(t) \to \vec{x}^\alpha(\vec{X},t) \tag{3.1}$$

of a set of discrete positions by a set of functions of the continuous variable $\vec{X}$. We shall use the notation x_i^α to represent the ith component of the position of sublattice α expressed in a Cartesian frame called the spatial frame. We shall use the notation X_A to represent the Ath Cartesian component of the name $\vec{X}$ in what we shall call the material frame. It will be noticed that upper case Latin letters will be used to denote the components in the material coordinate system and lower case Latin letters will be used to denote components in the spatial coordinate system. Greek letters are reserved to name the different sublattices or degrees of freedom.

It is particularly useful to regard the spatial and material frames as independent[31] in order to be able to discuss the invariance of the potential energy under separate rotations of the spatial frame (infinitesimal rotational invariance) and discrete rotations of the material frame (crystal symmetry invariance). After the symmetry properties of the potential energy are established, it is then convenient to refer all quantities to a common Cartesian frame. Indeed, if we define the center-of-mass position by

$$\vec{x}(\vec{X},t) \equiv \textstyle\sum_\alpha m^\alpha \vec{x}^\alpha(\vec{X},t) / \sum_\alpha m^\alpha \ , \tag{3.2}$$

it is customary to regard the material coordinate $\vec{X}$ as an unstrained or equilibrium position of the center-of-mass variable $\vec{x}$.

The distinction between the spatial and material frames is a familiar one.[32] A time derivative holding a position fixed is an ordinary partial derivative with respect to the time but a time derivative holding $\vec{X}$ fixed is referred to as a material time derivative or a substantive time derivative. It is the time derivative as one moves along with the particle. The relation between material and spatial time derivatives is explored in Appendix C.

In addition to maintaining the distinction between material and spatial frames, Truesdell,[33] Truesdell and Toupin,[34] and Toupin[4] write all equations in a covariant form applicable to arbitrary coordinate systems, e.g., spherical or cylindrical coordinate systems, in addition to Cartesian coordinate systems. We could do the same by suitably maintaining upper or lower positions of the component indices to denote contravariant and covariant components, respectively. However, no new physics follows from such a procedure, and for simplicity we shall restrict ourselves to Cartesian frames and use subscripts to denote all Cartesian components. Superscripts can then be reserved for sublattice names like α. We shall follow the Einstein summation convention with regard to our Cartesian subscript indices but summations over sublattice indices such as α must be indicated explicitly.

The passage to the continuum limit is effected by replacing sums by integrals:

$$\sum_n F(\vec{x}^{n\alpha}(t)) \to \frac{1}{\Omega_0}\sum_n F(\vec{x}^{n\alpha}(t))\Delta\vec{X} \to \frac{1}{\Omega_0}\int F(\vec{x}^\alpha(\vec{X},t))\,d\vec{X} \ , \tag{3.3}$$

where we have multiplied and divided by the cell volume $\Delta\vec{X} \equiv \Delta X_1\,\Delta X_2\,\Delta X_3 = \Omega_0$ in order to make use of the usual replacement of a Riemann sum by an integral. If the functions F^α contain no Fourier components outside the first Brillouin zone, then this replacement is exact. It is then an example of the use of the sampling theorem for band-limited functions.[35] In this paper, the replacement is a good approximation because we are seeking to deal with acoustic and optic waves whose wave vectors are small compared to the zone-boundary wave vectors.

As an example, we can replace the discrete kinetic energy T by its continuum limit:

$$T = \tfrac{1}{2}\sum_{n\alpha} m^\alpha [\dot{\vec{x}}^{n\alpha}(t)]^2 \to \tfrac{1}{2}\sum_{\alpha=1}^{N} \rho^\alpha \int [\dot{\vec{x}}^\alpha(\vec{X},t)]^2 d\vec{X} \ , \tag{3.4}$$

where

$$\rho^\alpha \equiv \frac{m^\alpha}{\Omega_0} \ , \qquad \dot{\vec{x}}^\alpha \equiv \left.\frac{\partial \vec{x}^\alpha(\vec{X},t)}{\partial t}\right|_{\vec{X}} \tag{3.5}$$

define the mass density ρ^α and the particle velocity $\dot{\vec{x}}^\alpha$. We use N to denote the total number of different particles both ions and electrons in the primitive unit cell. After the expression of our theory in terms of center of mass and internal coordinates the $3N$ degrees of freedom will include three describing the center-of-mass motion, and $3N-3$ describing internal degrees of freedom that may carry polarization. These latter degrees of freedom can be given a more general interpretation. For example, excitonic contributions to polarization[7] (in addition to the usual ionic contribution) can be described by such internal degrees of freedom.

IV. MACROSCOPIC LAGRANGIAN AND FIELD EQUATIONS

In order to complete our analysis, we must write down a form for the potential energy. We write the potential energy as

$$V = \rho^0 \int \bar{\Sigma}(\vec{x}^\beta(\vec{X},t),\ \vec{x}^\beta{}_{,A}(\vec{X},t))\,d\vec{X} \ , \tag{4.1}$$

where $\bar{\Sigma}$ is the stored energy per unit mass, and ρ^0 is the unperturbed mass density of the medium. The potential energy $\bar{\Sigma}$ is a function of all the continuum position variables $\vec{x}^\beta$, $\beta = 1, 2, \ldots, N$, and their first derivatives:

$$\vec{x}^\beta{}_{,A}(\vec{X},t) \equiv \frac{\partial \vec{x}^\beta(\vec{X},t)}{\partial X_A} \ , \quad A = 1, 2, 3 \ . \tag{4.2}$$

The $\{\ \}$ notation of Eq. (2.2) is implied but omitted in $\bar{\Sigma}$. The mass density ρ^0 is defined by

$$\rho^0 \equiv \textstyle\sum_\alpha \rho^\alpha = (\sum_\alpha m^\alpha)/\Omega_0 \ . \tag{4.3}$$

Since we are seeking to obtain a long-wavelength macroscopic theory, it is appropriate to neglect the dependence of $\bar{\Sigma}$ on higher derivatives than the first in Eq. (4.1). Indeed if wave-vector (spatial) dispersion is to be completely neglected, it is appropriate to neglect all first derivatives except those of the center-of-mass equation (3.2). The explicit separation of center-of-mass motion needed to accomplish this will be carried out in Sec. V. The particle Lagrangian density $\mathcal{L}_P$ is now defined by

$$L_P = \int \mathcal{L}_P\, d\vec{X} \ , \tag{4.4}$$

where

$$\mathfrak{L}_P=\frac{1}{2}\sum_{\alpha=1}^{N}\rho^\alpha[\dot{\vec{x}}^\alpha(\vec{X},t)]^2-\rho^0\,\overline{\Sigma}(\vec{x}^\beta(\vec{X},t),\,\vec{x}^\beta{}_{,A}(\vec{X},t))\,. \tag{4.5}$$

The interaction Lagrangian density can be obtained from Eq. (2.4) by converting the sum over n to an integral with the result

$$L_I=\int\mathfrak{L}_{\mathrm{PI}}\,d\vec{X}=\sum\nolimits_\alpha\int q^\alpha[\dot{\vec{x}}^\alpha(\vec{X},t)\cdot\vec{A}(\vec{x}^\alpha(\vec{X},t),t)-\Phi(\vec{x}^\alpha(\vec{X},t),t)]\,d\vec{X}\,. \tag{4.6}$$

The charge densities q^α are defined by

$$q^\alpha\equiv e^\alpha/\Omega_0\,. \tag{4.7}$$

The standard Lagrangian equation of motion for fields

$$\frac{d}{dt}\,\frac{\partial(\mathfrak{L}_P+\mathfrak{L}_{\mathrm{PI}})}{\partial\dot{\vec{x}}^\alpha}=\frac{\partial(\mathfrak{L}_P+\mathfrak{L}_{\mathrm{PI}})}{\partial\vec{x}^\alpha}-\frac{\partial}{\partial X_A}\,\frac{\partial(\mathfrak{L}_P+\mathfrak{L}_{\mathrm{PI}})}{\partial\vec{x}^\alpha{}_{,A}} \tag{4.8}$$

can be used to obtain the $3N$ matter equations of motion in the form

$$\rho^\alpha\ddot{\vec{x}}^\alpha=\vec{f}^\alpha+q^\alpha[\vec{E}(\vec{x}^\alpha)+\dot{\vec{x}}^\alpha\times\vec{B}(\vec{x}^\alpha)]\,. \tag{4.9}$$

Here the mechanical force $\vec{f}^\alpha$ is defined by

$$\vec{f}^\alpha\equiv-\rho^0\,\frac{\partial\overline{\Sigma}}{\partial\vec{x}^\alpha}+\rho^0\,\frac{\partial}{\partial X_A}\left(\frac{\partial\overline{\Sigma}}{\partial\vec{x}^\alpha{}_{,A}}\right)\,. \tag{4.10}$$

It should be no surprise that, when the Lagrangian equations of motion are used to obtain the equations of motion for the scalar and vector potential, they reduce to the Maxwell-Lorentz equations (2.10) and (2.11) with the continuum forms of the charge and current densities

$$q(\vec{z},t)=\sum\nolimits_\alpha q^\alpha\int\delta(\vec{z}-\vec{x}^\alpha(\vec{X},t))\,d\vec{X}\,, \tag{4.11}$$

$$\vec{j}(\vec{z},t)=\sum\nolimits_\alpha q^\alpha\int\dot{\vec{x}}^\alpha(\vec{X},t)\delta(\vec{z}-\vec{x}^\alpha(\vec{X},t))\,d\vec{X} \tag{4.12}$$

in place of the previous discrete forms Eqs. (2.8) and (2.9). In the long-wavelength limit, it is also appropriate to make a multipole expansion of the charge and current densities. This is done in Appendices A and B. The expression of the charge and current densities in terms of the polarization, quadrupolarization, and magnetization have already been noted in Eqs. (1.5) and (1.6).

V. INVARIANCE REQUIREMENTS ON STORED ENERGY

Among the conditions that the stored energy must obey are invariance against *uniform displacements* and *uniform rotations* of the whole crystal in the spatial coordinate system. These are needed to guarantee conservation of momentum and angular momentum, respectively. In addition, the stored energy must possess invariance against operations of the space group that describes the symmetry of the crystal considered. This symmetry results from the indistinguishability of atoms of the same element in equivalent sites. We will assume for simplicity that the medium under study is homogeneous; thus invariance against *translations* is required. This leads to conservation of crystal momentum. By translation we mean an operation in the material coordinate system of the form $\vec{X}\to\vec{X}+\vec{D}$, whereas by *displacement* we mean an operation in the spatial coordinate system of the form $\vec{x}\to\vec{x}+\vec{d}$. Invariance of the stored energy against *spatial inversion* is equivalent to parity conservation. Since experimental tests of such a conservation law are perhaps not yet definitive,[36] we will adopt a cautious approach and consider in Sec. V F the consequences of its violation. Invariance of the stored energy against *material inversion* of a crystal is distinct from parity invariance and depends on the presence or absence of the inversion operation in the crystal space group which distinguishes centrosymmetric from acentric crystals.

A. Displacement Invariance

A uniform displacement changes the position vectors $\vec{x}^\alpha$ and their derivatives $\vec{x}^\alpha{}_{,A}$ into

$$\vec{x}^\alpha\to\vec{x}^\alpha+\vec{d}\,,\qquad\vec{x}^\alpha{}_{,A}\to\vec{x}^\alpha{}_{,A}\,. \tag{5.1}$$

Invariance of the stored energy under this displacement leads to the condition

$$\overline{\Sigma}(\vec{x}^\alpha+\vec{d},\,\vec{x}^\alpha{}_{,A})=\overline{\Sigma}(\vec{x}^\alpha,\,\vec{x}^\alpha{}_{,A})\,. \tag{5.2}$$

If the displacement $\vec{d}$ is infinitesimal, we obtain the associated derivative condition

$$\sum_\alpha\frac{\partial\overline{\Sigma}}{\partial\vec{x}^\alpha}=0\,. \tag{5.3}$$

In order to display more precisely the influence of the displacement invariance condition, we introduce the center-of-mass coordinate $\vec{x}$ of Eq. (3.2) and a set of internal coordinates (see Appendix D)

$$\vec{y}^\mu(\vec{X})=\sum_{\alpha=1}^{N}U^{\mu\alpha}\vec{x}^\alpha(\vec{X})\,,\quad\sum_{\alpha=1}^{N}U^{\mu\alpha}=0,\qquad\mu=1,\,2,\,\ldots,\,N-1\,. \tag{5.4}$$

The second condition of Eq. (5.4) has been imposed to guarantee that under the transformation (5.1) the $\vec{y}^\mu$ variables remain unchanged and hence are true internal coordinates. Thus only the center-of-mass variable changes under the transformation (5.1):

$$\vec{x}\to\vec{x}+\vec{d}\,,\qquad\vec{y}^\mu\to\vec{y}^\mu\,. \tag{5.5}$$

Thus if the stored energy is expressed in terms of the new variables, invariance under uniform displacements requires the stored energy to be independent of the center-of-mass variable $\vec{x}$, though not of its derivatives:

$$\bar{\Sigma}(\vec{x}^{\alpha}, \vec{x}^{\alpha}{}_{,A}) \equiv \hat{\Sigma}(\vec{y}^{\mu}, \vec{x}_{,A}, \vec{y}^{\mu}{}_{,A}) . \qquad (5.6)$$

If all of the variables $\vec{x}^{\alpha}$ are given a common inhomogeneous displacement

$$\vec{x}^{\alpha} \to \vec{x}^{\alpha} + \vec{d}(\vec{X}) , \quad \vec{x} \to \vec{x} + \vec{d}(\vec{X}) , \quad \vec{y}^{\mu} \to \vec{y}^{\mu} \qquad (5.7)$$

[the last condition of Eq. (5.7) indicates why the $\vec{y}^{\mu}$ are called *internal* coordinates], then the change in the potential energy associated with this inhomogeneous displacement can be calculated in terms of the old stored energy $\bar{\Sigma}$ and the new stored energy $\hat{\Sigma}$:

$$\delta\bar{\Sigma} = \sum_{\alpha} \left(\frac{\partial \bar{\Sigma}}{\partial \vec{x}^{\alpha}{}_{,A}} \right) \cdot \vec{d}_{,A} , \qquad (5.8)$$

$$\delta\hat{\Sigma} = \left(\frac{\partial \hat{\Sigma}}{\partial \vec{x}_{,A}} \right) \cdot \vec{d}_{,A} . \qquad (5.9)$$

The equality between these two changes in potential energy leads to the requirement

$$\sum_{\alpha} \frac{\partial \bar{\Sigma}}{\partial \vec{x}^{\alpha}{}_{,A}} = \frac{\partial \hat{\Sigma}}{\partial \vec{x}_{,A}} . \qquad (5.10)$$

B. Rotational Invariance

Since the kinetic energy, field energy, and interaction energy are manifestly invariant under arbitrary infinitesimal rigid rotations of the body, our entire Lagrangian can be made invariant by requiring the stored energy to be rotationally invariant. This last objective can be accomplished by finding a complete set of rotational invariants constructed from the original position variables of the problem. An arbitrary rotational invariant must then be expressible as a function of these basis invariants.[37]

1. *Center of Mass Only*

For simplicity let us first consider the case in which only one sublattice is present, so that we need only consider the center-of-mass variable and can ignore internal variables. In this case, the theory of finite elastic deformations[38] will be obtained. The stored energy now depends only on the three vector variables $\vec{x}_{,1}$, $\vec{x}_{,2}$, and $\vec{x}_{,3}$. We can construct invariants under a rotation of the $\vec{x}$ frame by forming the scalar products

$$C_{AB} \equiv \vec{x}_{,A} \cdot \vec{x}_{,B} \equiv 2E_{AB} + \delta_{AB} . \qquad (5.11)$$

Since the deformation tensor C_{AB} is symmetric in the indices A and B, this leads to a set of six independent invariants. The quantity E_{AB} on the right-hand side of Eq. (5.11) is the measure of finite strain introduced by Green[39] into the theory of nonlinear elasticity.

Do these six invariants C_{AB} constitute a complete set? It is well known that with three vectors we can also form an invariant by means of the triple product or the determinant of the components of these vectors:

$$J(\vec{X}, t) \equiv \det x_{i,A} = \rho^0 / \rho(\vec{X}, t) . \qquad (5.12)$$

The quantity J is the Jacobian of the transformation from the $\vec{X}$ frame to the $\vec{x}$ frame. As such it is the ratio of the undistorted density ρ^0 to the distorted system density $\rho(\vec{X}, t)$. It might appear that J is a new invariant, independent of the previous six, but the rules of determinantal multiplication yield the result

$$J^2 = \det C_{AB} . \qquad (5.13)$$

Thus J is expressible up to a ± sign in terms of the finite strain tensor E_{AB}.

For a solid completely describable in terms of the center-of-mass variable $\vec{x}$, rotational invariance of the stored energy requires that the latter be expressible in terms of the complete set of invariants E_{AB}, J:

$$\bar{\Sigma}(\vec{x}_{,A}) = \Sigma_1(E_{AB}) + J\Sigma_2(E_{AB}) , \qquad (5.14)$$

where the magnitude of J but not its sign can be absorbed into Σ_2. If, however, one is not concerned with parity violations,[36] discussed in Sec. V F, the second term in Eq. (5.14) can be omitted.

To make connection with the ordinary theory of linear elasticity, we choose in the following equations a common Cartesian coordinate system for the material frame $\vec{X}$ and the spatial frame $\vec{x}$. In this common frame we can write

$$\vec{x}(\vec{X}, t) \equiv \vec{X} + \vec{u}(\vec{X}, t) , \qquad (5.15)$$

where $\vec{u}$ is commonly called the displacement vector, since it represents the displacement of the center of mass from its equilibrium or undistorted position $\vec{X}$. In this notation the finite strain tensor reduces to the conventional form

$$E_{AB} = \tfrac{1}{2}(u_{A,B} + u_{B,A}) + \tfrac{1}{2} u_{i,A} u_{i,B} . \qquad (5.16)$$

In the infinitesimal case, E_{AB} reduces to the usual expression for infinitesimal strain:

$$S_{AB} = \tfrac{1}{2}(u_{A,B} + u_{B,A}) . \qquad (5.17)$$

We have adopted the convention that the system is in equilibrium in the absence of strain. (See Sec. IX.) Thus if we expand the stored energy in powers of strain, the lowest-order term must be a quadratic term

$$\bar{\Sigma}(\vec{x}_{,A}) \equiv \Sigma(E_{AB}) = \tfrac{1}{2} c_{MANB} E_{MA} E_{NB} + \cdots . \qquad (5.18)$$

The coefficient c_{MANB} is the usual definition of the stiffness tensor.

2. *Several Internal Displacements*

We now generalize the stored energy of Toupin[4] by introducing a set $\alpha = 1, 2, \ldots, N$ of internal displacements

$$\vec{u}^{\alpha}(\vec{X}, t) \equiv \vec{x}^{\alpha}(\vec{X}, t) - \vec{x}(\vec{X}, t) . \qquad (5.19)$$

They are called *internal* displacements because for a pure deformation, i.e., $x^{\alpha}(X, t)$ independent of α, the $u^{\alpha}(X, t) = 0$. Since the three-dimensional space is already spanned by a set of three independent basis vectors $\vec{x}_{,1}$, $\vec{x}_{,2}$, $\vec{x}_{,3}$, the only new basic invariants that need be introduced are scalar products of the new vectors with these basis vectors:

$$\Gamma_A^{\alpha} \equiv \vec{x}_{,A} \cdot \vec{u}^{\alpha} . \qquad (5.20)$$

In order to show that the scalar products between these new vectors do not introduce new invariants we invert Eq. (5.20) to obtain

$$u_i^{\alpha} = X_{A,i}\, \Gamma_A^{\alpha} . \qquad (5.21)$$

If we then form the scalar product of a pair of such vectors, we obtain

$$\begin{aligned} u_i^{\alpha} u_i^{\beta} &= \Gamma_A^{\alpha} \Gamma_B^{\beta} X_{A,i} X_{B,i} \\ &= \Gamma_A^{\alpha} (\overleftrightarrow{C}^{-1})_{AB}\, \Gamma_B^{\beta} = \Gamma_A^{\alpha} [(\overleftrightarrow{1} + 2\overleftrightarrow{E})^{-1}]_{AB} \Gamma_B^{\beta} \\ &\approx \Gamma_A^{\alpha} \Gamma_A^{\beta} - 2\Gamma_A^{\alpha} E_{AB}\, \Gamma_B^{\beta} + 4\Gamma_A^{\alpha} E_{AC} E_{CB}\, \Gamma_B^{\alpha} \cdots . \end{aligned} \qquad (5.22)$$

We see that these invariants are not new but are expressible in terms of previous invariants. It might seem that we could also introduce as new invariants triple products of any three $\vec{u}^{\alpha}$ vectors. However knowledge of the scalar products of these $\vec{u}^{\alpha}$ vectors with the three vectors $\vec{x}_{,1}$, $\vec{x}_{,2}$, $\vec{x}_{,3}$ permits us to express the $\vec{u}^{\alpha}$ vectors in terms of the $\vec{x}_{,A}$. All triple products can then be expressed in terms of these scalar products and the one triple product J. The latter can be omitted in the parity conserving case, or retained, more generally, as discussed in Sec. VF.

Let us digress, for a moment, to introduce the rotation tensor of finite elasticity theory[40]:

$$R_{iA} \equiv x_{i,B}\, (\overleftrightarrow{C}^{-1/2})_{BA} . \qquad (5.23)$$

To first order in displacements

$$\begin{aligned} R_{iA} &= (\delta_{iB} + u_{i,B}) [(\overleftrightarrow{1} + 2\overleftrightarrow{E})^{-1/2}]_{BA} \\ &\approx (\delta_{iB} + u_{i,B}) (\delta_{BA} - E_{BA}) \\ &\approx \delta_{iA} + \tfrac{1}{2}(u_{i,A} - u_{A,i}) \end{aligned} \qquad (5.24)$$

reduces to the familiar expression for the rotation tensor in the infinitesimal case. Since the tensor $\overleftrightarrow{C}$ is invariant under rotations of the spatial frame, we see from Eq. (5.23) that R_{iA} has precisely the same transformation properties as $x_{i,A}$. Thus we can equally well define a set of invariants

$$\Lambda_A^{\alpha} \equiv u_i^{\alpha} R_{iA} = \Gamma_B^{\alpha} (\overleftrightarrow{C}^{-1/2})_{BA} . \qquad (5.25)$$

Just as the invariant in Eq. (5.22) can be written in more than one way by a rearrangement of the nonlinear terms in the expansion of the stored energy, so too the use of the variable Λ does not change the physics but merely rearranges the terms in the nonlinear expansion in a more convenient way so that nonlinear effects involving strain arise only from cubic (or higher-order) terms in the expansion.

If the stored energy is permitted to depend also on the derivatives of the various internal displacements, then we can define the additional set of invariants[41]

$$\Lambda_{B;C}^{\beta} \equiv R_{iB}\, u_{i,C}^{\beta} , \qquad (5.26)$$

so that the stored energy can finally be written in the manifestly invariant form

$$\Sigma = \Sigma\, (E_{AB}, \Lambda_A^{\alpha}, \Lambda_{B;C}^{\beta}) . \qquad (5.27)$$

Note that $\Lambda_{B;C}^{\alpha} \neq \partial \Lambda_B^{\alpha} / \partial X_C$. The latter involves second derivatives of x_i whereas the former does not. The semicolon notation was chosen because $\Lambda_{B;C}^{\alpha}$ is in fact a covariant derivative with respect to X_C.

The above choice of variables is not unique. One choice might appear to be better than another in the sense that a single term in one choice of variables requires an infinite expansion in the second choice, as in Eq. (5.22), with numerical coefficients that do not decrease. This possibility, however, is more apparent than real because the maximum strain that a crystal can sustain without fracture is of the order of 10^{-3}; thus expansions in the above variables converge quite rapidly. Thus a truncated power expansion in the Λ's [see Eq. (9.1)] and a truncated power expansion in the Γ's will agree if terms of the same order are kept in the underlying variables u^{α}, and if the expansion coefficients are appropriately related.

C. Crystal Symmetry

Under a space-group operation of a crystal containing a rotation matrix $\overleftrightarrow{S}$ as the rotational portion of the space-group operation, a particle of type α at reference position $\vec{X}$ is carried into a particle of type $S(\alpha)$ at position $\overleftrightarrow{S} \cdot \vec{X}$. Thus the new displacement of a particle of type α at $\vec{X}$ is determined by applying the appropriate rotation $\overleftrightarrow{S}$ to the displacement that the particle previously had when it was at the position $\overleftrightarrow{S}^{-1} \cdot \vec{X}$ and had the type $S^{-1}(\alpha) \equiv T(\alpha)$:

$$[u_i^{\alpha} (\vec{X}, t)]' = S_{ij} u_j^{T(\alpha)} (\overleftrightarrow{S}^{-1} \cdot \vec{X}, t) . \qquad (5.28)$$

From Eq. (5.28) we obtain the transformation properties of the invariants in the form

$$[\Lambda_A^{\alpha}(\vec{X}, t)]' = S_{AB} \Lambda_B^{T(\alpha)} (\overleftrightarrow{S}^{-1} \cdot \vec{X}, t) , \qquad (5.29)$$

$$[E_{AB} (\vec{X})]' = S_{AC} S_{BD} E_{CD} (\overleftrightarrow{S}^{-1} \cdot \vec{X}). \qquad (5.30)$$

Thus a body symmetry operation, Eq. (5.28), which acts on the spatial components behaves as if it were the associated material coordinate (name-changing) transformation on the Λ's and E's. What is to be invariant under a crystal symmetry operation, of course, is the total energy integrated over the crystal. Hence we obtain the relation

$$\int \Sigma \, d\vec{X} = \int \Sigma' \, d\vec{X} = \int \Sigma' \, d(\vec{S}^{-1} \cdot \vec{X}) \,, \tag{5.31}$$

where Σ' is the stored energy written as a function of the primed variables on the left-hand side of Eqs. (5.28)–(5.30). Comparing corresponding integrands we thus obtain the invariance relationship

$$\begin{aligned} &\Sigma(E_{AB}, \Lambda_A^\alpha, \Lambda_{B;C}^\beta) \\ &\quad = \Sigma(S_{AA'} S_{BB'} E_{A'B'}, \; S_{AA'} \Lambda_{A'}^{T(\alpha)}, \; S_{BB'} S_{CC'} \Lambda_{B';C'}^{T(\beta)}) \,. \end{aligned} \tag{5.32}$$

Let us examine a particular term in a polynomial expansion of Σ. For this term, Eq. (5.32) leads to the symmetry requirement

$$\begin{aligned} \sum_{\alpha\beta} H_{ABCD}^{\alpha\beta} \Lambda_A^\alpha \Lambda_B^\beta E_{CD} = \sum_{\alpha\beta} & H_{ABCD}^{\alpha\beta} S_{AA'} \Lambda_{A'}^{T(\alpha)} S_{BB'} \\ & \times \Lambda_{B'}^{T(\beta)} S_{CC'} S_{DD'} E_{C'D'} \,. \end{aligned} \tag{5.33}$$

Let us change the summation variables on the right-hand side of Eq. (5.33) from α, β into $S(\alpha)$, $S(\beta)$ so that $T(S(\alpha)) = \alpha$, $T(S(\beta)) = \beta$. Comparing corresponding terms we find that crystal symmetry has imposed the condition

$$H_{ABCD}^{\alpha\beta} = H_{A'B'C'D'}^{S(\alpha)S(\beta)} S_{A'A} S_{B'B} S_{C'C} S_{D'D} \tag{5.34}$$

on the expansion coefficient $H_{ABCD}^{\alpha\beta}$. Similar symmetry conditions can be imposed on all of the terms in the polynomial expansion which we display in Eq. (9.1).

D. Homogeneity

Homogeneity is a crystal or material symmetry. For a crystal it constitutes invariance of the stored energy under an arbitrary discrete lattice translation. In the continuum limit, it reduces to invariance of the stored energy under an arbitrary infinitesimal $\vec{X} \to \vec{X} + d\vec{X}$ translation of the material frame. As a consequence, the stored energy cannot depend explicitly on $\vec{X}$. Invariance under the *translation* $\vec{X} \to \vec{X} + d\vec{X}$ leads to crystal momentum conservation just as invariance under the *displacement* $\vec{x} \to \vec{x} + \vec{d}$ yields real momentum conservation.

E. Elimination of Redundancy

The set of $N+1$ vector variables $\vec{u}^\alpha, \vec{x}$ is redundant and should be replaced by the nonredundant set $\vec{x}, \vec{y}^\mu$ where the $\vec{y}^\mu$ are the $N-1$ internal vector variables of Eq. (5.5). We can thus define a nonredundant set of rotational invariants

$$\Lambda_A^\mu \equiv R_{iA} y_i^\mu \,, \quad \Lambda_{B;C}^\nu \equiv R_{iB} y_{i,C}^\nu \,, \tag{5.35}$$

so that the stored energy can be written[41]

$$\Sigma = \Sigma(E_{AB}, \Lambda_A^\mu, \Lambda_{B;C}^\nu) \,. \tag{5.36}$$

We use (in this paper only) later letters of the Greek alphabet λ, μ, ν, etc., to denote nonredundant internal variables and reserve early letters α, β, γ, etc., for Λ's associated with sublattice positions such as $\vec{x}^\alpha$ or $\vec{u}^\alpha$.

We sometimes refer to the Λ_A^μ as polarizationlike variables even though they more properly describe body components of internal coordinates (components relative to axes that rotate with a rotation of the body). These variables become body components of the true polarizations only when multiplied by the appropriate charge. Internal coordinates are used rather than polarizations since we must describe all vibrations in the solid including infrared-inactive ones which have no associated charge or polarization.

Let us now consider the symmetry requirements analogous to Eq. (5.34) on the material descriptors for the stored-energy expansion into nonredundant invariants. Under the transformation (D17) the sublattice invariant Λ_A^α of Eq. (5.25) is related to Λ_A^μ of Eq. (5.35) by

$$\Lambda_A^\alpha \equiv u_i^\alpha R_{iA} = \sum_{\mu=1}^{N-1} V^{\alpha\mu} \Lambda_A^\mu \,. \tag{5.37}$$

Thus a typical term in the stored energy becomes

$$\sum_{\alpha\beta=1}^{N} H_{ABCD}^{\alpha\beta} \Lambda_A^\alpha \Lambda_B^\beta E_{CD} = \sum_{\mu\nu=1}^{N-1} H_{ABCD}^{\mu\nu} \Lambda_A^\mu \Lambda_B^\nu E_{CD} \,, \tag{5.38}$$

where

$$H_{ABCD}^{\mu\nu} = \sum_{\alpha\beta=1}^{N} H_{ABCD}^{\alpha\beta} V^{\alpha\mu} V^{\beta\nu} \,. \tag{5.39}$$

Similar remarks apply to all the terms in the stored energy of Eq. (9.1).

The symmetry of $H_{ABCD}^{\alpha\beta}$ [see Eq. (5.34)] leads with the help of Eq. (5.39) to the corresponding symmetry

$$\begin{aligned} H_{ABCD}^{\mu\nu} = \sum_{\alpha\beta} & H_{A'B'C'D'}^{S(\alpha)S(\beta)} V^{\alpha\mu} V^{\beta\nu} \\ & \times S_{A'A} S_{B'B} S_{C'C} S_{D'D} \,. \end{aligned} \tag{5.40}$$

The inverse of Eq. (5.39), using Eq. (D5), can be written

$$H_{ABCD}^{\alpha\beta} = \sum_{\mu\nu} H_{ABCD}^{\mu\nu} U^{\mu\alpha} U^{\nu\beta} \,. \tag{5.41}$$

The limits in Eq. (5.41) extend from μ or $\nu = 0$ to $N-1$, but terms in which μ or ν (or both) are zero vanish if one uses Eqs. (D13), (5.39), and displacement invariance Eq. (5.2) in the form

$$\sum_\alpha H_{ABCD}^{\alpha\beta} = \sum_\beta H_{ABCD}^{\alpha\beta} = 0 \,. \tag{5.42}$$

Equation (5.41) permits us to eliminate $H^{S(\alpha)S(\beta)}$

from Eq. (5.40) with the result

$$H^{\mu\nu}_{ABCD}=\sum_{\mu'\nu'} H^{\mu'\nu'}_{A'B'C'D'}S_{A'A}S_{B'B}S_{C'C}S_{D'D}$$

$$\times\sum_{\alpha} V^{\alpha\mu}U^{\mu' S(\alpha)}\sum_{\beta} V^{\beta\nu}U^{\nu' S(\beta)}\ . \qquad (5.43)$$

For the *special case* in which the operation S does not interchange the sublattices $[S(\alpha)=\alpha, S(\beta)=\beta]$, Eq. (5.43) reduces to

$$H^{\mu\nu}_{ABCD}= H^{\mu\nu}_{A'B'C'D'}S_{A'A}S_{B'B}S_{C'C}S_{D'D}\ . \qquad (5.44)$$

This symmetry requirement is the same as for an ordinary fourth-rank tensor, i.e., the superscripts μ, ν can be ignored.

F. Spatial Inversion Invariance

Our discussion of the stored energy to this point has assumed *spatial inversion* invariance (parity conservation). Parity-violating terms can be considered by writing a stored energy in the form

$$\rho^0\Sigma=\rho^0[\Sigma_1(E_{AB}, \Lambda^\mu_c)+\eta\Sigma_2(E_{AB}, \Lambda^\mu_c)]\ , \qquad (5.45)$$

where η is a pseudoscalar which takes the values ± 1 for right- and left-handed spatial coordinate systems, respectively. We can, for example, visualize η as the sign of the Jacobian J of Eq. (5.12), the magnitude of J having been absorbed in Σ_2 in accord with Eq. (5.13). The term in Σ_2 is understood to be a small term arising from parity nonconserving terms in the microscopic Hamiltonian.

If we think of matter as having a handedness (i.e., chirality) associated with parity nonconservation, the symmetry operation of material inversion, which inverts both spatial and material coordinates as in Eq. (5.28), reverses this handedness. Thus if Σ_1 is invariant under a particular space group, Σ_2 is invariant only under the subgroup of this space group whose rotations are proper. Equations (5.34) and (5.43) determine the symmetry of the material descriptors in Σ_2 just as they do for those in Σ_1. Now, however, only the proper symmetry elements are used.

This reasoning leads to the interesting conclusion that crystals which are centrosymmetric when parity is conserved may be acentric when parity is violated. Such crystals could then possess odd-rank tensors (arising from the Σ_2) that are prohibited under parity conservation.

G. Neglect of Wave-Vector (Spatial) Dispersion

Since the objective of this paper is to create a macroscopic theory, that is to say, a theory which is appropriate for wavelengths much larger than the size of the unit cell in the crystal, it is appropriate to take the limit $ka\to 0$, where k is a typical wave vector and a a typical cell dimension. In the present language, this would consist in neglecting all material derivatives. Thus we discard the variables $\Lambda^\nu_{B;C}$ in Eq. (5.36) and obtain

$$\Sigma=\Sigma(E_{AB}, \Lambda^\mu_C)\ . \qquad (5.46)$$

Since Σ does not depend on the center-of-mass variable $\vec{x}$, but only its first derivatives, the latter cannot be neglected. The dependence on E_{AB}, indeed, is what yields the usual theory of nonlinear ("finite") elasticity.

In summary, the theory, from this point on, using Eq. (5.46) neglects spatial or wave-vector dispersion. A theory including wave-vector dispersion and dispersive effects such as optical rotation obtained by using Eq. (5.36) and the methods of this paper will be presented later.

VI. MULTIPOLE EXPANSION OF ELECTROMAGNETIC FORCES

We can rewrite Eq. (4.9) in a form

$$\rho^\alpha\ddot{\vec{x}}^\alpha(\vec{X}, t)=\vec{f}^{\,\alpha}(\vec{X}, t)+\vec{f}^{\,\alpha e}(\vec{X}, t), \qquad (6.1)$$

which separates the force into a mechanical part $\vec{f}^{\,\alpha}$, and an electromagnetic part $\vec{f}^{\,\alpha e}$. In this section our objective is to expand the electromagnetic force in powers of the internal displacements $\vec{u}^\alpha$ so that the result can subsequently be described in terms of the various multipole moments of the charge distribution or portions thereof. Thus the electromagnetic force can be written in the form

$$\vec{f}^{\,\alpha e}=q^\alpha[\vec{E}(\vec{x}+\vec{u}^\alpha)+(\dot{\vec{x}}+\dot{\vec{u}}^\alpha)\times\vec{B}(\vec{x}+\vec{u}^\alpha)]$$

$$=q^\alpha\vec{E}(\vec{x})+q^\alpha(\vec{u}^\alpha\cdot\vec{\nabla})\vec{E}(\vec{x})+\tfrac{1}{2}q^\alpha\vec{u}^\alpha\vec{u}^\alpha:\vec{\nabla}\vec{\nabla}\vec{E}(\vec{x})$$

$$+q^\alpha(\dot{\vec{x}}+\dot{\vec{u}}^\alpha)\times\vec{B}(\vec{x})+\dot{\vec{x}}\times(q^\alpha\vec{u}^\alpha\cdot\vec{\nabla})\vec{B}(\vec{x})$$

$$+q^\alpha\dot{\vec{u}}^\alpha\times(\vec{u}^\alpha\cdot\vec{\nabla})\vec{B}(\vec{x})+\cdots\ , \qquad (6.2)$$

where the ith component of the last term of Eq. (6.2) is given by

$$\epsilon_{ijk}q^\alpha\dot{u}^\alpha_j u^\alpha_m B_{k,m}=\tfrac{1}{2}\epsilon_{ijk}(d/dt)(q^\alpha u^\alpha_j u^\alpha_m)B_{k,m}$$

$$+\tfrac{1}{2}\epsilon_{jkm}q^\alpha u^\alpha_k\dot{u}^\alpha_m B_{j,i}\ . \qquad (6.3)$$

In the above equations, we use $\vec{\nabla}$ to stand for partial derivatives with respect to $\vec{x}$ rather than $\vec{X}$. The derivative $B_{k,m}$ in Eq. (6.3) is written using the lower-case letter to remind us that the derivative has been taken with respect to a spatial rather than a material variable.

If we sum Eq. (6.1) on the index α, we obtain the equation of motion of the center of mass

$$\rho^0\ddot{\vec{x}}(\vec{X}, t)=\vec{f}(\vec{X}, t)+\vec{f}^{\,e}(\vec{X}, t)\ . \qquad (6.4)$$

Making use of Eq. (4.10) for the force $\vec{f}^{\,\alpha}$ and the displacement invariance conditions (5.3) and (5.10), we find for the force on the center-of-mass variable

$$\vec{f}(\vec{X}, t) = \sum_{\alpha} \vec{f}^{\alpha}(\vec{X}, t) = \rho^0 \frac{\partial}{\partial X_A}\left(\frac{\partial \hat{\Sigma}}{\partial \vec{x}_{,A}}\right) . \tag{6.5}$$

A similar sum over α on the electromagnetic forces yields the total electromagnetic force

$$\begin{aligned} f_i^e = \sum_{\alpha} f_i^{\alpha e} = \{ &[\vec{p}(\vec{X}) \cdot \vec{\nabla}]\vec{E}(\vec{x}) + \tfrac{1}{2}[\overleftrightarrow{q}(\vec{X}) : \vec{\nabla}\vec{\nabla}]\vec{E}(\vec{x}) \\ &+ \dot{\vec{p}}(\vec{X}) \times \vec{B}(\vec{x}) + \dot{\vec{x}} \times [\vec{p}(\vec{X}) \cdot \vec{\nabla}]\vec{B}(\vec{x})\}_i \\ &+ \tfrac{1}{2}\epsilon_{ijk}[(d/dt)q_{ja}(\vec{X})]B_{k,a}(\vec{x}) \\ &+ m_k(\vec{X})B_{k,i}(\vec{x}) , \end{aligned} \tag{6.6}$$

where $\vec{p}$ represents the dipole moment, $\vec{m}$ represents the magnetic dipole moment, and $\overleftrightarrow{q}$ represents the electric quadrupole moment, all taken per unit volume in the material frame. The dipole and quadrupole moments are defined in Appendix A and the magnetic dipole moment is defined in Appendix B and these are simply sums of the corresponding terms in Eq. (6.2). When these moments per unit volume in the material frame are divided by the Jacobian, they reduce to the dipole, quadrupole, and magnetic dipole moment per unit volume in the spatial frame and so become the ordinary polarization, quadrupolarization, and magnetization. If Eq. (6.4) is divided by the Jacobian and evaluated at the spatial point $\vec{z} = \vec{x}(\vec{X}, t)$ and the lemma of Appendix C used to convert all material time derivatives (d/dt) to spatial time derivatives $(\partial/\partial t)$ on the right-hand side, then we obtain

$$\begin{aligned} &[\rho(\vec{X}, t)\ddot{x}_i(\vec{X}, t)]_{\vec{x}(\vec{X}, t) = \vec{z}} \\ &\quad = \Big[[\vec{P}(\vec{z}, t) \cdot \vec{\nabla}]\vec{E}(\vec{z}, t) + \left(\frac{\partial \vec{P}}{\partial t} + \vec{\nabla} \times (\vec{P} \times \dot{\vec{x}})\right) \times \vec{B} \\ &\qquad + (\vec{P} \cdot \vec{\nabla})(\dot{\vec{x}} \times \vec{B}) + (\dot{\vec{x}} \times \vec{B})(\vec{\nabla} \cdot \vec{P}) + \tfrac{1}{2}(\overleftrightarrow{Q} : \vec{\nabla}\vec{\nabla})\vec{E} \Big]_i \\ &\qquad + M_k B_{k,i} + \tfrac{1}{2}\epsilon_{iab}\left(\frac{\partial Q_{aj}}{\partial t} + \epsilon_{amn}\epsilon_{nrs}\frac{\partial}{\partial z_m}(Q_{rj}\dot{x}_s)\right) B_{b,j} \\ &\qquad + \tfrac{1}{2}\epsilon_{imn} Q_{aj} \frac{\partial \dot{x}_m}{\partial z_a} B_{n,j} + \tfrac{1}{2}\epsilon_{ijk} Q_{mr,m}\dot{x}_j B_{k,r} \\ &\qquad + \left(\frac{\rho(\vec{X}, t)\vec{f}(\vec{X}, t)}{\rho^0}\right)_{\vec{x}(\vec{X}, t) = \vec{z}} . \end{aligned} \tag{6.7}$$

All but the last term on the right-hand side represents the electromagnetic force density in a dielectric medium in the customary form. It is amusing to note that the convective contribution to the current $\vec{\nabla} \times (\vec{P} \times \dot{\vec{x}})$ which arises from the electric dipole moment and a corresponding convective contribution to the quadrupole current appear automatically when we make this transformation from material to spatial time derivatives. Thus these terms do not need to be derived by special arguments as in Panofsky and Phillips[42] or by appealing to Lorentz transformations. The reader is referred to Penfield and Haus[15] and to de Groot[16] for reviews of electrodynamics including such electromagnetic force terms as presented in Eq. (6.7). The force equation (6.7) agrees to terms of order v/c (all that can be expected for our nonrelativistic treatment) with the force in the Amperian formulation given by Penfield and Haus.[43]

A comparison of our Eq. (6.7) with Toupin's work[44] entails several considerations. First, we should ignore the electric quadrupole and magnetic dipole terms of our Eq. (6.7) in the comparison since Toupin has omitted such contributions. Next, the last term of our Eq. (6.7) is identical with the divergence of Toupin's local stress.[44] Further, if we make an adiabatic approximation in our internal coordinate equation (8.1), by which we mean the neglect of the inertial force term, and if we truncate the *Lagrangian* at the electric dipole level, then our Eq. (6.7) and Toupin's Eq. (5.2) agree. It should be remembered, however, that the portion of the total force in these equations which is "mechanical" or "electromagnetic" is somewhat arbitrary and is subject to the definition given to these terms. In order to explain the Faraday effect, Toupin makes an *ad hoc* addition to his constitutive equations. His extra term appears automatically as a $\vec{p}^{\mu} \times \vec{B}$ term in our Eq. (8.3) for the internal coordinates (other terms of comparable order also arise in that equation). This term can be shown to arise from the magnetic contribution $\vec{M} \cdot \vec{B}$ to the interaction Lagrangian. Such a term also makes contributions to the body force, the energy balance equation, and the stress tensor which do not appear in Toupin's treatment.

The term $M_k B_{k,i}$ has an interesting form, which contrasts with the corresponding electrostatic term $P_k E_{i,k}$. This difference arises because the magnetic dipole is generated by a current loop (electron spin is ignored in this paper) rather than a pair of magnetic poles. A summation of the forces over the elements of a current loop directly yields the force $M_k B_{k,i}$.

VII. EFFECTIVE FIELD CONTRIBUTIONS

Up to this point our handling of the electric field in the particle equations (2.12) and (6.2) has ignored self-field and local-field questions. In this section, we wish to clarify both of these issues. First, in calculating the electric field which acts on particle $n\alpha$ in Eq. (2.12) the self-field of the particle, which arises from its charge, must be omitted. Second the procedure of Eq. (6.2) in obtaining a multipole expansion of the electric and magnetic forces might be objected to since it involves expanding the electric and magnetic fields under the assumption that these are slowly varying functions. In truth, of course, the electromagnetic fields are slowly varying if one compares corresponding points in adjacent cells in a crystalline lattice, but within any cell these fields can vary rapidly. As a result, there are, in fact, local-field contributions.

We will henceforth use the term effective field to refer to that field acting on a particle which includes the local-field contribution but excludes the self-field contribution. Such effective field contributions imply, for example, that the electric force which acts on a sublattice α is not $q^\alpha\vec{E}$ but should be replaced instead by

$$q^\alpha\vec{E} \rightarrow q^\alpha(\vec{E}+\textstyle\sum_\beta \overleftrightarrow{L}^{\alpha\beta}\cdot\vec{p}^\beta)\ , \tag{7.1}$$

where $\vec{p}^\beta = q^\beta\vec{u}^\beta$. Matrices $\overleftrightarrow{L}^{\alpha\beta}$ are parameters that describe the strength of the effective field. We note, however, that if we were to add to the stored energy an additional term

$$\begin{aligned}\rho^0\overline{\Sigma}_{\text{local}} &= -\frac{1}{2}\sum_{\alpha\beta}\vec{p}^\alpha\cdot\overleftrightarrow{L}^{\alpha\beta}\cdot\vec{p}^\beta \\ &= -\frac{1}{2}\sum_{\alpha\beta} q^\alpha q^\beta\vec{u}^\alpha\cdot\overleftrightarrow{L}^{\alpha\beta}\cdot\vec{u}^\beta\ ,\end{aligned} \tag{7.2}$$

then this would lead to additional terms in the force equation of the form

$$\vec{f}^{\,\alpha}_{\text{local}} = -\frac{\partial}{\partial\vec{u}^\alpha}(\rho^0\overline{\Sigma}_{\text{local}}) = \sum_\beta q^\alpha\overleftrightarrow{L}^{\alpha\beta}\cdot\vec{p}^{\,\beta}\ , \tag{7.3}$$

in precise agreement with the effective field contributions of Eq. (7.1). Equation (7.2) can be rewritten in the rotationally invariant form

$$\rho^0\overline{\Sigma}_{\text{local}} = -\frac{1}{2}\sum_{\alpha\beta} q^\alpha q^\beta\Lambda^\alpha_A L^{\alpha\beta}_{AB}\Lambda^\beta_B\ . \tag{7.4}$$

Indeed Eq. (7.4) reduces to Eq. (7.2) when rotations are not present.

The addition of a term of the form (7.4) to the stored energy simply produces a modification of a term of the same form which is already present in the potential energy. If the parameters of the expansion of the stored energy are fitted against experiment the effective field contributions are all automatically included in these parameters and effective field contributions need not be separately stated. A corollary to this is that long-wavelength electromagnetic fields cannot be used to measure separately the effective fields *in perfect crystals* although short-wavelength fields (e.g., x rays or neutrons) can be used. The absorption of the effective field into the stored energy means that the $\vec{E}$ and $\vec{B}$ fields used in this paper are in fact the long-wavelength (conventional, macroscopic) portions of the corresponding total electric and magnetic fields. Our use of the continuum forms of the charge and current density, Eqs. (4.11) and (4.12), in the Maxwell-Lorentz equations has, in fact, guaranteed that we are computing just these macroscopic fields.

Of course, some of the force terms involved field derivatives, and in the presence of effective field contributions we must, for example, make a replacement such as

$$q^\alpha(\vec{u}^\alpha\cdot\vec{\nabla})\vec{E} \rightarrow q^\alpha(\vec{u}^\alpha\cdot\vec{\nabla})\vec{E}+\textstyle\sum_\beta q^\alpha(\vec{u}^\alpha\cdot\vec{\nabla})\overleftrightarrow{L}'^{\alpha\beta}\cdot\vec{p}^\beta\ , \tag{7.5}$$

where the parameters $\overleftrightarrow{L}'^{\alpha\beta}$ are not necessarily identical with $\overleftrightarrow{L}^{\alpha\beta}$. All such effective field contributions to the forces must in fact be derivable from stored-energy terms. When we insist that these stored-energy terms have a rotationally invariant form, then these terms must have the same form as terms already present in the stored energy and can again be absorbed. This means that all of the terms of the stored energy Σ are now understood to contain modifications associated with effective field contributions. A correction such as shown in Eq. (7.5) which involves gradients of the polarization will not appear, however, unless polarization derivatives are included in the stored energy, so that a fully consistent theory including effective field contributions may require the use of the stored energy of Eq. (5.36) which includes wave-vector dispersion effects.

VIII. EQUATIONS OF MOTION IN INTERNAL COORDINATES

By using Eqs. (D1) and (D12) of Appendix D and Eq. (6.1) we find that the matter equations of motion in the internal coordinates can be written in the form

$$m^\mu\ddot{\vec{y}}^\mu(\vec{X},\ t) = \textstyle\sum_\alpha V^{\alpha\mu}[\rho^\alpha\ddot{\vec{x}}^\alpha(\vec{X},\ t)] = \vec{f}^\mu+\vec{f}^{\mu e}\ , \tag{8.1}$$

valid for $\mu = 0, 1, 2, \ldots, N-1$, where

$$\vec{f}^\mu \equiv \sum_\alpha V^{\alpha\mu}\vec{f}^\alpha = -\rho^0\frac{\partial\hat{\Sigma}}{\partial\vec{y}^\mu}+\rho^0\frac{\partial[\partial\hat{\Sigma}/\partial\vec{y}^\mu{}_{,A}]}{\partial X_A} \tag{8.2}$$

and

$$\begin{aligned}f^{\mu e}_i &\equiv \textstyle\sum_\alpha V^{\alpha\mu}f^{\alpha e}_i \\ &= \{q^\mu\vec{E}(\vec{x})+[\vec{p}^\mu(\vec{X})\cdot\vec{\nabla}]\vec{E}(\vec{x}) \\ &\quad +\tfrac{1}{2}[\overleftrightarrow{q}^\mu(\vec{X}):\vec{\nabla}\vec{\nabla}]\vec{E}(\vec{x})+q^\mu\dot{\vec{x}}(\vec{X})\times\vec{B}(\vec{x}) \\ &\quad +\dot{\vec{p}}^\mu(\vec{X})\times\vec{B}(\vec{x})+\dot{\vec{x}}(\vec{X})\times[\vec{p}^\mu(\vec{X})\cdot\vec{\nabla}]\vec{B}(\vec{x})\}_i \\ &\quad +\tfrac{1}{2}\epsilon_{ira}\dot{q}^\mu_{rs}(\vec{X})B_{a,s}(\vec{x})+m^\mu_k(\vec{X})B_{k,i}(\vec{x})\ .\end{aligned} \tag{8.3}$$

The above equations are valid for $\mu = 0$, the center-of-mass case, as well as $\mu \neq 0$. For the case $\mu \neq 0$, and in the absence of wave-vector dispersion, the second term in Eq. (8.2) vanishes. The effective charge q^{μ} of the μth degree of freedom is defined by

$$q^{\mu} \equiv \textstyle\sum_{\alpha} q^{\alpha} V^{\alpha\mu} , \tag{8.4}$$

and the electric dipole moment $\vec{p}^{\,\mu}$ appearing in the force equation (8.3) is defined by

$$\vec{p}^{\,\mu} \equiv \textstyle\sum_{\alpha} q^{\alpha} \vec{u}^{\alpha} V^{\alpha\mu} = \sum_{\nu}' q^{\mu\nu} \vec{y}^{\,\nu} , \tag{8.5}$$

where a primed sum indicates omission of 0 from the summation variables. Note that this dipole moment is not the same as $q^{\mu}\vec{y}^{\,\mu}$. Instead, we see that the dipole moment of the μth degree of freedom has contributions from the displacements of other internal coordinates. Similarly, we define the elements of the quadrupole moment of the μth degree of freedom to be

$$q^{\mu}_{rs} = \textstyle\sum_{\alpha} q^{\alpha} u^{\alpha}_{r} u^{\alpha}_{s} V^{\alpha\mu} = \sum_{\nu\lambda}' q^{\mu\nu\lambda} y^{\nu}_{r} y^{\lambda}_{s} = q^{\mu}_{sr} , \tag{8.6}$$

and the magnetic dipole moment of the μth degree of freedom to be

$$\vec{m}^{\mu} \equiv \tfrac{1}{2} \textstyle\sum_{\alpha} q^{\alpha} (\vec{u}^{\alpha} \times \dot{\vec{u}}^{\alpha}) V^{\alpha\mu} = \tfrac{1}{2} \sum_{\nu\lambda}' q^{\mu\nu\lambda} (\vec{y}^{\,\nu} \times \dot{\vec{y}}^{\,\lambda}) . \tag{8.7}$$

The set of effective charges $q^{\mu\nu}$ (dipole moments per unit change of internal coordinate) is defined by

$$q^{\mu\nu} = \textstyle\sum_{\alpha} q^{\alpha} V^{\alpha\mu} V^{\alpha\nu} = q^{\nu\mu} = q^{(\mu\nu)} , \tag{8.8}$$

and the corresponding effective charges appropriate to quadrupole and magnetic dipole moments are defined by

$$q^{\mu\nu\lambda} \equiv \textstyle\sum_{\alpha} q^{\alpha} V^{\alpha\mu} V^{\alpha\nu} V^{\alpha\lambda} = q^{(\mu\nu\lambda)} . \tag{8.9}$$

The parentheses displayed in Eqs. (8.8) and (8.9) are to remind us these effective charges are symmetric on all interchanges of the indices enclosed in the parentheses. Moreover, we obtain the special relations

$$q^{\mu 0} = q^{0\mu} = q^{\mu} , \quad q^{\mu\nu 0} = q^{0\mu\nu} = q^{\mu 0\nu} = q^{\mu\nu} . \tag{8.10}$$

If we specialize Eq. (8.1) to the center-of-mass equation ($\mu = 0$) and make use of the fact that the center-of-mass charge $q^{0} = 0$, we obtain the center-of-mass equation

$$m^{0} \ddot{\vec{x}} = \rho^{0} \frac{\partial(\partial\hat{\Sigma}/\partial\vec{x}_{,A})}{\partial X_{A}} + \vec{f}^{\,e} , \tag{8.11}$$

where the electromagnetic force $\vec{f}^{\,e}$ is defined by Eq. (6.6). The electric and magnetic moments and the quadrupole tensor can now be expressed in terms of the internal coordinates by

$$\vec{p} = \textstyle\sum_{\nu}' q^{\nu} \vec{y}^{\,\nu} = \vec{p}^{\,0} = \vec{P} J , \tag{8.12}$$

$$q_{rs} = \sum_{\nu\lambda}{}' q^{\nu\lambda} y^{\nu}_{r} y^{\lambda}_{s} = q^{0}_{rs} = Q_{rs} J , \tag{8.13}$$

$$\vec{m} = \tfrac{1}{2} \sum_{\nu\lambda}{}' q^{\nu\lambda} (\vec{y}^{\,\nu} \times \dot{\vec{y}}^{\,\lambda}) = \vec{m}^{0} = \vec{M} J , \tag{8.14}$$

where $J = | \partial\vec{x}/\partial\vec{X} |$ is the Jacobian as before and $\vec{P}$, $\overleftrightarrow{Q}$, and $\vec{M}$ are the usual polarization, electric quadrupolarization, and magnetization of the medium.

IX. NONLINEAR INTERACTIONS AND FORCES

As discussed in Sec. V, the stored energy can always be expressed as a single-valued function of a set of basic rotationally invariant variables E_{AB}, Λ^{μ}_{C} as shown in Eq. (5.46). For our purposes, it is sufficient to expand the stored energy in polynomial form

$$\begin{aligned}
\rho^{0}\Sigma = {} & \sum_{\mu} {}^{(1,0)}H^{\mu}_{A} \Lambda^{\mu}_{A} + {}^{(0,1)}H_{AB} E_{AB} \\
& + \sum_{\mu\nu} {}^{(2,0)}H^{\mu\nu}_{AB} \Lambda^{\mu}_{A} \Lambda^{\nu}_{B} + \sum_{\mu} {}^{(1,1)}H^{\mu}_{ABC} \Lambda^{\mu}_{A} E_{BC} \\
& + {}^{(0,2)}H_{ABCD} E_{AB} E_{CD} + \sum_{\mu\nu\lambda} {}^{(3,0)}H^{\mu\nu\lambda}_{ABC} \Lambda^{\mu}_{A} \Lambda^{\nu}_{B} \Lambda^{\lambda}_{C} \\
& + \sum_{\mu\nu} {}^{(2,1)}H^{\mu\nu}_{ABCD} \Lambda^{\mu}_{A} \Lambda^{\nu}_{B} E_{CD} \\
& + \sum_{\mu} {}^{(1,2)}H^{\mu}_{ABCDE} \Lambda^{\mu}_{A} E_{BC} E_{DE} \\
& + \sum_{\mu\nu\lambda\gamma} {}^{(4,0)}H^{\mu\nu\lambda\gamma}_{ABCD} \Lambda^{\mu}_{A} \Lambda^{\nu}_{B} \Lambda^{\lambda}_{C} \Lambda^{\gamma}_{D} \\
& + \sum_{\mu\nu\lambda} {}^{(3,1)}H^{\mu\nu\lambda}_{ABCDE} \Lambda^{\mu}_{A} \Lambda^{\nu}_{B} \Lambda^{\lambda}_{C} E_{DE} \\
& + \sum_{\mu\nu} {}^{(2,2)}H^{\mu\nu}_{ABCDEF} \Lambda^{\mu}_{A} \Lambda^{\nu}_{B} E_{CD} E_{EF} + \cdots .
\end{aligned} \tag{9.1}$$

The terms in Eq. (9.1) are written up to the fourth order, but terms no higher than the second in the strain field E_{AB} have been retained. Clearly, additional strain terms can be added, but our primary interest in this and subsequent papers will be in the intense fields associated with laser beams so that it is more important to retain high-order nonlinearities in the Λ^{μ} polarization variables. The H coefficients, called material descriptors, contain numerical presuperscripts (m, n) where m denotes the number of polarizationlike factors Λ^{μ} and n denotes the number of strain factors E in the term in question.

We can define the natural state of the medium as the equilibrium state where no external field or stress has been applied. In the absence of initial stress, such as produced by bending a bar into a circle and welding it into a single piece, both the stress and strain will be zero in the natural state in a nonferroelastic material. Similarly, if the material is not ferroelectric or antiferroelectric, etc., no spontaneous polarization contributions $\vec{p}^{\,\mu}$ or displacements $\vec{y}^{\,\mu}$ will be present. Thus, the electromagnetic field will vanish. In order for the natural state to be an equilibrium state, all forces must vanish, which implies that

$$\frac{\partial \Sigma}{\partial \Lambda^{\mu}_{C}} = \frac{\partial \Sigma}{\partial E_{AB}} = 0 \qquad (9.2)$$

in the natural state, i.e., where $\Lambda^{\mu}_{C} = E_{AB} = 0$. We can thus conclude, since we use a natural state as our reference state, that the coefficients of the linear terms, ${}^{(1,0)}H^{\mu}_{C}$ and ${}^{(0,1)}H_{AB}$, must vanish. A similar choice was made by Toupin.[4]

By assuming the existence of a stored energy, [Eq. (9.1)] we have automatically introduced parameters H which are independent of frequency. When we calculate various higher-order susceptibilities, these will be related to the H parameters by various frequency factors, closely related to the linear susceptibility. The frequency dependence arises from a solution of the dynamical equations of the particular problem. The H parameters play a role analogous to the frequency-independent Miller[45] constant δ derived from second-harmonic generation coefficients (see Sec. XIII).

As we demonstrated in Sec. V, for example Eq. (5.22), there is more than one way to construct a set of basic rotationally invariant variables, so that the choice of these basic invariants is not unique. However, any complete set of basic invariants is expressible in terms of any other complete set. Thus it is adequate for us to represent the stored energy in the form of Eq. (9.1). A different choice of basis invariants—for example, the use of the parameter Γ of Eq. (5.20) in place of Λ of Eq. (5.25)—in the current expansion consists essentially in a rearrangement of the terms in the expansion Eq. (9.1). The present choice in terms of Λ was made to reduce the number of appearances of low-order H coefficients (m, n small) in nonlinear effects to a minimum and so simplifies the form of results. We have already shown,[2] however, that certain nonlinear effects must in fact arise from the quadratic terms. Indeed, the rotational invariance of the theory assures that the rotation associated with an acoustic shear wave produces a change in the dielectric tensor in addition to the change brought about by strain. This causes the photoelasticity tensor to lack the symmetry upon interchange in its two elastic indices assumed since the work of Pöckels.[11]

The solution of the nonlinear dynamical equations for the polarizationlike variables $\vec{y}^{\mu}$ by an iteration procedure automatically leads to all the two-step and higher-step contributions to whatever tensor is being calculated. This is another advantage of our formulation of the energy in terms of polarizationlike variables and strains rather than fields and strains. If fields were used, multistep contributions would have to be introduced in an *ad hoc* manner. For example, the term involving ${}^{(2,1)}H$ describes a one-step interaction in which a light wave is scattered by a sound wave. Our more detailed analysis of the photoelasticity tensor,[2] however, shows that the same scattering can also be produced by combining the terms ${}^{(3,0)}H$ and ${}^{(1,1)}H$. This two-step internal process can be interpreted as the creation of an internal displacement field by a ${}^{(1,1)}H$ interaction followed by a ${}^{(3,0)}H$ interaction of this low-frequency internal displacement field with the input electromagnetic field to produce the scattered electromagnetic field. The ${}^{(1,1)}H$ interaction is related to the piezoelectric tensor while the ${}^{(3,0)}H$ interaction is related to the electrooptic tensor. (See Secs. X and XIII.) It will sometimes be possible to express the two-step effects in terms of tensors deduced from other experiments. When this is so, we will refer to it as a two-step *indirect* effect; when it is not, as a two-step *internal* contribution to the *direct* effect.

In order to evaluate the forces in Eqs. (8.2) and (8.11), we need the following derivatives:

$$\frac{\partial \hat{\Sigma}}{\partial y^{\mu}_{i}} = \frac{\partial \Sigma}{\partial \Lambda^{\mu}_{A}} R_{iA} , \qquad (9.3)$$

$$\frac{\partial \hat{\Sigma}}{\partial x_{i,A}} = \frac{\partial \Sigma}{\partial E_{AB}} x_{i,B} + \sum_{\mu=1}^{N-1} y^{\mu}_{j} \frac{\partial \Sigma}{\partial \Lambda^{\mu}_{B}} \frac{\partial R_{jB}}{\partial x_{i,A}} . \qquad (9.4)$$

By utilizing the definition (5.23), the rotation tensor can be expressed in the form

$$\begin{aligned} R_{jB} &= x_{j,D}[(\overleftrightarrow{1} + 2\overleftrightarrow{E})^{-1/2}]_{DB} \\ &= x_{j,D}(\delta_{DB} - E_{DB} + \tfrac{3}{2} E_{DC} E_{CB} \\ &\qquad - \tfrac{5}{2} E_{DA} E_{AC} E_{CB} + \cdots) , \qquad (9.5) \end{aligned}$$

so that its derivative can be written to second order in the displacement $\vec{u}$ as

$$\begin{aligned} \frac{\partial R_{jB}}{\partial x_{i,A}} &= \tfrac{1}{2}(\delta_{ij} \delta_{AB} - \delta_{jA} \delta_{iB}) \\ &\quad + \tfrac{1}{4}[\delta_{jA}(3\delta_{iC} S_{CB} - 2u_{i,B}) - \delta_{ij} S_{AB} \\ &\quad + \delta_{iB}(3\delta_{jD} S_{DA} - 2u_{j,A}) - \delta_{AB} S_{CD} \delta_{iC} \delta_{jD}] \\ &\quad + [\tfrac{3}{2} \delta_{jD}(S_{DC} u_{i,(B} \delta_{C)A} + \delta_{i(D} \delta_{C)A} u_{m,C} u_{m,B}) \\ &\quad + \tfrac{3}{2} u_{j,D}(\delta_{i(D} \delta_{C)A} S_{CB} + S_{DC} \delta_{i(C} \delta_{B)A}) \\ &\quad - \tfrac{5}{2} \delta_{jD}(\delta_{i(D} \delta_{F)A} S_{FG} S_{GB} + S_{DF} \delta_{i(F} \delta_{G)A} S_{GB} \\ &\quad + S_{DF} S_{FG} \delta_{i(G} \delta_{B)A})] . \qquad (9.6) \end{aligned}$$

Note that $\delta_{iC} S_{CB} \neq S_{IB}$. (See Appendix E.) In the absence of wave-vector dispersion, the force on any internal coordinate $\vec{y}^{\mu}$ is given by the first term in Eq. (8.2) which we can rewrite in the form

$$f_i^\mu = -R_{iA}\,\rho^0\,\frac{\partial\Sigma}{\partial\Lambda_A^\mu}$$

$$= -(R_{iA}-\delta_{iA})\,\rho^0\,\frac{\partial\Sigma}{\partial\Lambda_A^\mu} - \delta_{iA}\,\rho^0\,\frac{\partial\Sigma'}{\partial\Lambda_A^\mu}$$

$$-\delta_{iA}\,\Big({}^{(1,1)}H_{ABC}^\mu E_{BC} + 2\sum_\nu {}^{(2,0)}H_{AB}^{\mu\nu}\Lambda_B^\nu\Big)\ , \quad (9.7)$$

where we have used the abbreviation Σ' to represent the portion of Σ above and beyond the quadratic terms:

$$\rho^0\Sigma' = \rho^0\Sigma - \sum_{\mu\nu} {}^{(2,0)}H_{AB}^{\mu\nu}\,\Lambda_A^\mu\,\Lambda_B^\nu - {}^{(0,2)}H_{ABCD}\,E_{AB}\,E_{CD}$$

$$-\sum_\mu {}^{(1,1)}H_{ABC}^\mu\,\Lambda_A^\mu\,E_{BC}\ , \qquad (9.8)$$

$$R_{iA}-\delta_{iA} = \tfrac{1}{2}\,u_{i,A} - \tfrac{1}{2}\delta_{iB}\,u_{A,B} - \tfrac{1}{2}\delta_{iB}\,u_{k,B}\,u_{k,A}$$

$$+\tfrac{3}{2}\delta_{iB}S_{BC}S_{CA} - u_{i,B}\,S_{BA} + \cdots\ , \quad (9.9)$$

where S_{BA} is the infinitesimal strain defined in Eq. (5.17). Note that $\delta_{iB}\,u_{A,B} \neq u_{A,i}$ [see Eq. (E5) of Appendix E].

By using Eq. (9.4) the force in the center-of-mass equation (8.11) can be written more explicitly

$$\frac{f_i}{\rho^0} = \frac{\partial}{\partial X_A}\,\frac{\partial\hat{\Sigma}}{\partial x_{i,A}}$$

$$= u_{i,BA}\,\frac{\partial\Sigma}{\partial E_{AB}} + \sum_\mu y_{j,A}^\mu\,\frac{\partial\Sigma}{\partial\Lambda_B^\mu}\,\frac{\partial R_{jB}}{\partial x_{i,A}} + (\delta_{iB}+u_{i,B})\left(\frac{\partial^2\Sigma}{\partial E_{AB}\,\partial E_{CD}}\,E_{CD,A} + \sum_\mu \frac{\partial^2\Sigma}{\partial E_{AB}\,\partial\Lambda_C^\mu}\,\Lambda_{C,A}^\mu\right)$$

$$+\sum_\mu y_j^\mu\,\frac{\partial R_{jB}}{\partial x_{i,A}}\left(\frac{\partial^2\Sigma}{\partial\Lambda_B^\mu\,\partial E_{CD}}\,E_{CD,A} + \sum_\nu \frac{\partial^2\Sigma}{\partial\Lambda_B^\mu\,\partial\Lambda_C^\nu}\,\Lambda_{C,A}^\nu\right) + \sum_\mu y_j^\mu\,\frac{\partial\Sigma}{\partial\Lambda_B^\mu}\,\frac{\partial}{\partial X_A}\left(\frac{\partial R_{jB}}{\partial x_{i,A}}\right)\ . \quad (9.10)$$

The matter equations of motion (8.1) are written with the variable $\vec{X}$ as independent variable. Since these equations are coupled to the electromagnetic field and it is the electromagnetic field at the position $\vec{x}$ of the particle which is relevant, it is convenient to introduce x as the independent variable of the matter equations. To differentiate between the same physical quantity with $\vec{x}$ as independent variable rather than $\vec{X}$ we add a caret as in

$$\vec{u}(\vec{X},t) \equiv \hat{\vec{u}}(\vec{x},t)\ , \qquad (9.11)$$

$$\vec{y}^\mu(\vec{X},t) \equiv \hat{\vec{y}}(\vec{x},t)\ . \qquad (9.12)$$

Having made this transformation, we write the mechanical equation for the internal degree of freedom $\hat{\vec{y}}^\mu$ in the form

$$m^\mu\,\frac{\partial^2\hat{y}_i^\mu}{\partial t^2} + 2\textstyle\sum_\nu {}^{(2,0)}H_{ib}^{\mu\nu}\,\hat{y}_b^\nu + {}^{(1,1)}H_{ibc}^\mu\,\hat{u}_{b,c} - q^\mu E_i = F_i^\mu\ . \qquad (9.13)$$

We have segregated on the left-hand side of Eq. (9.13) all of the linear terms and have collected in the force F_i^μ, on the right-hand side, all nonlinear terms to be given below. Similarly, we write the equation for the center of mass in the form

$$\rho^0\,\frac{\partial^2\hat{u}_i}{\partial t^2} - 2\,{}^{(0,2)}H_{aicd}\,\hat{u}_{c,da} - \textstyle\sum_\mu {}^{(1,1)}H_{cai}^\mu\,\hat{y}_{c,a}^\mu = G_i\ , \qquad (9.14)$$

where all nonlinear terms are collected in G_i. Equations (1.18) and (1.21) for the electromagnetic field can be combined to give the driven wave equation

$$n^2(\overleftrightarrow{1} - \vec{s}\vec{s})\cdot\vec{E} - \vec{E} - \vec{P}^L/\epsilon_0 = \vec{\mathcal{P}}/\epsilon_0\ . \qquad (9.15)$$

Here we have explicitly displayed the linear portion of the polarization P^L since the latter at low frequencies will contain a piezoelectric contribution to be evaluated in Eq. (10.10). This piezoelectric contribution is not important in the optical region but will be in the low-frequency region. $\vec{\mathcal{P}}$ is the effective nonlinear polarization defined in Eq. (1.21).

From Eq. (9.7) we obtain the nonlinear internal force term of Eq. (9.13):

$$F_i^\mu = -(R_{iA}-\delta_{iA})\,\rho^0\,\frac{\partial\Sigma}{\partial\Lambda_A^\mu} - \rho^0\,\delta_{iA}\,\frac{\partial\Sigma'}{\partial\Lambda_A^\mu}$$

$$- {}^{(1,1)}H_{iBC}^\mu\,[E_{BC} - \tfrac{1}{2}(\hat{u}_{b,c}+\hat{u}_{c,b})]$$

$$-2\sum_\nu {}^{(2,0)}H_{iB}^{\mu\nu}\,y_j^\nu\,(R_{jB}-\delta_{jB})$$

$$+ f_i^{\mu e} - q^\mu E_i - m^\mu\left(\ddot{y}_i^\mu - \frac{\partial^2\hat{y}_i^\mu}{\partial t^2}\right)\ , \quad (9.16)$$

where the electromagnetic force $\vec{f}^{\mu e}$ is given by Eq. (8.3). The last term in Eq. (9.16) arises from kinematic corrections associated with the transformation (9.12). These kinematic corrections are evaluated in Eq. (E16) of Appendix E. With the help of Eq. (E5) the third term on the right-hand side of Eq. (9.16) can be reexpressed with the help of

$$E_{BC} - \tfrac{1}{2}(\hat{u}_{b,c}+\hat{u}_{c,b})$$

$$= \tfrac{1}{4} u_{j,B} u_{j,C} + \tfrac{1}{2}(u_{b,C} - \hat{u}_{b,c})$$

$$+ \text{interchange of } B \text{ with } C \text{ and } b \text{ with } c$$

$$= \tfrac{1}{4}(\hat{u}_{j,b} + \hat{u}_{j,k}\hat{u}_{k,b} + \cdots) \times (\hat{u}_{j,c} + \hat{u}_{j,l}\hat{u}_{l,c} + \cdots)$$

$$+ \tfrac{1}{2}(\hat{u}_{b,j}\hat{u}_{j,c} + \hat{u}_{b,j}\hat{u}_{j,k}\hat{u}_{k,c} + \cdots)$$

$$+ \text{interchange of } b \text{ with } c\ . \qquad (9.17)$$

Similarly the nonlinear force that enters the center-of-mass equation of motion can be written in the form

$$G_i = u_{i,BA} \frac{\partial(\rho^0\Sigma)}{\partial E_{AB}} + \sum_\mu y^\mu_{j,A} \frac{\partial(\rho^0\Sigma)}{\partial \Lambda^\mu_B} \frac{\partial R_{jB}}{\partial x_{i,A}}$$

$$+ \sum_\mu y^\mu_j \frac{\partial R_{jB}}{\partial x_{i,A}} \left(\frac{\partial^2(\rho^0\Sigma)}{\partial \Lambda^\mu_B \, \partial E_{CD}} E_{CD,A} + \sum_\nu \frac{\partial^2(\rho^0\Sigma)}{\partial \Lambda^\mu_B \, \partial \Lambda^\nu_C} \Lambda^\nu_{C,A} \right)$$

$$+ \sum_\mu y^\mu_j \frac{\partial(\rho^0\Sigma)}{\partial \Lambda^\mu_B} \frac{\partial}{\partial X_A} \left(\frac{\partial R_{jB}}{\partial x_{i,A}} \right)$$

$$+ u_{i,B} \left(\frac{\partial^2(\rho^0\Sigma)}{\partial E_{AB} \, \partial E_{CD}} E_{CD,A} + \frac{\partial^2(\rho^0\Sigma)}{\partial E_{AB} \, \partial \Lambda^\mu_C} \Lambda^\mu_{C,A} \right)$$

$$+ \delta_{iB} \left(\frac{\partial^2(\rho^0\Sigma')}{\partial E_{AB} \, \partial E_{CD}} E_{CD,A} + \frac{\partial^2(\rho^0\Sigma')}{\partial E_{AB} \, \partial \Lambda^\mu_C} \Lambda^\mu_{C,A} \right)$$

$$+ {}^{(0,2)}H_{AiCD}(E_{CD} - u_{c,d})_{,A}$$

$$+ \sum_\mu {}^{(1,1)}H^\mu_{CAi} \left[(y^\mu_j R_{jC})_{,A} - y^\mu_{c,a} \right] + f^e_i$$

$$- \rho^0 \left(\ddot{\vec{x}}_i - \frac{\partial^2 \hat{\vec{u}}_i}{\partial t^2} \right) . \qquad (9.18)$$

The kinematic correction term [the last term in Eq. (9.18)] is evaluated in Eq. (E15). We have not chosen here to express these forces completely in terms of the variables $\hat{\vec{y}}$ and $\hat{\vec{u}}$. That is done in connection with the various applications we shall present in subsequent papers. The forms quoted here are sufficiently general to permit the evaluation of all desired nonlinear effects.

X. MACROSCOPIC NONLINEAR EQUATIONS OF MOTION

In Eqs. (9.13) and (9.14), all mechanical and field variables are evaluated at the point $\vec{x}$ whereas the field in the electromagnetic wave Eq. (9.15) are evaluated at the point $\vec{z}$. Since the electric field which enters the mechanical equations is $\vec{E}(\vec{z})$ evaluated at $\vec{z} = \vec{x}$ and the polarization which enters the field equation involves $\vec{y}(\vec{z})$ evaluated at $\vec{x} = \vec{z}$, the two variables $\vec{x}$ and $\vec{z}$ can be identified for purposes of solving the coupled equations. They are both spatial variables and we shall denote both by $\vec{z}$ from here on. Since we are interested in individual frequency components of the fields, we can simplify our equations by taking Fourier components. Thus we shall write each field in the form

$$\hat{y}^\mu_i(\vec{z}, t) = y^\mu_i(\vec{z}, \omega) e^{-i\omega t}, \quad \hat{u}_i(\vec{z}, t) = u_i(\vec{z}, \omega) e^{-i\omega t} . \qquad (10.1)$$

Equation (9.13) can thus be rewritten in the form

$$\textstyle\sum_\nu \left(2\,{}^{(2,0)}H^{\mu\nu}_{ib} - m^\mu \omega^2 \delta^{\mu\nu} \delta_{ib}\right) y^\nu_b$$

$$= q^\mu E_i - {}^{(1,1)}H^\mu_{ibc} u_{b,c} + F^\mu_i , \qquad (10.2)$$

where all fields without carets are now understood to be a function of a single frequency ω as defined by Eq. (10.1). Let us now introduce a mechanical admittance matrix $\overleftrightarrow{\Upsilon}$ by

$$\epsilon_0 \textstyle\sum_\nu \Upsilon^{\mu\nu}_{ij}(\omega) \left(2\,{}^{(2,0)}H^{\nu\lambda}_{jk} - m^\nu \omega^2 \delta^{\nu\lambda} \delta_{jk}\right) = \delta^{\mu\lambda} \delta_{ik} . \qquad (10.3)$$

From the symmetry of the ${}^{(2,0)}H$ matrix we see that the $\overleftrightarrow{\Upsilon}$ matrix has the corresponding symmetry

$$\Upsilon^{\mu\nu}_{ij}(\omega) = \Upsilon^{\nu\mu}_{ji}(\omega) . \qquad (10.4)$$

Comparison of Eqs. (10.2) and (10.3) permits us to write an expression for $\vec{y}^\mu$ useful in iterative solutions of nonlinear problems (see Sec. XIII):

$$y^\mu_i = \epsilon_0 \textstyle\sum_\nu \Upsilon^{\mu\nu}_{ij}(\omega) \left(q^\nu E_j - {}^{(1,1)}H^\nu_{jbc} u_{b,c} + F^\nu_j\right) . \qquad (10.5)$$

The dipole moment per unit volume (in the material frame) is therefore given by

$$p_i = \textstyle\sum_\mu q^\mu y^\mu_i = \epsilon_0 \chi_{ij}(\omega) E_j + e_{ibc}(\omega) u_{b,c}$$

$$+ \epsilon_0 \textstyle\sum_\nu \chi^\nu_{ij}(\omega) F^\nu_j / q^\nu , \qquad (10.6)$$

where the susceptibility $\overleftrightarrow{\chi}$ and the dielectric tensor $\overleftrightarrow{\kappa}$ are expressible in terms of the admittance matrix by

$$\chi_{ij}(\omega) \equiv \sum_{\mu\nu} q^\mu \Upsilon^{\mu\nu}_{ij}(\omega) q^\nu, \quad \kappa_{ij}(\omega) \equiv \delta_{ij} + \chi_{ij}(\omega) , \qquad (10.7)$$

and the piezoelectric tensor is defined by

$$e_{ibc}(\omega) = -\epsilon_0 \sum_{\mu\nu} q^\mu \Upsilon^{\mu\nu}_{ij}(\omega)\, {}^{(1,1)}H^\nu_{jbc} . \qquad (10.8)$$

Clearly ${}^{(1,1)}H^\nu_{jbc}$ must be nonvanishing in a piezoelectric material. It can vanish in a nonpiezoelectric material (e.g., the NaCl structure). However, when it does not vanish in a nonpiezoelectric material (e.g., the diamond structure) the summation guarantees the vanishing of the piezoelectric tensor in accord with the point-group symmetry of the crystal. The partial susceptibility $\overleftrightarrow{\chi}^\nu$ in Eq. (10.6) is defined by

$$\chi^\nu_{ij} \equiv \textstyle\sum_\mu q^\mu \Upsilon^{\mu\nu}_{ij}(\omega) q^\nu . \qquad (10.9)$$

The polarization P_i can be expressed in terms of the dipole moment per unit volume p_i (in the material frame) by making use of the Jacobian:

$$P_i = p_i/\hat{J} = \epsilon_0 \chi_{ij} E_j + e_{ibc} u_{b,c} + P_i^{\mathrm{NL}} , \qquad (10.10)$$

where the nonlinear contribution to the polarization can be separated off in the form

$$P_i^{\mathrm{NL}} = (\hat{J}^{-1} - 1)(\epsilon_0 \chi_{ij} E_j + e_{ibc} u_{b,c}) + \frac{1}{\hat{J}} \epsilon_0 \sum_\nu \frac{\chi_{ij}^\nu F_j^\nu}{q^\nu} , \qquad (10.11)$$

and the Jacobian itself is expressible in terms of the displacement field by means of Eq. (E9):

$$\hat{J} = 1 + \hat{u}_{i,i} + \tfrac{1}{2}(\hat{u}_{i,i}\hat{u}_{j,j} + \hat{u}_{i,j}\hat{u}_{j,i}) + \cdots . \qquad (10.12)$$

The electromagnetic wave equation (9.15) which contains the piezoelectric contribution can be rewritten in the form

$$[\vec{\nabla} \times (\vec{\nabla} \times \vec{\mathrm{E}}) - (\omega/c)^2 \overleftrightarrow{\kappa} \cdot \vec{\mathrm{E}}]_i - (\omega/c)^2 e_{ibc} u_{b,c}/\epsilon_0 = \left(\frac{\omega}{c}\right)^2 \mathcal{P}_i/\epsilon_0 , \qquad (10.13)$$

where the effective nonlinear polarization $\vec{\mathcal{P}}$ of Eq. (1.21) is rewritten as

$$\mathcal{P}_i = P_i^{\mathrm{NL}} - \frac{1}{2} \frac{\partial Q_{ij}}{\partial z_j} + \frac{i}{\omega} \epsilon_{ijk} \frac{\partial}{\partial z_j} \times \left[M_k^{\mathrm{NL}} + \epsilon_{klm} \left(P_l \dot{x}_m - \frac{1}{2} \frac{\partial (Q_{ln} \dot{x}_m)}{\partial z_n} \right) \right] . \qquad (10.14)$$

If we substitute Eq. (10.5) for the internal variables into Eq. (9.14) for the displacement field, we obtain elasticity equations in the form

$$-\rho^0 \omega^2 u_i - c_{aicd} u_{c,da} + e_{jia} E_{j,a} = \mathcal{G}_i , \qquad (10.15)$$

where the usual stiffness tensor is now expressed in terms of the fundamental parameters by means of

$$c_{aicd} \equiv 2\, {}^{(0,2)}H_{aicd} - \epsilon_0 \sum_{\mu\nu} {}^{(1,1)}H_{eai}^{\mu} \Upsilon_{ej}^{\mu\nu}\, {}^{(1,1)}H_{jcd}^{\nu} . \qquad (10.16)$$

The second term in Eq. (10.16) is the usual negative internal contribution to the elasticity tensor produced by the coupling between strain and internal displacements. This contribution does not depend on the material being piezoelectric but merely on having internal coordinates that couple to the strain. For instance, this term makes a contribution in germanium comparable to the first term.[46] The new nonlinear force $\mathcal{G}$ in Eq. (10.15) is expressible in terms of the original nonlinear force by means of

$$\mathcal{G}_i = G_i + \epsilon_0 \sum_{\mu\nu} {}^{(1,1)}H_{eai}^{\mu} \Upsilon_{ej}^{\mu\nu} F_{j,a}^{\nu} . \qquad (10.17)$$

The above equations have not assumed that we have an infinite medium or plane-wave solutions. If the latter are assumed, the electromagnetic equation (10.13) can be rewritten in the simpler-looking form

$$\alpha_{ij}(\vec{\mathrm{k}}, \omega) E_j - e_{icd} u_{c,d}/\epsilon_0 = \mathcal{P}_i/\epsilon_0 , \qquad (10.18)$$

where the dyadic $\overleftrightarrow{\alpha}$ is defined by Eq. (1.22) but with $\vec{\mathrm{k}}$ a number here rather than an operator. Before proceeding with a discussion of nonlinear equations and techniques, it would be useful to indicate in our notation the appropriate solution of the linear equations of motion.

XI. LINEAR ACOUSTIC EQUATIONS OF MOTION

We are concerned in this section with that simultaneous solution of Eqs. (10.13) and (10.15) (with nonlinear terms $\vec{\mathcal{P}}$ and $\mathcal{G}$ removed) which resembles acoustic waves. Thus we wish to eliminate the electric field $\vec{\mathrm{E}}$ from Eq. (10.15) by means of Eq. (10.13). Unfortunately, this elimination requires, in general, the solution of a complicated boundary value problem. Measurements of sound velocity, however, are usually made at acoustic wavelengths small compared to the specimen size. In this limit, the electromagnetic response to the acoustic displacement field can be approximated by that appropriate for an infinite medium. In this case, we can replace Eq. (10.13) by Eq. (10.18) appropriate to plane waves with $\vec{\mathcal{P}} = 0$. We can then eliminate the electric field using Eq. (10.18) to obtain the result

$$E_j = (\overleftrightarrow{\alpha}^{-1})_{jk} e_{kcd} u_{c,d}/\epsilon_0 . \qquad (11.1)$$

Inserting this result into Eq. (10.15), we obtain an effective acoustic equation of motion

$$-\rho^0 \omega^2 u_i - \{ c_{aicd} - \epsilon_0^{-1} e_{jai}(\omega) [\overleftrightarrow{\alpha}^{-1}(k, \omega)]_{jq} e_{qcd}(\omega) \} u_{c,da} = 0 . \qquad (11.2)$$

To make this result useful we need an explicit form for the inverse matrix $\overleftrightarrow{\alpha}^{-1}$. In Appendix F the inverse matrix is found to be

$$\overleftrightarrow{\alpha}^{-1} = \overleftrightarrow{\Gamma} + \frac{(\overleftrightarrow{\Gamma} \cdot \vec{\mathrm{s}}\vec{\mathrm{s}} \cdot \overleftrightarrow{\Gamma})}{(1/n^2) - \vec{\mathrm{s}} \cdot \overleftrightarrow{\Gamma} \cdot \vec{\mathrm{s}}} , \qquad (11.3)$$

where the dyadic $\overleftrightarrow{\Gamma}$ is defined by

$$\overleftrightarrow{\Gamma} \equiv [n^2 \overleftrightarrow{1} - \overleftrightarrow{\kappa}(\omega)]^{-1} \qquad (11.4)$$

and the refractive index n in this acoustic regime is defined by

$$n = ck_A/\omega_A = c/v_A \sim 10^5 . \qquad (11.5)$$

Because of this enormous value of n, the inverse dyadic of Eq. (11.3) can be replaced with negligible error by its limiting value when $n \to \infty$:

$$\overleftrightarrow{\alpha}^{-1} \to -\vec{\mathrm{s}}\vec{\mathrm{s}}/(\vec{\mathrm{s}} \cdot \overleftrightarrow{\kappa} \cdot \vec{\mathrm{s}}) . \qquad (11.6)$$

Inserting this inverse dyadic into Eq. (11.2) we obtain the final result

$$-\rho^0\omega^2 u_i - \left(c_{aicd} + \frac{e_{jai}(\omega)\, s_j\, s_q\, e_{qcd}(\omega)}{\epsilon_0\, s_m\, \kappa_{mn}(\omega) s_n} \right) u_{c,da} = 0 \ , \tag{11.7}$$

where the s_j are components of a unit vector

$$\vec{s} = \vec{k}_A / |\vec{k}_A| \ , \quad \omega = \omega_A \tag{11.8}$$

in the direction of propagation of the sound wave. Equation (11.7) demonstrates that for a piezoelectric material the elasticity tensor is modified by a term proportional to the square of the piezoelectric constant and inversely proportional to the dielectric constant.[47] It may not be generally appreciated that this well-known piezoelectric modification does not have the symmetry of the fourth-rank tensor c_{aicd}. Rather it has the symmetry of a fourth-rank tensor which is a function of the unit vector $\vec{s}$ whose direction is arbitrary. Thus the piezoelectric modification to the elasticity tensor may have components for which the original tensor vanishes.

XII. LINEAR OPTICAL EQUATIONS OF MOTION

In this section we wish to obtain a set of effective optical equations of motion by eliminating the sound field from Eqs. (10.15) and (10.18) again with $\vec{\mathcal{P}}$ and $\vec{\mathcal{G}}$ set to zero. This elimination is easiest to perform when the wavelength of sound at the frequency ω_0 of the electromagnetic wave is small compared to the specimen size. In this case, the piezoelectric term in Eq. (10.18) can be eliminated with the help of Eq. (10.15) using a plane-wave description in the latter equation. We have the relationships

$$\omega_0 \sim ck_0 \ , \quad c_{aicd} \sim \rho^0 (v^A)^2 \ .$$

From this it is possible to deduce that the elasticity term in Eq. (10.15) is about 10^{-10} smaller than the inertia term. Thus the displacement field can immediately be solved in the form

$$u_i \approx (\rho^0 \omega_0^2)^{-1} e_{jai}(\omega) E_{j,a} \ . \tag{12.1}$$

When this displacement field is inserted into the piezoelectric term in Eq. (10.18), we see that this term is of negligible importance, that is, it is smaller than the dominant terms by a factor $(v_A/c)^2 \sim 10^{-10}$. Thus the effective optical equation of motion (10.18) reduces to

$$\overleftrightarrow{\alpha}(\vec{k}, \omega) \cdot \vec{E} = 0 \quad \text{or} \quad (n^2 \overleftrightarrow{1} - \overleftrightarrow{\kappa}) \cdot \vec{E} = n^2 \vec{s}(\vec{s} \cdot \vec{E}) \ . \tag{12.2}$$

The conventional discussion of linear crystal optics (see Born and Wolf[48]) based on this equation considers only the two freely propagating electric field solutions. Since the third solution (infinite refractive index and hence not freely propagating) can exist as a forced wave and be important in coupling various optical processes in high-order nonlinear optical interactions, it is important for us to use a formulation which includes this solution on an equal footing with the other two. Thus we are led to introduce the real electric field eigenvectors $\vec{\mathcal{E}}^\varphi = \vec{\mathcal{E}}^\varphi(\vec{s}, \omega)$ with eigenvalues $[1/n^\varphi(\vec{s}, \omega)]^2$ defined by

$$[\overleftrightarrow{1} - \vec{s}\,\vec{s}] \cdot \vec{\mathcal{E}}^\varphi = (1/n^\varphi)^2 \overleftrightarrow{\kappa}(\omega) \cdot \vec{\mathcal{E}}^\varphi \quad (\varphi = 1, 2, \infty) \ . \tag{12.3}$$

We find these eigenvectors more convenient than those introduced by Kleinman.[49] $\vec{\mathfrak{D}}^\varphi$ corresponding to the eigenvectors $\vec{\mathcal{E}}^\varphi$ are defined by

$$\vec{\mathfrak{D}}^\varphi \equiv \overleftrightarrow{\kappa} \cdot \vec{\mathcal{E}}^\varphi \ . \tag{12.4}$$

As discussed in Appendix F, these eigenvectors necessarily obey a biorthogonality requirement of the form

$$\vec{\mathcal{E}}^\varphi \cdot \vec{\mathfrak{D}}^\theta \propto \delta^{\varphi\theta} \ . \tag{12.5}$$

Inspection of Eq. (12.3) immediately reveals the existence of one nonpropagating longitudinal solution with infinite refractive index

$$\vec{\mathcal{E}}^\infty \parallel \vec{s} \ , \quad (1/n^\infty) = 0 \ . \tag{12.6}$$

The orthogonality relation (12.5) now immediately yields that the $\vec{\mathfrak{D}}^\varphi$ vectors of the propagating solutions are necessarily orthogonal to the direction of propagation:

$$\vec{s} \cdot \vec{\mathfrak{D}}^\varphi = 0 \ , \quad \varphi \neq \infty \ . \tag{12.7}$$

If $\theta \neq \infty$, then the scalar product of Eq. (12.3) with $\vec{\mathfrak{D}}^\theta$ yields

$$(1/n^\varphi)^2 \vec{\mathfrak{D}}^\theta \cdot \vec{\mathfrak{D}}^\varphi = \vec{\mathfrak{D}}^\theta \cdot (\overleftrightarrow{1} - \vec{s}\,\vec{s}) \cdot \vec{\mathcal{E}}^\varphi = 0 \ , \quad \varphi \neq \theta \ . \tag{12.8}$$

The right-hand side of Eq. (12.8) vanishes because of Eqs. (12.7) and (12.5). Thus we conclude

$$\vec{\mathfrak{D}}^1 \perp \vec{\mathfrak{D}}^2, \quad \vec{\mathfrak{D}}^1 \perp \vec{s} \ , \quad \vec{\mathfrak{D}}^2 \perp \vec{s} \ , \tag{12.9}$$

where the propagating solutions $\vec{\mathfrak{D}}^1$ and $\vec{\mathfrak{D}}^2$ are referred to as ordinary and extraordinary solutions in a uniaxial crystal.

Equation (12.2) can be used to show that the eigenvectors possess components in the principal coordinate system

$$\mathcal{E}_i^\varphi = \frac{s_i}{[(n^\varphi)^2 - \kappa_{ii}] N^\varphi} \ , \tag{12.10}$$

where the dielectric tensor $\overleftrightarrow{\kappa}$ is diagonal in that system with elements κ_{ii}. Summation over i is not implied in Eq. (12.10). The normalization factor N^φ is chosen in accord with

$$N^\varphi = \left(\sum_i \frac{\kappa_{ii} s_i^2}{[(n^\varphi)^2 - \kappa_{ii}]^2} \right)^{1/2} \tag{12.11}$$

to ensure the orthonormality condition

$$\vec{\mathcal{E}}^{\varphi} \cdot \vec{\mathfrak{D}}^{\theta} = \delta^{\varphi\theta} . \tag{12.12}$$

Equation (12.12) is a biorthonormality condition since it states that the three vectors $\vec{\mathcal{E}}^1$, $\vec{\mathcal{E}}^2$, and $\vec{\mathcal{E}}^{\infty} \propto \vec{s}$ are not orthogonal to each other but to the corresponding set $\vec{\mathfrak{D}}^1$, $\vec{\mathfrak{D}}^2$, and $\vec{\mathfrak{D}}^{\infty} \propto \overleftrightarrow{\kappa} \cdot \vec{s}$ as illustrated in Fig. 1.

If we solve Eq. (12.2) for $\vec{E}$ on the left-hand side and take a scalar product of the resulting equation with $\vec{s}$, then we obtain an equation for $\vec{s} \cdot \vec{E}$ which is satisfied provided

$$\frac{1}{n^2} = \sum_i \frac{s_i^2}{n^2 - \kappa_{ii}} . \tag{12.13}$$

Equation (12.13) can be regarded as an equation for the index of refraction using the dielectric tensor $\overleftrightarrow{\kappa}$ at a given frequency ω for a given direction $\vec{s}$ of propagation. An alternative form of Eq. (12.13) can be obtained by subtracting $1/n^2$ from the left-hand side and $(1/n^2)(s_1^2 + s_2^2 + s_3^2)$ from the right-hand side with the result

$$0 = \frac{\kappa_{11} s_1^2}{n^2 - \kappa_{11}} + \frac{\kappa_{22} s_2^2}{n^2 - \kappa_{22}} + \frac{\kappa_{33} s_3^2}{n^2 - \kappa_{33}} . \tag{12.14}$$

It is clear that Eq. (12.14) is satisfied by $n = \infty$, the nonpropagating solution previously found in Eq. (12.6). The two remaining solutions can be obtained by rationalizing Eq. (12.14) with the result

$$n^4(\kappa_{11}s_1^2 + \kappa_{22}s_2^2 + \kappa_{33}s_3^2) + \kappa_{11}\kappa_{22}\kappa_{33} - n^2[\kappa_{22}\kappa_{33}(1 - s_1^2) + \kappa_{33}\kappa_{11}(1 - s_2^2) + \kappa_{11}\kappa_{22}(1 - s_3^2)] = 0 , \tag{12.15}$$

which is a quadratic equation in n^2 for the two propagating wave roots. All of the above results are valid in arbitrary crystals, that is to say, biaxial, uniaxial, and optically isotropic crystals.

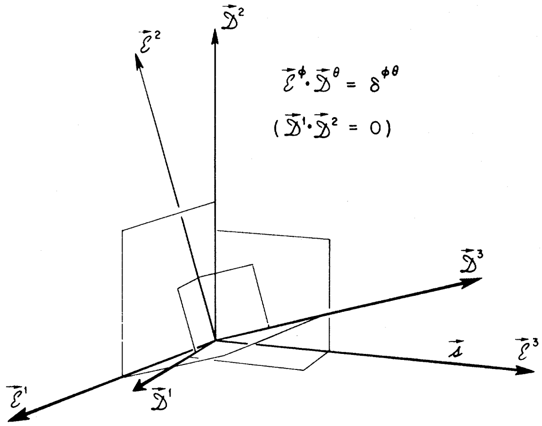

FIG. 1. The biorthogonality of the electric field eigenvectors $\vec{\mathcal{E}}^{\varphi}$ and the associated electric displacement eigenvectors $\vec{\mathfrak{D}}^{\varphi} \equiv \overleftrightarrow{k} \cdot \vec{\mathcal{E}}^{\varphi}$ is displayed, as well as the orthogonality of the three vectors $\vec{\mathfrak{D}}^1$, $\vec{\mathfrak{D}}^2$, and the propagation direction vector $\vec{s}$.

Although results for the uniaxial case can be obtained from the general results above by taking the appropriate limit, the limiting process can be a tricky one and it is therefore efficacious to indicate here directly the solutions for the uniaxial case. The uniaxial case is described by the condition

$$\kappa_{11} = \kappa_{22} , \quad s_3 \equiv (\vec{s} \cdot \vec{c}) , \tag{12.16}$$

where $\vec{c}$ is a unit vector in the direction of the optic axis. In this case, the quadratic equation for n^2 [Eq. (12.15)] factors readily and yields the two roots

$$(n^o)^2 = \kappa_{11} , \quad (n^e)^2 = \frac{\kappa_{11}\kappa_{33}}{\kappa_{11}[1 - (\vec{s} \cdot \vec{c})^2] + \kappa_{33}(\vec{s} \cdot \vec{c})^2} . \tag{12.17}$$

These roots are labeled with superscripts o and e corresponding to the ordinary (n^2 independent of $\vec{s}$) and extraordinary (n^2 dependent on $\vec{s}$) solutions. If the electric vector is in the plane perpendicular to $\vec{c}$ then the dielectric tensor in Eq. (12.4) merely produces a factor κ_{11}. Moreover, in this plane $\vec{\mathfrak{D}}$ must be parallel to $\vec{\mathcal{E}}$. By Eq. (12.7), however, $\vec{\mathfrak{D}} \perp \vec{s}$ so that $\vec{\mathcal{E}} \perp \vec{s}$ and $\vec{\mathcal{E}} \perp \vec{c}$. This leads to the ordinary solution:

$$\vec{\mathcal{E}}^o = (\vec{s} \times \vec{c})/N^o, \quad \vec{\mathfrak{D}}^o = \kappa_{11}\vec{\mathcal{E}}^o , \tag{12.18}$$

since Eq. (12.2) yields $n^2 = \kappa_{11}$ independent of $\vec{s}$. By the orthogonality condition (12.12), the extraordinary vector $\vec{\mathfrak{D}}^e$ must be perpendicular both to $\vec{s}$ and to $\vec{\mathcal{E}}^o$. Thus it must be parallel to the cross product of these two vectors and the extraordinary solution is

$$\vec{\mathcal{E}}^e = \overleftrightarrow{\kappa}^{-1} \cdot \vec{\mathfrak{D}}^e , \quad \vec{\mathfrak{D}}^e = \vec{s} \times (\vec{s} \times \vec{c})/N^e . \tag{12.19}$$

The normalization condition (12.12) permits us to determine the normalization factors in the form

$$(N^o)^2 = (n^o)^2[1 - (\vec{s} \cdot \vec{c})^2] , \quad (N^e)^2 = [1 - (\vec{s} \cdot \vec{c})^2]/(n^e)^2 . \tag{12.20}$$

A. Polariton Dispersion Curves

The dispersion relation Eq. (12.15) conceals a great deal of physics because the frequency dependence of the dielectric tensor $\overleftrightarrow{\kappa}(\omega)$ has not been explicitly displayed there. Equations (10.7) and (10.3) indicate that $\overleftrightarrow{\kappa}$ will have resonances associated with each internal normal coordinate, e.g., ionic, electronic, or excitonic degrees of freedom. When these resonances are taken into account, the dispersion relation yields a branch associated with each resonance, e.g., an optical-phonon branch and an excitonic branch in addition to the electromagnetic and acoustic phonon branches previously discussed.

If the coupling between the polarization of one of these branches and the electromagnetic field is neglected, the dispersion curve for that branch crosses the one for electromagnetic waves. In the "crossing region," the interaction is important. It causes a repulsion between the branches (eliminates the crossing) and a mixing of the polarization mode with the electromagnetic field[50] to produce what is usually referred to as a polariton.[7] Away from the "crossing region," the interaction is unimportant, and a given mode will be nearly electromagnetic or nearly excitonic (or nearly phononlike).

To illustrate these ideas in a semiquantitative manner, let us consider the case of a biaxial crystal with $s_2=1$. The dispersion equation (12.15) now factors into

$$\kappa_{22}(\omega)[n^2-\kappa_{11}(\omega)][n^2-\kappa_{33}(\omega)]=0\ . \tag{12.21}$$

If we seek a transverse solution in which $\vec{\mathcal{E}}$ is parallel to the x axis, then the corresponding index of refraction obeys

$$n^2=(ck/\omega)^2=\kappa_{11}=\kappa^b_{11}+\chi^i_{11}+\chi^e_{11}\ . \tag{12.22}$$

As a specific example, we shall assume that the dielectric tensor component κ_{11} has in addition to a relatively nondispersive electronic background component κ^b_{11}, an ionic component χ^i_{11} associated with optical-phonon polarization, and a component χ^e_{11} associated with exciton polarization. In particular, each of these components can be assumed to have a single pole in ω^2 as in

$$\chi^i_{11}\approx(2\,{}^{(2,0)}H^{ii}_{11}-m^i\omega^2)^{-1}(q^i)^2/\epsilon_0=A^i/(\omega^2-\omega_i^2)\ , \tag{12.23}$$

$$\chi^e_{11}=(2\,{}^{(2,0)}H^{ee}_{11}-m^e\omega^2)^{-1}(q^e)^2/\epsilon_0=A^e/(\omega^2-\omega_e^2)\ . \tag{12.24}$$

In this example, the interaction ${}^{(2,0)}H^{ie}_{11}$ between the oscillators has been neglected. This interaction is unimportant since these oscillators are well separated in frequency [see Eq. (13.32)]. Our qualitative conclusions would be unmodified if such an interaction were included. Using Eq. (12.22), we see that

$$k\rightarrow\infty \ \text{ as } \ \omega\rightarrow\omega_e \ \text{ or } \ \omega\rightarrow\omega_i\ . \tag{12.25}$$

Also Eq. (12.22) reduces for small ω to

$$\omega=ck/[\kappa_{11}(0)]^{1/2}\ . \tag{12.26}$$

In addition when $\omega\gg\omega_i$ and $\omega\gg\omega_e$, only the background contribution to the dielectric constant remains and we obtain the dispersion relation

$$\omega\rightarrow ck/(\kappa^b_{11})^{1/2}\ . \tag{12.27}$$

These conditions permit us to sketch in Fig. 2 a plot of a dispersion curve, in other words, a plot of ω vs k. The result is that the dispersion curve has two asymptotic regions that approach ω_i and ω_e, as $k\rightarrow\infty$ does not depend on the detailed form of the dielectric constant in Eqs. (12.23) and (12.24). It depends only on the existence of poles

$$\kappa_{11}(\omega_i)=\kappa_{11}(\omega_e)=\infty \tag{12.28}$$

associated with the natural internal frequencies of the system.

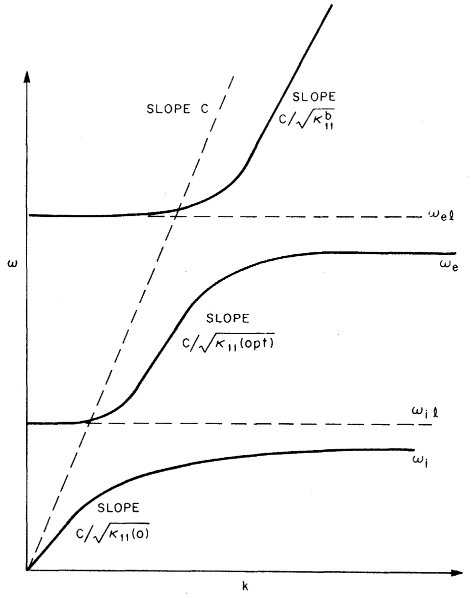

FIG. 2. Typical polariton dispersion curves. Frequency ω is plotted versus wave number k for electromagnetic waves coupled to ionic motion i and excitonic motion e. The large-k limit displays the longitudinal resonances ω_{il} and ω_{el} and the transverse resonances ω_i and ω_e appropriate to ionic and excitonic vibration with negligible electromagnetic contribution. By large k we mean k large compared to the crossover region, but still negligible compared to the Brillouin-zone boundary. The longitudinal frequencies ω_{il} and ω_{el} are shown as independent of k which is appropriate for the case of propagation along a symmetry axis. The solid curves where labeled with slopes are predominantly electromagnetic in character.

If we set the first factor in Eq. (12.21) equal to zero, we obtain the longitudinal solution

$$s_2=1\ ,\quad \vec{\mathrm{E}}\parallel y\ ,\quad \kappa_{22}(\omega)=0\ . \tag{12.29}$$

If we interchange the indices 1 and 2 in Eq. (12.29), we obtain an alternative longitudinal solution obeying

$$s_1=1\ ,\quad \vec{\mathrm{E}}\parallel x\ ,\quad \kappa_{11}(\omega)=0\ . \tag{12.30}$$

A comparison of Eqs. (12.28) and (12.30) shows that we have a case in which the transverse solutions are poles and the longitudinal solutions are roots of the same function of frequency. Such a relationship is what leads to the Lyddane-Sachs-Teller theorem.[28]

B. Lyddane-Sachs-Teller Theorem

If we have an arbitrary even function $\kappa(\omega)$ with a finite number of simple poles ω_p, and a finite high-frequency limit, then it can be represented in the form

$$\frac{\kappa(\omega)}{\kappa(\infty)}=1+\sum_{p=1}^{m} A_p\Big/(\omega_p^2-\omega^2)=\left(\prod_{p=1}^{m}(\omega_p^2-\omega^2)+\sum_{p=1}^{m}A_p\prod_{j\neq p}^{m}(\omega_j^2-\omega^2)\right)\Big/\prod_{p=1}^{m}(\omega_p^2-\omega^2)\quad, \tag{12.31}$$

where $m=3N-3$ is the number of nonacoustic degrees of freedom. The above result can be rewritten in the form

$$\frac{\kappa(\omega)}{\kappa(\infty)}=\prod_{r=1}^{m}(\omega_r^2-\omega^2)\Big/\prod_{p=1}^{m}(\omega_p^2-\omega^2)\,, \tag{12.32}$$

which makes evident the roots ω_r of the function of ω as well as its poles. If we set $\omega=0$ in Eq. (12.32) we obtain

$$\frac{\kappa(0)}{\kappa(\infty)}=\prod_{r=1}^{m}\omega_r^2\Big/\prod_{p=1}^{m}\omega_p^2\ , \tag{12.33}$$

which yields a relationship between the ratio of the analytical function of zero and infinite frequencies and the set of roots and poles of this function. When the poles correspond to transverse solutions and the roots to longitudinal solutions of the same analytic function, Eq. (12.33) is then the usual statement of the Lyddane-Sachs-Teller theorem originally proven for cubic crystals.[28]

Although we have demonstrated such a relationship for a biaxial crystal with special directions of propagation, this relationship is *not valid* for general directions in biaxial crystals. The internal frequencies of vibration of the crystal are, in general, given by the frequencies on the dispersion curves as k approaches infinity. We may obtain these frequencies by letting n become large in Eq. (12.14). If we multiply Eq. (12.14) by n^2 and take the limit as $n\to\infty$, we obtain the condition

$$\vec{s}\cdot\overleftrightarrow{\kappa}(\omega)\cdot\vec{s}=0\ . \tag{12.34}$$

Thus for a general direction of propagation *all* the natural internal vibration frequencies *are roots* of a function (12.34). Since all these modes have a longitudinal electric field component, it is not surprising that their frequencies are given as roots. In a general direction there are no solutions which are purely transverse and no solutions which are obtainable as poles of some analytic function. To understand the behavior as the special direction $s_2=1$ is approached Eq. (12.34) is rewritten in the form

$$\frac{s_1^2}{\kappa_{33}(\omega)}+\frac{\kappa_{22}(\omega)}{\kappa_{11}(\omega)\kappa_{33}(\omega)}\,s_2^2+\frac{s_3^2}{\kappa_{11}(\omega)}=0\ , \tag{12.35}$$

so that when $s_2=1$, $s_1=s_3=0$ the frequencies obey

$$\frac{\kappa_{22}(\omega)}{\kappa_{11}(\omega)\kappa_{33}(\omega)}=0\ . \tag{12.36}$$

Thus they are the roots of $\kappa_{22}(\omega)$ and the poles of $\kappa_{11}(\omega)$ and $\kappa_{33}(\omega)$, i.e., the longitudinal and purely transverse modes previously discussed following Eq. (12.21).

By the reasoning that led to Eq. (12.32) we can, however, write

$$\frac{\vec{s}\cdot\overleftrightarrow{\kappa}(\omega)\cdot\vec{s}}{\vec{s}\cdot\overleftrightarrow{\kappa}(\infty)\cdot\vec{s}}=\frac{\Pi_r[\omega_r(\vec{s})^2-\omega^2]}{\Pi_p(\omega_p^2-\omega^2)}\quad, \tag{12.37}$$

where $\omega_r(\vec{s})$ now includes *all* resonant frequencies of the crystal "transverse" as well as "longitudinal." (The quotes remind us that in a general direction the modes do not have a pure transverse or longitudinal character.) The poles ω_p of $\vec{s}\cdot\overleftrightarrow{\kappa}(\omega)\cdot\vec{s}$ do not correspond to resonant frequencies for direction $\vec{s}$ but instead are poles of the three terms $\kappa_{11}(\omega)$, $\kappa_{22}(\omega)$, and $\kappa_{33}(\omega)$ contained in $\vec{s}\cdot\overleftrightarrow{\kappa}\cdot\vec{s}$ and are independent of the direction of $\vec{s}$. Thus

$$\frac{\vec{s}\cdot\overleftrightarrow{\kappa}(0)\cdot\vec{s}}{\vec{s}\cdot\overleftrightarrow{\kappa}(\infty)\cdot\vec{s}}=A^{-1}\prod_{r}[\omega_r(\vec{s})]^2\,, \tag{12.38}$$

$$A=\prod_{j=1}^{3}\prod_{t=1}^{N-1}\omega_{tj}^2\ , \tag{12.39}$$

where ω_{tj} is the observable transverse resonant frequency associated with a wave polarized in the principal direction j and propagating in either of the other principal directions. As a symmetry direction is approached, the generalized Lyddane-Sachs-Teller theorem (12.38) reduces by the use of Eq. (12.36) to the simpler form Eq. (12.33).

The form (12.38) of the Lyddane-Sachs-Teller relation has been derived by Cochran and Cowley.[29] These authors express A as a product $\Pi_p\,\Omega_p^2$, where the Ω_p are all the resonant frequencies appropriate to the same crystal in which all electric fields are suppressed (a condition which cannot be realized experimentally in the infrared by boundary conditions in normal-sized crystals). Our expression (12.39) for A involves readily measurable frequencies.

The Cochran-Cowley derivation[29] makes use of the electrostatic approximation and makes extensive use of the properties of determinants. Our derivation avoids the electrostatic approximation and achieves its simplicity by using only the existence of poles and zeros of the longitudinal dielectric constant $\vec{s}\cdot\overleftrightarrow{\kappa}(\omega)\cdot\vec{s}$. We have, of course, made the usual assumptions, made also by Cochran and Cowley, that (i) $\kappa(\omega)$ is an even function of ω, (ii) $\overleftrightarrow{\kappa}(\infty)$ = finite = $\overleftrightarrow{\kappa}^b$, (iii) $\overleftrightarrow{\kappa}(\omega)$ has a finite number of poles on the real axis and no other singularities. The first of these can be justified by time reversal. Assumption (ii) implies that there is a frequency well above the ionic resonances, but well below the electronic resonances (i.e., in the optical region) in which frequency dispersion is negligible so that $\overleftrightarrow{\kappa}^b=\overleftrightarrow{\kappa}$ (optical) is the background dielectric tensor produced by the electronic degrees of freedom. Assumption (iii) is merely the statement that the infrared-active ionic modes constitute a finite number of degrees of freedom and that damping is neglected.

C. Piezoelectric Modification of Low-Frequency Dielectric Tensor

At low frequencies, at which wavelengths can be comparable to specimen dimensions, Eq. (12.1) is no longer valid and we must return to Eq. (10.15) in the form

$$-\rho^0\omega^2u_i=T_{ia,a}\ , \tag{12.40}$$

where the stress tensor in the linear regime is defined by

$$T_{ia}=c_{aicd}u_{c,d}-e_{jai}E_j\ . \tag{12.41}$$

The boundary condition at the surface of a traction-free crystal can be written in the form

$$T_{ia}n_a=0\ , \tag{12.42}$$

where the n_a are components of a vector normal to the surface of the crystal. In the vicinity of what is known as the fundamental piezoelectric resonance (pr) in a crystal of thickness L, the wave vector and frequency are given by

$$k\sim\pi/L\ ,\quad \omega_{pr}\sim\pi v_A/L\ . \tag{12.43}$$

A comparison of the importance of the inertial term to the elasticity term in the elastic equation of motion is given by

$$\rho^0\omega^2u_i/c_{aicd}k_dk_au_c\sim\rho^0\omega^2/\rho^0(v_A)^2(\pi/L)^2\sim(\omega/\omega_{\mathrm{pr}})^2. \tag{12.44}$$

Thus we see that, if the frequency ω is much below the frequency ω_{pr} of the piezoelectric resonance, the inertial term in the elasticity equation can be discarded. In this case Eq. (12.40) can be rewritten in the corresponding form

$$T_{ia,a}=0. \tag{12.45}$$

When combined with the boundary condition Eq. (12.42) and the uniqueness of solutions to the elasticity equations,[51] we can conclude that the stress tensor must vanish everywhere within the crystal:

$$0=T_{ia}=c_{aicd}u_{c,d}-e_{jai}E_j\ . \tag{12.46}$$

Thus we can solve for the symmetric part of the displacement gradient in the form

$$u_{(c,d)}=s_{cdab}e_{jab}E_j\ , \tag{12.47}$$

where $\overleftrightarrow{s}$ is the compliance tensor, the reciprocal of the stiffness tensor $\overleftrightarrow{c}$. Since the electromagnetic wave equation (10.18) depends only on the strain, Eq. (12.47) can be inserted to yield

$$\{[n^2(\overleftrightarrow{1}-\overrightarrow{ss})-\overleftrightarrow{\kappa}(\omega)]\cdot\vec{E}\}_i=e_{icd}s_{cdab}e_{jab}E_j/\epsilon_0\ . \tag{12.48}$$

The term on the right-hand side of Eq. (12.48) can be interpreted as a piezoelectric modification of the dielectric tensor[52]

$$\kappa_{ij}(\omega_L)=\kappa_{ij}(\omega_H)+e_{icd}s_{cdab}e_{jab}/\epsilon_0\ . \tag{12.49}$$

Here L stands for low and H for high frequencies as compared to the piezoelectric resonance frequency of the crystal under study.

XIII. ITERATIVE TECHNIQUES FOR SOLUTION OF NONLINEAR EQUATIONS

In this section we shall obtain the form of the nonlinear polarization responsible for mixing of two electromagnetic fields, at least one of which is optical. This will include optical harmonic generation (where both fields have the same optical frequency), optical mixing (where the frequencies are different), the high-frequency (clamped) electro-optic effect (where one frequency lies between the ionic and piezoelectric resonances), and the low-frequency (unclamped) electro-optic effect (where one frequency is below the piezoelectric resonance frequency). The difference between the low- and high-frequency electro-optic effects involves the piezoelectric and photoelastic effects illustrating the effect of acoustic interactions on what otherwise would be described as purely electromagnetic phenomena. We have applied the technique to be used here to the photoelastic interaction[2] and to acoustically induced harmonic generation.[3]

The important nonlinear terms in the polarization can be obtained through the use of the following approximations: (i) To obtain the mixing of two electromagnetic fields as discussed above, terms involving a product of three or more fields in the equations of motion must be discarded. (ii) Terms arising from electric quadrupole, magnetic dipole, and higher multipole moments are found to be negligible in a dielectric in comparison to the interactions considered here and are discarded from Eq. (8.3). (iii) Two field terms in the forces involving a product of two displacement fields $[\vec{u}(\vec{x}, t)]$ can be immediately discarded since one of these fields must be at an optical frequency and hence minute for the interactions considered. (iv) Remaining forces that involve the magnetic field $\vec{B}$, such as $\vec{p}\times\vec{B}$ and gradient forces such as $(\vec{p}\cdot\vec{\nabla})\vec{E}$ can also be discarded, as they are of order (lattice constant × wavelength) times the dominant forces. (v) Correction terms that arise in the transformation of time derivatives from the material to the spatial frame (see Appendix E) are found to be negligible. (vi) Two field terms in which the acoustic displacement is evaluated at an optical frequency can be discarded as negligible. (vii) All terms in the acoustic nonlinear driving force $\vec{G}$ enter the polarization equations through a piezoelectric term involving the displacement $\vec{u}$ at an optical frequency. Since the latter is small, the nonlinear driving term $\vec{G}$ gives a negligible contribution to the optical output and so can be neglected in this section. (viii) The convective current term $(i/\omega)\vec{\Delta}\times(\vec{P}\times\vec{u})$ of Eq. (1.21) is omitted since it is of order ω_A/ω_0 compared to terms retained. These approximations, the terms discarded, and estimates of their size are given in Ref. 2. With these approximations Eq. (10.11) becomes

$$\mathcal{P}_i \approx P_i^{\mathrm{NL}} \approx -u_{c,c}\epsilon_0\chi_{ij}E_j + \epsilon_0\textstyle\sum_\nu \chi_{im}^{\;\nu} F_m^\nu/q^\nu\,, \tag{13.1}$$

where with the help of Eq. (9.16) we get

$$\begin{aligned} F_m^\nu = &-3\sum_{\lambda\mu} {}^{(3,0)}H_{mbf}^{\nu\lambda\mu}\, y_b^\lambda y_f^\mu \\ &-2\sum_{\lambda} {}^{(2,1)}H_{mbcd}^{\nu\lambda}\, y_b^\lambda u_{c,d} \\ &-2\sum_{\lambda} {}^{(2,0)}H_{db}^{\nu\lambda}\, y_b^\lambda u_{[m,d]} \\ &-2\sum_{\lambda} {}^{(2,0)}H_{md}^{\nu\lambda}\, y_b^\lambda u_{[b,d]}\,, \end{aligned} \tag{13.2}$$

where we have used the brackets to denote an antisymmetrization in the enclosed indices:

$$u_{[c,d]} \equiv \tfrac{1}{2}(u_{c,d} - u_{d,c})\,. \tag{13.3}$$

We are considering a problem in which we have two driving fields: one at the frequency ω_0 which we shall normally consider to be an optical frequency, and another at another frequency ω_A which may be optical or at a lower frequency. The latter field is applied as an electromagnetic field in an electro-optic experiment, and as an acoustic field in a photoelastic experiment. It is then rigorous to expand any field variable $\vec{Z}(\vec{y}^\nu,\ \vec{u},\ \vec{E},\ \text{or}\ \vec{B})$ in a Fourier expansion

$$\vec{Z}(\vec{z}, t) = \frac{1}{2}\sum_{m,n=-\infty}^{+\infty} \vec{Z}(\vec{z},\ t;\ m,\ n)\,, \tag{13.4}$$

where the individual terms have the form

$$\vec{Z}(\vec{z},\ t;\ m,\ n) = \vec{Z}(\vec{z};\ m,\ n)\,e^{-i(m\omega_0 + n\omega_A)t}\,. \tag{13.5}$$

Reality of the original variable $\vec{Z}$ is guaranteed by the requirement

$$\vec{Z}(\vec{z};\ -m,\ -n) = \vec{Z}^*(\vec{z};\ m,\ n)\,. \tag{13.6}$$

We have included the factor $\frac{1}{2}$ in Eq. (13.4) so that the magnitude of $\vec{Z}(\vec{z};\ m,\ n)$ represents the amplitude at its associated frequency. It can be omitted from the $m = n = 0$ term. Other conventions have also been used in the literature.[26]

If the expansion Eq. (13.4) is applied to Eq. (13.1) and the corresponding coefficients with the frequency $\omega_0 + \omega_A$, i.e., the $(m,\ n) = (1,\ 1)$ coefficients, are compared, we obtain the result

$$\begin{aligned} \tfrac{1}{2}\mathcal{P}_i(1,\ 1) = &-(\tfrac{1}{2})^2 u_{c,c}(0,\ 1)\,\epsilon_0\chi_{ij}(\omega_0)E_j(1,\ 0) \\ &+\tfrac{1}{2}\epsilon_0\textstyle\sum_\nu \chi_{im}^{\;\nu}(\omega_B)F_m^\nu(1,\ 1)/q^\nu\,, \end{aligned} \tag{13.7}$$

where all field variables are understood to be functions of $\vec{z}$ and

$$\omega_B = \omega_0 + \omega_A\,. \tag{13.8}$$

Similarly, the nonlinear driving force can be written in the form

$$\begin{aligned} \tfrac{1}{2}F_m^\nu(1,\ 1) = \left(\frac{1}{2}\right)^2 \Big(&-6\sum_{\lambda\mu} {}^{(3,0)}H_{mbf}^{\nu\lambda\mu}\, y_b^\lambda(1,\ 0)\, y_f^\mu(0,\ 1) - 2\sum_{\lambda} {}^{(2,1)}H_{mbcd}^{\nu\lambda}\, y_b^\lambda(1,\ 0)u_{c,d}(0,\ 1) \\ &-2\sum_{\lambda} {}^{(2,0)}H_{db}^{\nu\lambda}\, y_b^\lambda(1,\ 0)u_{[m,d]}(0,\ 1) - 2\sum_{\lambda} {}^{(2,0)}H_{md}^{\nu\lambda}\, y_b^\lambda(1,\ 0)u_{[b,d]}(0,\ 1)\Big)\,, \end{aligned} \tag{13.9}$$

where the interchange of the (0, 1) and (1, 0) arguments has been omitted in the last three terms but included in the first. This accounts for the extra factor of 2 in the first term.

We now continue the procedure used in Sec. X of eliminating the internal displacements $\vec{y}^\nu$ in favor of the electric field $\vec{E}$ and displacement gradients $u_{c,d}$. This elimination is to be made by the use of Eq. (10.5). Since the expression (13.9) is already bilinear in the field variables, we must omit the last term in Eq. (10.5). Moreover, the second term in Eq. (10.5) can be neglected at the optical frequency ω_0 but must be retained at the acoustic frequency ω_A when that is a low frequency. Thus we can write

$$y_b^\lambda(1, 0) = \epsilon_0 \chi_{jb}^\lambda(\omega_0) E_j(1, 0)/q^\lambda , \tag{13.10}$$

$$y_f^\mu(0, 1) = \epsilon_0 \chi_{kf}^\mu(\omega_A) E_k(0, 1)/q^\mu - \epsilon_0 \sum_\nu \Upsilon_{fg}^{\mu\nu}(\omega_A)\, {}^{(1,1)}H_{gcd}^\nu u_{c,d}(0, 1). \tag{13.11}$$

When these results are inserted into Eq. (13.9) and the latter in turn inserted into Eq. (13.7), we see that the effective nonlinear polarization is expressible in terms of field amplitudes and displacement gradients alone:

$$\mathcal{P}_i(1, 1) = 2\epsilon_0 d_{ijk} E_j(1, 0) E_k(0, 1) + \epsilon_0 \chi_{ij(cd)} E_j(1, 0) u_{(c,d)}(0, 1) + \epsilon_0 \chi_{ij[cd]} E_j(1, 0) u_{[c,d]}(0, 1) , \tag{13.12}$$

where our subscript indices correspond to the frequencies according to

$$j \rightarrow (1, 0) \rightarrow \omega_0, \quad k \rightarrow (0, 1) \rightarrow \omega_A, \quad i \rightarrow (1, 1) \rightarrow \omega_B . \tag{13.13}$$

When Eqs. (13.10) and (13.11) are inserted into Eq. (13.7), the coefficients in Eq. (13.12) can be read off as

$$d_i^{\omega_B}{}_j^{\omega_0}{}_k^{\omega_A} = -\tfrac{3}{2}\epsilon_0^2 \sum_{\nu\lambda\mu} \chi_{im}^\nu(\omega_B) \chi_{jb}^\lambda(\omega_0) \chi_{kf}^\mu(\omega_A) \times {}^{(3,0)}H_{mbf}^{\nu\lambda\mu}/q^\nu q^\lambda q^\mu, \tag{13.14}$$

$$\chi_i^{\omega_B}{}_j^{\omega_0}{}_{(cd)}^{\omega_A} = -\tfrac{1}{2}\chi_{ij}(\omega_0)\delta_{cd} - \epsilon_0 \sum_{\nu\lambda} \chi_{im}^\nu(\omega_B)\chi_{jb}^\lambda(\omega_0) \frac{{}^{(2,1)}H_{mbcd}^{\nu\lambda}}{q^\nu q^\lambda} + 3\epsilon_0^2 \sum_{\nu\lambda\mu\rho} \chi_{im}^\nu(\omega_B)\chi_{jb}^\lambda(\omega_0)\, {}^{(3,0)}H_{mbf}^{\nu\lambda\mu} \Upsilon_{fg}^{\mu\rho}(\omega_A) \frac{{}^{(1,1)}H_{gcd}^\rho}{q^\nu q^\lambda q^\mu q^\rho} , \tag{13.15}$$

$$\chi_i^{\omega_B}{}_j^{\omega_0}{}_{[cd]}^{\omega_A} = -\epsilon_0 \sum_{\mu\beta} \chi_{im}^\mu(\omega_B)\chi_{jb}^\beta(\omega_0)\, \mathcal{A}(c, d) \frac{{}^{(2,0)}H_{db}^{\mu\beta}\delta_{cm} + {}^{(2,0)}H_{md}^{\mu\beta}\delta_{bc}}{q^\mu q^\beta} . \tag{13.16}$$

We have used the symbol $\mathcal{A}(c, d)$ to represent an antisymmetrization operation defined by

$$\mathcal{A}(c, d) f_{cd} \equiv \tfrac{1}{2}(f_{cd} - f_{dc}) . \tag{13.17}$$

The terms $\chi_{ij(cd)}$ and $\chi_{ij[cd]}$ are the symmetric and antisymmetric contributions to the direct photoelastic tensor. We have previously emphasized the importance of the heretofore neglected antisymmetric term[10] and note that when Eq. (13.17) is inserted into Eq. (13.16) we obtain the result quoted in Eq. (4.16) of our paper on the photoelastic interaction.[2] In that paper we note that the linear interaction matrix ${}^{(2,0)}H$ can be eliminated by means of Eq. (10.3) of this paper. Neglecting terms of order ω_A/ω_0, Eq. (13.16) can be reduced to the simple form

$$\chi_{ij[cd]} = \tfrac{1}{2}\mathcal{A}(c, d)\left[\chi_{ic}(\omega_B)\delta_{jd} + \chi_{jc}(\omega_0)\delta_{id}\right] . \tag{13.18}$$

We have already shown how Eq. (13.18) (ignoring the minor difference between ω_B and ω_0) can be derived using elementary arguments relating χ to the change in the dielectric tensor of anisotropic crystals under rigid rotations.[10] Equation (13.18), with predictable sign and magnitude, can be combined with acousto-optic or Brillouin scattering measurements of $|\chi_{ijkl}|$ and $|\chi_{ijlk}|$ to determine the sign of χ_{ijkl}.

A. Optical Mixing Tensor

The tensor responsible for mixing two input electric fields is defined by means of the relationship

$$\mathcal{P}_i = D\epsilon_0 d_i^{\omega_B}{}_j^{\omega_0}{}_k^{\omega_A} E_j^{\omega_0} E_k^{\omega_A} , \tag{13.19}$$

where the factor D is given the values

$$D = 1 \text{ if } \omega_0 = \omega_A , \quad D = 2 \text{ if } \omega_0 \neq \omega_A . \tag{13.20}$$

This factor takes into account the fact that when ω_0 does not equal ω_A two terms arise in this theory whereas only one term can arise if ω_0 is exactly equal to ω_A. The inclusion of the factor D then makes the mixing tensor $d_i^{\omega_B}{}_j^{\omega_0}{}_k^{\omega_A}$ a continuous function of its frequency arguments. A comparison between Eqs. (13.19) and (13.12) shows that the coefficient d_{ijk} is indeed identical to the mixing tensor used in Eq. (13.12) where the two frequencies were assumed to be different.

When both frequencies ω_0 and ω_A are identical optical frequencies, $d_i^{\omega_B}{}_j^{\omega_0}{}_k^{\omega_A}$ is referred to as the second-harmonic generation tensor, and it is necessarily symmetric on its last two indices. Thus it has the same symmetry as the piezoelectric tensor for the material in question. If ω_0 and ω_A are different optical frequencies, $d_i^{\omega_B}{}_j^{\omega_0}{}_k^{\omega_A}$ is referred to as the optical mixing tensor. As discussed by Giordmaine,[53] $\omega_0 - \omega_A$ can be large enough for dispersive effects to destroy the symmetry on the indices j and k, thus permitting d_{ijk} to exist for all (and only for) acentric groups (including the acentric, nonpiezoelectric group 432). If the low frequency ω_A lies above the piezoelectric resonances of the crystal (of course, ω_0 is still optical) then the tensor $d^{\omega_B}_{i}{}^{\omega_0}_{j}{}^{\omega_A}_{k}$ is referred to as the high-frequency (clamped) electro-optic tensor still expressed in the form conventional to the optic mixing tensor. If the low frequency ω_A is below the fundamental piezoelectric resonance, the tensor plus the indirect electro-optic term (derived in Sec. XIII B below) is referred to as the low-frequency (unclamped) electro-optic tensor in the optical mixing form.

The form of the d_{ijk} tensor given in Eq. (13.14) is similar to, but somewhat more general than, corresponding expressions used by Kleinman[54] and Miller.[45] Of course, the general symmetry requirements

$$d^{\omega_B}_{i}{}^{\omega_0}_{j}{}^{\omega_A}_{k} = d^{\omega_0}_{j}{}^{\omega_B}_{i}{}^{\omega_A}_{k} = d^{\omega_B}_{i}{}^{\omega_A}_{k}{}^{\omega_0}_{j} \tag{13.21}$$

follow from the symmetry of ${}^{(3,0)}H^{\nu\lambda\mu}_{mbf}$ under the interchange of any lower pair of indices coupled with the simultaneous interchange of the corresponding upper pair. [This symmetry can be assumed without loss of generality since nonsymmetric portions of ${}^{(3,0)}H$ do not contribute to the potential-energy sum in Eq. (9.1).]

In a dispersion-free region, in which $\chi^{\nu}_{im}(\omega)$ has the same value at the three frequencies ω_B, ω_0, ω_A, the just-described symmetry of the ${}^{(3,0)}H^{\nu\lambda\mu}_{mbf}$ immediately leads to the Kleinman[54] rule of symmetry with respect to any permutation of the subscripts:

$$d_{ijk} = d_{(ijk)} \; . \tag{13.22}$$

This reasoning is the same as Kleinman's except that many degrees of freedom can be involved.

Equation (13.14) can be written in a form

$$d^{\omega_B}_{i}{}^{\omega_0}_{j}{}^{\omega_A}_{k} = \sum_{\lambda\mu\nu} \chi^{\lambda}_{ia}(\omega_B)\,\chi^{\mu}_{jb}(\omega_0)\,\chi^{\nu}_{kc}(\omega_A)\,\delta^{\lambda\mu\nu}_{abc} \; , \tag{13.23}$$

representing a generalization of the Miller relationship[45] to the case of several degrees of freedom. The partial susceptibility $\overleftrightarrow{\chi}^{\lambda}$ associated with $\vec{y}^{\lambda}$ is defined by

$$\chi^{\lambda}_{ia}(\omega) \equiv \textstyle\sum_{\xi} q^{\xi}\, \Upsilon^{\xi\lambda}_{ia}(\omega)\, q^{\lambda} \; , \tag{13.24}$$

where the generalized Miller δ can be identified as

$$\delta^{\lambda\mu\nu}_{abc} = -\tfrac{3}{2}\epsilon_0^2 \; {}^{(3,0)}H^{\lambda\mu\nu}_{abc}/(q^{\lambda} q^{\mu} q^{\nu}) \; . \tag{13.25}$$

That the $\overleftrightarrow{\chi}^{\lambda}$ are partial susceptibilities is evident from the relationship

$$\chi_{ia}(\omega) = \textstyle\sum_{\lambda} \chi^{\lambda}_{ia}(\omega) \; . \tag{13.26}$$

Equation (13.23) has not been specialized to principal directions of $\overleftrightarrow{\chi}$ as Miller did, since in monoclinic and triclinic crystals these directions are frequency dependent. If there is (effectively) a single electronic (e) and a single ionic (i) contribution to the susceptibility, Eq. (13.23) can be rewritten in a form which generalizes that suggested by Garrett[20] and used by Boyd, Bridges, Pollack, and Turner[55]:

$$\begin{aligned} d^{\omega_B}_{r}{}^{\omega_0}_{s}{}^{\omega_A}_{t} = {} & \chi^{e}_{ra}(\omega_B)\,\chi^{e}_{sb}(\omega_0)\,\chi^{e}_{tc}(\omega_A)\,\delta^{eee}_{abc} \\ & + [\chi^{e}_{ra}(\omega_B)\,\chi^{e}_{sb}(\omega_0)\,\chi^{i}_{tc}(\omega_A) \\ & + \chi^{e}_{ra}(\omega_B)\,\chi^{e}_{st}(\omega_A)\,\chi^{i}_{sc}(\omega_0) \\ & + \chi^{e}_{ta}(\omega_A)\,\chi^{e}_{sb}(\omega_0)\,\chi^{i}_{rc}(\omega_B)\,]\,\delta^{eei}_{abc} \\ & + \text{interchange of } e \text{ and } i \; . \end{aligned} \tag{13.27}$$

By Eq. (13.25) $\delta^{\lambda\mu\nu}_{abc}$ has the same symmetry as ${}^{(3,0)}H^{\lambda\mu\nu}_{abc}$:

$$\delta^{\lambda\mu\nu}_{abc} = \delta^{\mu\lambda\nu}_{bac} = \delta^{\mu\nu\lambda}_{bca} \; . \tag{13.28}$$

Thus δ^{eee} and δ^{iii} must have Kleinman symmetry

$$\delta^{eee}_{abc} = \delta^{eee}_{(abc)} , \quad \delta^{iii}_{abc} = \delta^{iii}_{(abc)} , \tag{13.29}$$

whereas the remaining δ's have piezoelectric symmetry

$$\delta^{eei}_{abc} = \delta^{eei}_{(ab)c} , \quad \delta^{eii}_{abc} = \delta^{eii}_{a(bc)} \; . \tag{13.30}$$

In the optical region, in which all frequencies are well above the ionic resonance, only the first term in Eq. (13.27) contributes since $\overleftrightarrow{\chi}^{i}$ is small. Miller's rule[45] states that although the optical mixing tensor d varies by orders of magnitude from one material to another, the (Miller) δ's vary much less. It is large variations in the susceptibilities that are responsible for the dramatic variations in d. The Miller δ which is essentially our ${}^{(3,0)}H$ is a "chemical" property of the crystal which should not vary strikingly as one moves through the Periodic Table. Levine's bond charge model[56] has accounted well for the variation of the Miller δ in different crystals.

If one of the frequencies, say ω_A, is infrared, and the other two are optical as in the Faust-Henry[57] experiment, or an electro-optic experiment (discussed more carefully later), then the only contributing terms are

$$\begin{aligned} d^{\omega_B}_{r}{}^{\omega_0}_{s}{}^{\omega_A}_{t} = {} & \chi^{e}_{ra}(\omega_B)\,\chi^{e}_{sb}(\omega_0) \\ & \times[\chi^{e}_{tc}(\omega_A)\,\delta^{eee}_{abc} + \chi^{i}_{tc}(\omega_A)\,\delta^{eei}_{abc}] \; . \end{aligned} \tag{13.31}$$

For all except triclinic and monoclinic crystals, principal axes (for which χ_{ij} is diagonal) are defined by symmetry and the d_{rst} are understood to be expressed in such a principal coordinate system. Since all force constants are comparable $H^{ei} \sim H^{ee} \sim m^{e}(\omega^{e})^2$, the effective coupling between electronic and ionic motions

$$\frac{{}^{(2,0)}H^{ei}}{(m^e m^i)^{1/2}[(\omega^e)^2-(\omega^i)^2]} \sim \frac{m^e(\omega^e)^2}{(m^e m^i)^{1/2}[(\omega^e)^2-(\omega^i)^2]} \sim \left(\frac{m^e}{m^i}\right)^{1/2} \tag{13.32}$$

is negligible. Thus the partial susceptibilities

$$\chi_{ra}^e \approx \chi_{aa}^e \delta_{ra}, \quad \chi_{tc}^i \approx \chi_{cc}^i \delta_{tc} \tag{13.33}$$

are also diagonal with respect to the same axes. Faust and Henry in their experiment in which ω_A passes through the restrahl region of the crystal obtain excellent agreement assuming (i) that the partial susceptibilities are diagonal, Eq. (13.33), (ii) that $\overleftrightarrow{\chi}^e$ can be approximated as a frequency-independent background, and (iii) that $\overleftrightarrow{\chi}^i$ is described by a single damped resonance. Their experiment, in conjunction with clamped electro-optic experiments,[58] permits the determination of the two Miller parameters δ^{eee} and δ^{eei}.

An experiment with two frequencies near the infrared resonance ω_i would depend on δ^{eii}. However, the sum frequency would still not be much above ω_i so that δ^{iii} terms would also enter in addition to δ^{eee} and δ^{eei}. Nevertheless, measurements at several frequencies can be combined with harmonic generation and electro-optic data to determine all four constants.

Extensive measurements of microwave frequency mixing have been made by Boyd, Bridges, Pollack, and Turner[55] with results expressed in terms of all four parameters discussed here. Their data in combination with second harmonic generation and electro-optic effect data were sufficient to determine δ^{eee}, δ^{eei}, and a susceptibility weighted combination of δ^{eii} and δ^{iii}.

B. Electro-Optic Tensor

In a piezoelectric material, the term in Eq. (13.12) involving the strain components $u_{(c,d)}$ contribute to the electro-optic effect. Below the piezoelectric resonance, we can use Eq. (12.47) to calculate the strain induced by an electric field. Since the piezoelectric effect via Eq. (12.47) only induces a strain and not a rotation, the last term in Eq. (13.12) vanishes while the middle term yields the indirect electro-optic effect. Thus Eq. (13.12) becomes

$$\mathcal{P}_i(1,1) = \epsilon_0(2d_{ijk} + \chi_{ij(cd)} s_{cdab} e_{kab}) E_j(1,0) E_k(0,1)\,, \tag{13.34}$$

where the first and second terms are the direct and indirect electro-optic effects. Note that only the symmetric part of the photoelastic tensor contributes to the indirect effect. Moreover, the indirect effect, in this low-frequency region, has the same symmetry as the direct effect.

At frequencies well above the piezoelectric resonance, Eq. (12.47) does not apply. The crystal responds only weakly to the applied field as seen from Eq. (12.1), so that the indirect effect in Eq. (13.34) should be omitted. In the piezoelectric resonance region, where acoustic wavelengths are comparable to crystal dimensions, neither Eq. (12.47) nor Eq. (12.1) is applicable, and a boundary-value problem must be solved. In the latter case, the indirect electro-optic effect *loses the (infinite medium) symmetry of the direct effect, and depends on the shape and orientation of the specimen.*[58]

C. Indirect Photoelastic Effect

In a piezoelectric material a strain induces an electric field. Equations (11.1) and (11.6) yield the induced field

$$E_k(0,1) = -\frac{a_k a_m}{\vec{a}\cdot\overleftrightarrow{\kappa}(\omega_A)\cdot\vec{a}}\,\frac{e_{mcd}u_{c,d}(0,1)}{\epsilon_0}\,, \tag{13.35}$$

where

$$\vec{a} = \vec{k}_A/|\vec{k}_A| \tag{13.36}$$

is a unit vector in the direction of propagation of the sound wave. If the electric field (13.35) is eliminated from Eq. (13.12), the total nonlinear polarization induced by an applied electromagnetic field and an applied acoustic field is given by

$$\mathcal{P}'_i = \epsilon_0\left(\chi_{ijcd} - \frac{2d_{ijk}a_k a_m}{\epsilon_0\vec{a}\cdot\overleftrightarrow{\kappa}(\omega_A)\cdot\vec{a}}e_{mcd}\right)E_j(1,0)u_{c,d}(0,1)\,, \tag{13.37}$$

where χ_{ijcd} is the sum of the symmetric and antisymmetric contributions previously defined:

$$\chi_{ijcd} = \chi_{ij(cd)} + \chi_{ij[cd]}\,. \tag{13.38}$$

As discussed in more detail elsewhere,[2,59] the piezoelectric correction to the measured photoelastic tensor does not transform as an ordinary tensor of fourth rank, but rather as a tensor function of the unit vector $\vec{a}$. As a consequence, the indirect photoelastic susceptibility can have nonvanishing components forbidden by bulk symmetry to the direct photoelastic susceptibility. These piezoelectric corrections must be subtracted off from the experimental results to obtain the material tensor χ_{ijcd}. The situation we describe here with regard to the photoelastic interaction is completely parallel to the situation of piezoelectric corrections to the elasticity tensor (see Sec. XI).

XIV. FAR-FIELD DYADIC GREEN'S FUNCTION IN ANISOTROPIC MEDIA

When the experimental geometry is such that the electromagnetic field is not properly or conveniently described as a plane wave, the electromagnetic equation

$$\overleftrightarrow{\alpha}(-i\vec{\nabla},\omega)\cdot\vec{\mathrm{E}}(\vec{\mathrm{r}},\omega)=\vec{\mathcal{P}}(\vec{\mathrm{r}})e^{-i\omega t}/\epsilon_0 \tag{14.1}$$

is best solved by the Green's-function technique:

$$\vec{\mathrm{E}}(\vec{\mathrm{r}},\omega)=\int\overleftrightarrow{\mathrm{G}}(\vec{\mathrm{r}},\vec{\mathrm{r}}')\cdot\vec{\mathcal{P}}(\vec{\mathrm{r}}')d\vec{\mathrm{r}}'e^{-i\omega t}/\epsilon_0\,. \tag{14.2}$$

Here the dyadic Green's function is given by

$$\overleftrightarrow{\mathrm{G}}(\vec{\mathrm{r}},\vec{\mathrm{r}}')=\int_{-\infty}^{+\infty}\frac{e^{i\vec{\mathrm{k}}\cdot(\vec{\mathrm{r}}-\vec{\mathrm{r}}')}}{\overleftrightarrow{\alpha}(\vec{\mathrm{k}},\omega)}\,\frac{d\vec{\mathrm{k}}}{(2\pi)^3}\,, \tag{14.3}$$

and the reciprocal of $\overleftrightarrow{\alpha}(\vec{\mathrm{k}},\omega)$ has been given in (F17) as

$$\frac{1}{\overleftrightarrow{\alpha}(\vec{\mathrm{k}},\omega)}=\sum_{\varphi=1,2}\frac{\vec{\mathcal{E}}^{\varphi}(\vec{\mathrm{s}},\omega)\vec{\mathcal{E}}^{\varphi}(\vec{\mathrm{s}},\omega)}{[(ck/\omega)^2/n^{\varphi}(\vec{\mathrm{s}},\omega)^2]-1}-\frac{\vec{\mathrm{s}}\vec{\mathrm{s}}}{\vec{\mathrm{s}}\cdot\overleftrightarrow{K}(\omega)\cdot\vec{\mathrm{s}}}\,, \tag{14.4}$$

where $\vec{\mathrm{s}}=\vec{\mathrm{k}}/|\vec{\mathrm{k}}|$ is the usual unit propagation vector and $\vec{\mathcal{E}}^{\varphi}(\vec{\mathrm{s}},\omega)$ are the eigenvectors introduced in Eq. (12.3) for the driving frequency ω and the propagation direction $\vec{\mathrm{s}}$. We note that the denominators in Eq. (14.4) vanish only when k is "on the energy shell," i.e., appropriate to a free plane-wave solution. A small negative imaginary part $-i\eta$ is understood to be added to these denominators, so as to yield the usual outgoing Green's function.[60]

A common experimental geometry is one in which the source polarization $\vec{\mathcal{P}}(\vec{\mathrm{r}}')$ is confined to a finite volume (the region of overlap of the driving fields) and the point of observation $\vec{\mathrm{r}}$ is in the far-field ("Fraunhofer") region. In this case, the $\vec{\mathrm{k}}$ integral in Eq. (14.3) can be simplified by using asymptotic methods.[61] For any function

$$F(\vec{\mathrm{k}})\equiv F(k\vec{\mathrm{s}})\equiv f(k,\xi,\mu)\,, \tag{14.5}$$

where $\mu=\vec{\mathrm{k}}\cdot\vec{\mathrm{R}}/kR=\cos(\vec{\mathrm{k}},\vec{\mathrm{R}})$, $\vec{\mathrm{R}}\equiv\vec{\mathrm{r}}-\vec{\mathrm{r}}'$, $R=|\vec{\mathrm{R}}|$, and ξ is an azimuthal angle about the direction of $\vec{\mathrm{k}}$. Thus $d\vec{\mathrm{k}}=k^2dk\,d\xi\,d\mu$. Writing $f(\mu)$ briefly for $f(k,\xi,\mu)$, we can simplify the integration over μ by integrating by parts:

$$\int_{-1}^{1}e^{ikR\mu}f(\mu)d\mu=\left(\frac{f(1)e^{ikR}}{ikR}-\frac{f(-1)e^{-ikR}}{ikR}\right)-\int_{-1}^{+1}\frac{df(\mu)}{d\mu}\,\frac{e^{ikR\mu}}{ikR}\,d\mu\,. \tag{14.6}$$

The first term on the right-hand side is of order $1/kR$. The second term like the left-hand side contains a rapidly oscillating factor and can, by another integration by parts, be shown to be of order $(1/kR)^2$ and hence negligible in the far field. We note, however, that at $\mu=\pm1$, the vector $\vec{\mathrm{k}}$ must be parallel or antiparallel to $\vec{\mathrm{R}}$, and $f(\pm 1)$ is independent of ξ. Thus

$$\int_0^{\infty}k^2dk\int_0^{2\pi}d\xi\int_{-1}^{1}d\mu\,e^{ikR\mu}F(k\vec{\mathrm{s}})$$

$$\approx 2\pi\int_0^{\infty}k^2dk\left(F(k\hat{\mathrm{R}})\frac{e^{ikR}}{ikR}-F(-k\hat{\mathrm{R}})\frac{e^{-ikR}}{ikR}\right)$$

$$=2\pi\int_{-\infty}^{\infty}k^2dk\,F(k\hat{\mathrm{R}})\frac{e^{ikR}}{ikR}\,, \tag{14.7}$$

where $\hat{R}=\vec{\mathrm{R}}/|\vec{\mathrm{R}}|$ is a unit vector in the direction of $\vec{\mathrm{r}}-\vec{\mathrm{r}}'$ and we have used the evenness in k of the quantity in parentheses.

The Green's dyadic [Eq. (14.3)], evaluated with the help of Eq. (14.7), becomes in the first far-field approximation

$$\overleftrightarrow{\mathrm{G}}^{(1)}(\vec{\mathrm{r}},\vec{\mathrm{r}}')=\sum_{\varphi=1,2}\vec{\mathcal{E}}\varphi(\hat{R},\omega)\,\vec{\mathcal{E}}^{\phi}(\hat{R},\omega)(k^{\varphi})^2g^{\varphi}(R)\,, \tag{14.8}$$

$$g^{\varphi}(R)\equiv\lim_{\eta\to0}\frac{1}{R}\,\frac{1}{(2\pi)^2i}\int_{-\infty}^{\infty}\frac{e^{ikR}k\,dk}{k^2-(k^{\varphi})^2-i\eta}=\frac{e^{ik^{\varphi}R}}{4\pi R}\,, \tag{14.9}$$

$$k^{\varphi}\equiv\omega n^{\varphi}(\hat{R},\omega)/c\,. \tag{14.10}$$

The nonpropagating mode [last term in Eq. (14.4)] does not contribute to the far-field Green's dyadic. The approximation involved in obtaining $\overleftrightarrow{\mathrm{G}}$, namely, $kR\gg1$, is an excellent one in the optical region. A second approximation to the Green's dyadic $\overleftrightarrow{\mathrm{G}}^{(2)}(\vec{\mathrm{s}},\vec{\mathrm{s}}')$, valid when the source dimensions are small compared to the observation distance ($r'\ll r$), may be obtained by replacing $\hat{R}$ in Eq. (14.8) by $\hat{\mathrm{r}}=\vec{\mathrm{r}}/|\vec{\mathrm{r}}|$. In this case, the electric field is given by

$$\vec{\mathrm{E}}(\vec{\mathrm{r}},t)=\frac{e^{-i\omega t}}{\epsilon_0}\sum_{\varphi=1,2}(k^{\varphi})^2\vec{\mathcal{E}}^{\varphi}(\hat{r},\omega)\,\vec{\mathcal{E}}^{\varphi}(\hat{r},\omega)\cdot\int g^{\varphi}(|\vec{\mathrm{r}}-\vec{\mathrm{r}}'|)\vec{\mathcal{P}}(\vec{\mathrm{r}}')d\vec{\mathrm{r}}'\,, \tag{14.11}$$

and now $k^{\varphi}=\omega n^{\varphi}(\hat{r},\omega)/c$. If, in addition, one is in the Fraunhofer region $r\gg k(r')^2$, it is legitimate to make the customary sagittal approximation

$$R\approx r-\hat{r}\cdot\vec{\mathrm{r}}' \tag{14.12}$$

[with an error of order $k(r')^2/r$ in the exponent] to obtain

$$\vec{\mathrm{E}}=\sum_{\varphi=1,2}\frac{e^{i(k^{\varphi}r-\omega t)}}{4\pi\epsilon_0 r}[k^{\varphi}(\hat{r},\omega)]^2\vec{\mathcal{E}}^{\varphi}(\hat{r},\omega)C^{\varphi}\,, \tag{14.13}$$

$$C^{\varphi}\equiv\vec{\mathcal{E}}^{\varphi}(\hat{r},\omega)\cdot\int e^{-ik^{\varphi}\hat{r}\cdot\vec{\mathrm{r}}'}\vec{\mathcal{P}}(\vec{\mathrm{r}}')d\vec{\mathrm{r}}'\,. \tag{14.14}$$

With neglect of terms of order $(kr)^{-1}$, the magnetic field is given by

$$\vec{\mathrm{H}}=\sum_{\theta}\frac{e^{i(k^{\theta}r-\omega t)}}{4\pi\epsilon_0 r}\,\frac{[k^{\theta}(\hat{r},\omega)]^3}{\omega\mu_0}\,\hat{r}\times\vec{\mathcal{E}}^{\theta}(\hat{r},\omega)C^{\theta}\,. \tag{14.15}$$

The time-averaged Poynting vector $\frac{1}{2}\mathrm{Re}\,[\vec{\mathrm{E}}^{*}\times\vec{\mathrm{H}}]$ is

$$\vec{S}=\sum_{\varphi\theta}\frac{c^2(k^\varphi)^2(k^\theta)^3}{32\pi^2\epsilon_0 r^2\omega}\left[\hat{r}(\vec{\mathcal{E}}^\varphi\cdot\vec{\mathcal{E}}^\theta)-\vec{\mathcal{E}}^\theta(\vec{\mathcal{E}}^\varphi\cdot\hat{r})\right]$$

$$\times\operatorname{Re}\left[(C^\varphi)^* C^\theta e^{i(k^\theta-k^\varphi)r}\right], \quad (14.16)$$

where c is the velocity of light in vacuum. We are concerned, however, with the component $\vec{S}\cdot\hat{r}$ of $\vec{S}$ in the direction $\hat{r}$ of observation. If we make use of Eq. (12.3) and orthonormality [Eq. (12.12)]

$$(n^\theta)^2\,\vec{\mathcal{E}}^\varphi(\hat{r},\omega)\cdot(1-\hat{r}\hat{r})\cdot\vec{\mathcal{E}}^\theta(\hat{r},\omega)=\vec{\mathcal{E}}^\varphi\cdot\overleftrightarrow{\kappa}\cdot\vec{\mathcal{E}}^\theta=\delta^{\varphi\theta}, \quad (14.17)$$

we obtain

$$\vec{S}\cdot\hat{r}=\frac{\omega^4}{32\pi^2\epsilon_0 c^3 r^2}\sum_{\varphi=1,2}[n^\varphi(\hat{r},\omega)]^3|C^\varphi|^2, \quad (14.18)$$

with no cross terms between the two polarization modes excited by $\vec{\mathcal{P}}$. The total radiated power in watts is then given by

$$W=\frac{\omega^4}{8\pi\epsilon_0 c^3}\sum_{\varphi=1,2}\langle[n^\varphi(\hat{r},\omega)]^3|C^\varphi|^2\rangle, \quad (14.19)$$

where $\langle\,\rangle$ denotes an average over all orientations of the observation unit vector $\hat{r}$.

A check on the numerical accuracy can be made by specializing Eq. (14.19) to the case of a point dipole in an isotropic medium in which case $\vec{\mathcal{E}}^\varphi$ is transverse to the direction $\hat{r}$ of propagation and

$$C^\varphi=\vec{\mathcal{E}}^\varphi\cdot\vec{p}^{(1)}, \quad (14.20)$$

where $\vec{p}^{(1)}=\int\vec{\mathcal{P}}\,d\vec{r}'$ is the total electric dipole moment. The normalization requirement [Eq. (12.12)] requires $\vec{\mathcal{E}}^\varphi$ to be a vector of magnitude $1/n$, where $n=n^\varphi$ is independent of orientation. Thus

$$\langle|\vec{\mathcal{E}}^\varphi\cdot\vec{p}^{(1)}|^2\rangle=\tfrac{1}{3}|\vec{p}^{(1)}|^2/n^2, \quad (14.21)$$

and the total radiated power

$$W=\frac{\omega^4}{12\pi}\frac{n}{\epsilon_0 c^3}|\vec{p}^{(1)}|^2 \quad (14.22)$$

is in agreement with Stratton's formula[62] with the magnetic permeability of the medium set to unity.

The nonlinear polarization arises as in Eq. (13.12) from products of linear driving fields. If these are describable by plane waves over the volume V in which they overlap, then the integrand of Eq. (14.14) is

$$e^{-i\vec{k}^\varphi\cdot\vec{r}'}\vec{\mathcal{P}}(r')=\vec{\mathcal{P}}(0)e^{i\Delta\vec{k}\cdot\vec{r}'},\quad \Delta\vec{k}=\vec{k}-\vec{k}^\varphi. \quad (14.23)$$

Here the driving $\vec{k}$ will be the sum of the $\vec{k}$ vectors of the input fields and $\vec{k}^\varphi=k^\varphi\hat{r}$ is a vector in the direction of observation $\hat{r}$ with a propagation constant $k^\varphi=k^\varphi(\hat{r},\omega)$, that is, it is "on the energy shell" for that frequency and direction of propagation. If the interaction volume is a rectangular parallelepiped ($V=L_1L_2L_3$), the power into a detector at r with solid angle $d\Omega$ is given by

$$\vec{S}\cdot\hat{r}r^2\,d\Omega=\frac{d\Omega\,\omega^4}{32\pi^2\epsilon_0 c^3}$$

$$\times\sum_{\varphi=1,2}(n^\varphi)^3|\vec{\mathcal{E}}^\varphi(\hat{r},\omega)\cdot\vec{\mathcal{P}}(0)|^2V^2\Phi^2, \quad (14.24)$$

where Φ^2 is the reduction in power produced by imperfect phase match

$$\Phi=\frac{\sin(\frac{1}{2}\Delta k_1L_1)}{\frac{1}{2}\Delta k_1L_1}\frac{\sin(\frac{1}{2}\Delta k_2L_2)}{\frac{1}{2}\Delta k_2L_2}\frac{\sin(\frac{1}{2}\Delta k_3L_3)}{\frac{1}{2}\Delta k_3L_3}, \quad (14.25)$$

where $\Delta k_i=k_i-k_i^\varphi$ is the degree of mismatch in component i of the wave vector. We note that at phase match ($\Phi^2=1$), the power increases with V^2, the square of the volume of the interaction region.

ACKNOWLEDGMENT

We wish to thank R. A. Toupin for useful correspondence in connection with this manuscript.

APPENDIX A: CHARGE DENSITY AND POLARIZATION

By expressing the position $\vec{x}^\alpha$ in terms of the internal displacements $\vec{u}^\alpha$

$$\vec{x}^\alpha(\vec{X},t)\equiv\vec{x}(\vec{X},t)+\vec{u}^\alpha(\vec{X},t), \quad (A1)$$

Eq. (4.11) for the charge density can be written

$$q(\vec{z},t)=\textstyle\sum_\alpha q^\alpha\int\delta(\vec{z}-\vec{x}(\vec{X},t)-\vec{u}^\alpha(\vec{X},t))\,d\vec{X}. \quad (A2)$$

A multipole expansion can then be accomplished by expanding the δ function in powers of $\vec{u}^\alpha$:

$$\delta(\vec{z}-\vec{x}-\vec{u}^\alpha)=\delta(\vec{z}-\vec{x})-(\vec{u}^\alpha\cdot\vec{\nabla})\,\delta(\vec{z}-\vec{x})$$

$$+\tfrac{1}{2}\vec{u}^\alpha\vec{u}^\alpha:\vec{\nabla}\vec{\nabla}(\vec{z}-\vec{x})-\cdots, \quad (A3)$$

where the gradient operator, defined by

$$(\vec{\nabla})_i\equiv\frac{\partial}{\partial z_i}, \quad (A4)$$

acts on the spatial coordinate $\vec{z}$. Equation (4.11) then yields for the total charge density

$$q(\vec{z})=q_D(\vec{z})-\vec{\nabla}\cdot\vec{P}(\vec{z})+\tfrac{1}{2}\vec{\nabla}\vec{\nabla}:\overleftrightarrow{Q}(\vec{z})+\cdots. \quad (A5)$$

The three terms explicitly displayed in Eq. (A5) are the contribution to the charge density produced by deformation, polarization, and quadrupolarization, respectively.

The deformation contribution, given by

$$q_D(\vec{z})=\frac{1}{\hat{J}}\textstyle\sum_\alpha q^\alpha=0 \quad (A6)$$

vanishes in a charge-free dielectric. The polarization density or electric dipole moment per unit volume in the spatial frame is given by

$$\vec{P}(\vec{z})=\vec{p}(\vec{X})/J(\vec{X})\,\big|_{\vec{x}(\vec{X},t)=\vec{z}}\equiv\hat{\vec{p}}(\vec{z})/\hat{J}(\vec{z},t) \quad (A7)$$

in terms of the dipole moment $\vec{p}$ per unit volume in the material frame. The correction factor $1/\hat{J}$ in Eqs. (A6) and (A7) accounts for the density change associated with the elastic distortion. It is defined by

$$\int \delta(\vec{z}-\vec{x}(\vec{X},t))\,d\vec{X}=\left(\frac{1}{J(\vec{X})}\right)_{\vec{x}(\vec{X},t)=\vec{z}} \equiv \frac{1}{\hat{J}(\vec{z},t)}\ , \tag{A8}$$

where $J(\vec{X})=\det(x_{i,A})$ is the Jacobian of the transformation from the material to the spatial frame. The total polarization can be written as a sum of contributions from the individual sublattices in accordance with

$$\vec{p}(\vec{X})=\textstyle\sum_\alpha \vec{p}^{\,\alpha}(\vec{X}),\quad \vec{p}^{\,\alpha}(\vec{X})=q^\alpha\,\vec{u}^{\,\alpha}(\vec{X})\ . \tag{A9}$$

Similarly, the quadrupole moment per unit spatial frame volume is given by

$$Q_{ij}(\vec{z})=q_{ij}(\vec{X})/J(\vec{X})\big|_{\vec{x}(\vec{X},t)=\vec{z}} \tag{A10}$$

in terms of the quadrupole moment tensor per unit material frame volume q_{ij}. The latter also can be written as a sum of contributions over the different sublattices in the form

$$q_{ij}(\vec{X})\equiv\textstyle\sum_\alpha q^\alpha u_i^\alpha(\vec{X})\,u_j^\alpha(\vec{X})\ . \tag{A11}$$

Since the Coulomb interactions in this paper are originally those due to a set of nonoverlapping point charges, it is appropriate to use only the traceless part of q_{ij}, as is conventionally done.[63]

APPENDIX B: CURRENT DENSITY

We rewrite Eq. (4.12) for the current density in the form

$$\begin{aligned}\vec{j}(\vec{z},t)&=\textstyle\sum_\alpha q^\alpha \int[\dot{\vec{x}}(\vec{X},t)+\dot{\vec{u}}^{\alpha}(\vec{X},t)]\\ &\qquad\times\delta(\vec{z}-\vec{x}(\vec{X},t)-\vec{u}^{\,\alpha}(\vec{X},t))\,d\vec{X}\\ &=\vec{j}_D(\vec{z},t)+\vec{j}_P(\vec{z},t)+\vec{j}_Q(\vec{z},t)+\vec{j}_M(\vec{z},t)\end{aligned} \tag{B1}$$

and note that this current density automatically obeys the charge conservation relationship

$$\vec{\nabla}\circ\vec{j}+\frac{\partial q}{\partial t}=0\ , \tag{B2}$$

with the charge described in Eq. (4.11) and Appendix A. After expanding the δ function as in Eq. (A3) the deformation contribution to the current becomes

$$\vec{j}_D(\vec{z},t)=\textstyle\sum_\alpha q^\alpha\int\dot{\vec{x}}(\vec{X},t)\delta(\vec{z}-\vec{x}(\vec{X},t))\,d\vec{X}=0\ , \tag{B3}$$

which vanishes in a charge-free dielectric. The polarization contribution to the current, which involves the internal displacements $\vec{u}^{\,\alpha}$ linearly, can be written as

$$\begin{aligned}\vec{j}_P(\vec{z},t)&=\textstyle\sum_\alpha q^\alpha\int[\dot{\vec{u}}(\vec{X},t)-\dot{\vec{x}}(\vec{X},t)\,\vec{u}^{\,\alpha}(\vec{X},t)\cdot\vec{\nabla}]\\ &\qquad\times\delta(\vec{z}-\vec{x}(\vec{X},t))\,d\vec{X}\ .\end{aligned} \tag{B4}$$

Performing the summation over α and utilizing Eqs. (A8) and (A9) for the polarization, we can reexpress the polarization current in the form

$$\begin{aligned}\vec{j}_P(\vec{z},t)&=\frac{1}{\hat{J}(\vec{z},t)}\frac{d}{dt}[\hat{J}(\vec{z},t)\vec{P}(\vec{z},t)]\\ &\qquad-\frac{\partial}{\partial z_i}[\dot{\vec{x}}(\vec{z},t)P_i(\vec{z},t)]\ ,\end{aligned} \tag{B5}$$

where we have followed the customary notation of representing a material time derivative ($\vec{X}$ fixed) of an arbitrary function by

$$\begin{aligned}\dot{f}(\vec{z},t)&\equiv\frac{d}{dt}f(\vec{z},t)\equiv\frac{d}{dt}f(\vec{x}(\vec{X},t),t)\Big|_{\vec{x}(\vec{X},t)=\vec{z}}\\ &=\frac{\partial f(\vec{z},t)}{\partial t}+\dot{\vec{x}}(\vec{z},t)\cdot\vec{\nabla}f(\vec{z},t)\ .\end{aligned} \tag{B6}$$

Of course, the velocity itself is the material time derivative

$$\dot{\vec{x}}(\vec{z},t)\equiv\frac{\partial\vec{x}(\vec{X},t)}{\partial t}\bigg|_{\vec{x}(\vec{X},t)=\vec{z}}\ . \tag{B7}$$

In a similar way the quadrupole contribution to the current density involves all terms bilinear in the $\vec{u}^{\,\alpha}$ and can be written in terms of the $\vec{u}^{\,\alpha}$ in the form

$$\begin{aligned}(j_Q)_i&=\sum_\alpha q^\alpha\int\left(-\frac{1}{2}\frac{(\dot{u}_i^\alpha u_j^\alpha+\dot{u}_j^\alpha u_i^\alpha)\partial}{\partial z_j}+\frac{\dot{x}_i u_j^\alpha u_k^\alpha\partial^2}{\partial z_j\partial z_k}\right)\\ &\qquad\times\delta(\vec{z}-\vec{x}(\vec{X},t))\,d\vec{X}\ .\end{aligned} \tag{B8}$$

After summing again over α the quadrupolarization contribution to the current can be expressed in the form

$$\begin{aligned}[\vec{j}_Q(\vec{z},t)]_i&=-\frac{1}{2}\frac{\partial}{\partial z_j}\left(\hat{J}^{-1}\frac{d}{dt}(\hat{J}Q_{ij})\right)\\ &\qquad+\frac{1}{2}\frac{\partial^2}{\partial z_j\partial z_k}(\dot{x}_i Q_{jk})\end{aligned} \tag{B9}$$

in terms of the quadrupolarization Q_{ij} of Eq. (A10). The remaining term that arises in the unfolding of Eq. (B1) is the current associated with the magnetization

$$\begin{aligned}[\vec{j}_M(\vec{z},t)]_i&=-\sum_\alpha\frac{1}{2}q^\alpha\int(\dot{u}_i^\alpha u_j^\alpha-\dot{u}_j^\alpha u_i^\alpha)\\ &\qquad\times\frac{\partial}{\partial z_j}\delta(\vec{z}-\vec{x}(\vec{X},t))\,d\vec{X}\\ &=\frac{\partial M_{ij}}{\partial z_j}\equiv(\vec{\nabla}\cdot\overleftrightarrow{M})_i=\epsilon_{ijk}\frac{\partial}{\partial z_j}M_k\ ,\end{aligned} \tag{B10}$$

where the magnetization tensor $\overleftrightarrow{M}$ and the usual magnetization vector $\vec{M}$ are given in terms of the internal displacements by

$$M_{ij} \equiv \epsilon_{ijk} M_k = \frac{1}{2} \sum_{\alpha} \frac{q^{\alpha}(u_i^{\alpha} \dot{u}_j^{\alpha} - u_j^{\alpha} \dot{u}_i^{\alpha})}{J} \bigg|_{\vec{x}(\vec{X},t)=\vec{z}} . \tag{B11}$$

Alternatively, the magnetization can be related to its material form by

$$\vec{M}(\vec{z}, t) = [\vec{m}(\vec{X}, t)/J(\vec{X}, t)]\big|_{\vec{x}(\vec{X},t)=\vec{z}} . \tag{B12}$$

The magnetic moment per unit volume in the material coordinate system is given by

$$\vec{m}(\vec{X}, t) \equiv \textstyle\sum_{\alpha} \vec{m}^{\alpha}(\vec{X}, t), \quad \vec{m}^{\alpha}(\vec{X}, t) = \frac{1}{2} q^{\alpha}(\vec{u}^{\alpha} \times \dot{\vec{u}}^{\alpha}) . \tag{B13}$$

By transforming material-frame time derivatives into spatial-frame time derivatives (see Appendix C), the polarization current of Eq. (B5) can be rewritten as

$$\vec{j}_P(\vec{z}, t) = \frac{\partial \vec{P}(\vec{z}, t)}{\partial t} + \vec{\nabla} \times [\vec{P}(\vec{z}, t) \times \dot{\vec{x}}(\vec{z}, t)] . \tag{B14}$$

The second term on the right-hand side of Eq. (B14) is referred to as the convective current. A typical derivation of this convective current considers the time derivative of the integrated flux through a closed surface. The convective current is that part which arises because of the motion of the surface.[42] In our case, the convective current arises because of a transformation from material time derivatives to spatial time derivatives. This, of course, contains the same physical content as the previous derivation since the extra term arises because of the motion of one coordinate frame relative to another which is a manifestation of the motion of the body. A further use of the theorem to be derived in Appendix C when applied to Eq. (B9) yields an expression for the quadrupole contribution to the current in the form of

$$\vec{j}_Q(\vec{z}, t) = -\frac{1}{2} \frac{\partial(\vec{\nabla} \cdot \overleftrightarrow{Q})}{\partial t} - \frac{1}{2} \vec{\nabla} \times \vec{W} , \tag{B15}$$

$$W_i = \{[(\vec{\nabla} \cdot \overleftrightarrow{Q}) + \overleftrightarrow{Q} \cdot \vec{\nabla}] \times \dot{x}\}_i = \epsilon_{ijk}(Q_{jm,m} \dot{x}_k + Q_{jm} \dot{x}_{k,m}) .$$

It is thus possible to write the total current in a form

$$\vec{j}(\vec{z}, t) = \frac{\partial \vec{P}'}{\partial t} + \vec{\nabla} \times \vec{M}' , \tag{B16}$$

which is in agreement with Eq. (1.6) used in the Introduction. There and here the effective polarization is given by

$$\vec{P}' = \vec{P} - \tfrac{1}{2} \vec{\nabla} \cdot \overleftrightarrow{Q} , \tag{B17}$$

and the effective magnetization is given by

$$\vec{M}' = \vec{M} + [\vec{P} - \tfrac{1}{2}(\vec{\nabla} \cdot \overleftrightarrow{Q}) - \tfrac{1}{2} \overleftrightarrow{Q} \circ \vec{\nabla}] \times \dot{\vec{x}} . \tag{B18}$$

APPENDIX C: RELATION BETWEEN MATERIAL AND SPATIAL TIME DERIVATIVES

Any physical quantity $\gamma(\vec{X}, t)$ in the material frame [e.g., a dipole moment per unit material volume $\vec{p}(\vec{X}, t)$] and the corresponding quantity $\Gamma(\vec{z}, t)$ in the spatial frame [e.g., the polarization $\vec{P}(\vec{z}, t)$] are related by

$$\begin{aligned} \Gamma(\vec{z}, t) &= \int \gamma(\vec{X}, t)\, \delta(\vec{z} - \vec{x}(\vec{X}, t))\, d\vec{X} \\ &= \gamma(\vec{X}, t)/J(\vec{X}, t)\big|_{\vec{x}(\vec{X},t)=\vec{z}} \equiv \hat{\gamma}(\vec{z}, t)/\hat{J}(\vec{z}, t) . \end{aligned} \tag{C1}$$

The spatial time derivative (i.e., holding $\vec{z}$ fixed) is then

$$\begin{aligned} \frac{\partial \Gamma(\vec{z}, t)}{\partial t} &= \int \frac{d\gamma(\vec{X}, t)}{dt} \delta(\vec{z} - \vec{x}(\vec{X}, t))\, d\vec{X} \\ &\quad - \int \gamma(\vec{X}, t) \dot{x}_i(\vec{X}, t) \frac{\partial \delta(\vec{z} - \vec{x}(\vec{X}, t))}{\partial z_i}\, d\vec{X} \\ &= [\hat{J}(\vec{z}, t)]^{-1} \frac{d\gamma(\vec{X}, t)}{dt} \bigg|_{\vec{x}(\vec{X},t)=\vec{z}} \\ &\quad - \frac{\partial}{\partial z_i} \left(\frac{\dot{x}_i(\vec{z}, t) \hat{\gamma}(\vec{z}, t)}{\hat{J}(\vec{z}, t)} \right) . \end{aligned} \tag{C2}$$

We rewrite this in the form of a continuity equation

$$\frac{\partial \Gamma(\vec{z}, t)}{\partial t} + \frac{\partial[\Gamma(\vec{z}, t) \dot{x}_i]}{\partial z_i} = (\hat{J})^{-1} \frac{d(\hat{J}\Gamma)}{dt} , \tag{C3}$$

the right-hand side describing creation of Γ. The substantive or material time derivative on the right-hand side is understood as usual to mean a derivative holding $\vec{X}$ ("particle name") fixed, with the result reexpressed as a function of the spatial position $\vec{z}$ as in (B6). If we set $\Gamma = (\hat{J})^{-1}$, we find that the latter obeys the conservation-of-matter equation

$$\frac{\partial(\hat{J}^{-1})}{\partial t} + \frac{\partial[\hat{J}^{-1} \dot{x}_i]}{\partial z_i} = 0 . \tag{C4}$$

Thus it is appropriate to regard

$$\hat{J}^{-1}(\vec{z}, t) \equiv n(\vec{z}, t) \tag{C5}$$

as a mass density (normalized to unit density in the material frame). Indeed, if the conservation equation (C4) is assumed, it is a trivial matter to derive the seemingly more general equation (C3).

If $\vec{x}$, $\vec{X}$, and $\vec{z}$ are measured relative to a common Cartesian coordinate system, we may apply the identity (C3) to a vector Γ_i to obtain

$$\begin{aligned} &\hat{J}^{-1} \frac{d(\hat{J}\Gamma_i)}{dt} - \frac{\partial(\dot{x}_i \Gamma_a)}{\partial z_a} \\ &\quad = \frac{\partial \Gamma_i}{\partial t} + \frac{\partial(\Gamma_i \dot{x}_a)}{\partial z_a} - \frac{\partial(\dot{x}_i \Gamma_a)}{\partial z_a} = \left(\frac{\partial \vec{\Gamma}}{\partial t} + \vec{\nabla} \times (\vec{\Gamma} \times \dot{\vec{x}}) \right)_i . \end{aligned} \tag{C6}$$

The curl term of Eq. (C6) illustrates the automatic appearance of a convective contribution to a current when material time derivatives are transformed into spatial time derivatives.

If Γ is replaced by a component Γ_{ij} of a tensor, we obtain a corresponding relationship

$$\hat{J}^{-1}\frac{d}{dt}(\hat{J}\Gamma_{ij})-\frac{\partial}{\partial z_a}(\dot{x}_i\Gamma_{aj})=\frac{\partial\Gamma_{ij}}{\partial t}+\epsilon_{imn}\frac{\partial}{\partial z_m}(\epsilon_{npq}\Gamma_{pj}\dot{x}_q)\ . \tag{C7}$$

Equations (B5) and (B9) were formed to correspond to the left-hand sides of Eqs. (C6) and (C7), respectively. Making use of these relationships we obtain the previously quoted polarization and quadrupolarization contributions to the current in Eqs. (B14) and (B15).

APPENDIX D: INTERNAL COORDINATES

Let us introduce a new set of coordinates $\vec{y}^\mu$:

$$\vec{y}^\mu(\vec{X})\equiv\sum_{\alpha=1}^{N}U^{\mu\alpha}\vec{x}^\alpha(\vec{X}),\quad \mu=0,1,2,\ldots,N-1\ . \tag{D1}$$

If we define the first row of the $\overleftrightarrow{U}$ matrix to have the elements

$$U^{0\alpha}\equiv\rho^\alpha/\rho^0\ , \tag{D2}$$

then the first coordinate $\vec{y}^0$ is identical to the center-of-mass coordinate $\vec{x}$. The inverse transformation to Eq. (D1) can be written in the form

$$\vec{x}^\alpha(\vec{X})\equiv\sum_{\mu=0}^{N-1}V^{\alpha\mu}\vec{y}^\mu(\vec{X}),\quad \alpha=1,2,\ldots,N\ . \tag{D3}$$

The matrix $\overleftrightarrow{U}$ and its inverse $\overleftrightarrow{V}$ are related by both

$$\sum_{\alpha=1}^{N}U^{\mu\alpha}V^{\alpha\nu}=\delta^{\mu\nu}\ , \tag{D4}$$

$$\sum_{\mu=0}^{N-1}V^{\alpha\mu}U^{\mu\beta}=\delta^{\alpha\beta}\ . \tag{D5}$$

Let us assume that this transformation is chosen so as to preserve the diagonality of the kinetic energy

$$\sum_{\alpha=1}^{N}\rho^\alpha(\dot{\vec{x}}^\alpha)^2=\sum_{\mu=0}^{N-1}m^\mu(\dot{\vec{y}}^\mu)^2\ ,\quad m^0\equiv\rho^0\ . \tag{D6}$$

This leads to the relationships

$$\sum_{\alpha=1}^{N}\rho^\alpha V^{\alpha\mu}V^{\alpha\nu}=m^\mu\,\delta^{\mu\nu}\ , \tag{D7}$$

$$\sum_{\mu=0}^{N-1}m^\mu U^{\mu\alpha}U^{\mu\beta}=\rho^\alpha\,\delta^{\alpha\beta}\ . \tag{D8}$$

Alternatively, the invariance of the quadratic form displayed in Eq. (D6) ensures that an orthogonal transformation can be made from the set of variables $(\rho^\alpha)^{1/2}\vec{x}^\alpha$ to $(m^\mu)^{1/2}\vec{y}^\mu$:

$$(\rho^\alpha)^{1/2}\vec{x}^\alpha=\textstyle\sum_\mu O^{\alpha\mu}(m^\mu)^{1/2}\vec{y}^\mu\ , \tag{D9}$$

where $\overleftrightarrow{O}$ is an orthogonal matrix, that is, $\overleftrightarrow{O}^{-1}=\tilde{\overleftrightarrow{O}}$. By expressing the transformation matrices $\overleftrightarrow{V}$ and $\overleftrightarrow{U}$ in terms of the orthogonal matrix

$$\overleftrightarrow{V}=(\overleftrightarrow{\rho})^{-1/2}\cdot\overleftrightarrow{O}\cdot(\overleftrightarrow{m})^{1/2}\ ,\quad \overleftrightarrow{U}=\overleftrightarrow{V}^{-1}=(\overleftrightarrow{m})^{-1/2}\cdot\tilde{\overleftrightarrow{O}}\cdot(\vec{\rho})^{1/2}\ , \tag{D10}$$

where

$$(\overleftrightarrow{\rho})^{\alpha\beta}\equiv\delta^{\alpha\beta}\rho^\alpha,\quad (\overleftrightarrow{m})^{\mu\nu}=m^\mu\,\delta^{\mu\nu}\ , \tag{D11}$$

the orthogonality of $\overleftrightarrow{O}$ leads to the relationship

$$\overleftrightarrow{V}=\overleftrightarrow{\rho}^{-1}\cdot\tilde{\overleftrightarrow{U}}\cdot\overleftrightarrow{m},\quad V^{\alpha\mu}=(m^\mu/\rho^\alpha)U^{\mu\alpha}\ . \tag{D12}$$

If we substitute the relationship (D2) into the explicit or second relationship (D12), we obtain the condition

$$V^{\alpha 0}=1\ . \tag{D13}$$

This is perhaps the simplest representation of the requirement that the variable $\vec{y}^0$ is the center-of-mass position $\vec{x}$. If we substitute Eq. (D13) into Eq. (D4), we derive the relationship

$$\textstyle\sum_\alpha U^{\mu\alpha}=\delta^{\mu 0}\ . \tag{D14}$$

If we substitute Eq. (D2) into Eq. (D4), we obtain

$$\sum_\alpha\frac{\rho^\alpha}{\rho^0}V^{\alpha\nu}=\delta^{0\nu}\ . \tag{D15}$$

If we use Eqs. (D2) and (D13), we can rewrite Eq. (D5) in the form

$$\sum_{\mu\neq 0}V^{\alpha\mu}U^{\mu\beta}+\frac{\rho^\beta}{\rho^0}=\delta^{\alpha\beta}\ . \tag{D16}$$

Let us note that the condition Eq. (D14) for $\mu\neq 0$ is what was used in Eqs. (5.4) and (5.5) to display the fact that the variables $\vec{y}^\mu$ for $\mu\neq 0$ are indeed internal coordinates unaffected by a displacement of the crystal as a whole.

With the help of Eq. (D13), Eq. (D3) can be written in a form

$$\vec{u}^\alpha\equiv\vec{x}^\alpha-\vec{x}=\sum_{\mu=1}^{N-1}V^{\alpha\mu}\vec{y}^\mu\ , \tag{D17}$$

which displays the internal character of $\vec{u}^\alpha$ previously pointed out in Sec. V B.

The internal coordinates $\vec{y}^\mu$ are not normal coordinates unless they obey the eigenvalue equation

$$2\textstyle\sum_\nu H^{\mu\nu}_{ij}y^\nu_j=m^\mu\omega^2 y^\mu_i\ . \tag{D18}$$

For all except triclinic and monoclinic crystals, there exists a unique set of principal axes such that

$$H^{\mu\mu}_{ij}=H^{\mu\mu}_{ii}\,\delta_{ij}\ . \tag{D19}$$

If the crystal space group possesses a subgroup G

of operations S that leave the sublattices invariant, then as in Eq. (5.44)

$$H^{\mu\nu}_{ij}=H^{\mu\nu}_{i'j'}S_{i'i}S_{j'j}\ , \tag{D20}$$

so that $H^{\mu\nu}_{ij}$ transforms as an ordinary second-rank tensor under this subgroup. If the subgroup G is sufficient to require a second-rank tensor to be diagonal in a special frame, then with respect to these principal axes

$$H^{\mu\nu}_{ij}=H^{\mu\nu}_{ii}\delta_{ij}\ . \tag{D21}$$

If, moreover, the subgroup G belongs to one of the cubic crystal classes, then $H^{\mu\nu}_{ii}$ will be independent of i and the transformation $V^{\alpha\nu}$ may be chosen to diagonalize $H^{\mu\nu}$. In this case, the $\vec{y}^{\mu}$ will be normal coordinates. For the noncubic case, normal coordinates w^{φ} can be obtained by a transformation

$$y^{\mu}_{i}=\textstyle\sum_t M^{\mu\varphi}_{i}w^{\varphi} \tag{D22}$$

chosen to diagonalize $H^{\mu\nu}_{ii}$ for each i.

APPENDIX E: KINEMATIC CORRECTIONS

Kinematic corrections are corrections which arise as a consequence of the transformation between the material and spatial coordinate systems. A general function F of the material coordinates can be rewritten as a function $\hat{F}$ of the corresponding spatial coordinates

$$F(\vec{X},t)\equiv\hat{F}(\vec{x}(\vec{X},t),t)\ . \tag{E1}$$

When we use a common Cartesian coordinate system for both spatial and material systems, there is no distinction between a vector component y_a and a corresponding vector y_A. There is nevertheless a distinction between derivatives with respect to the spatial and material coordinates. In particular, we have

$$\frac{\partial F}{\partial X_A}=\frac{\partial\hat{F}}{\partial x_j}\frac{\partial x_j}{\partial X_A}=\frac{\partial\hat{F}}{\partial x_j}(\delta_{jA}+u_{j,A})\equiv\frac{\partial\hat{F}}{\partial x_a}+\frac{\partial\hat{F}}{\partial x_j}u_{j,A}\ , \tag{E2}$$

where $\vec{u}$ is the displacement vector defined in Eq. (5.15). This equation appears to transform a general material derivative into a general spatial derivative; unfortunately, the correction factor on the right-hand side of Eq. (E2) contains the term $u_{j,A}$ which has the same form as the terms we are trying to eliminate. If we specialize Eq. (E2) by replacing F by the variable u_i, we obtain

$$u_{i,A}=\hat{u}_{i,j}(\delta_{jA}+u_{j,A})=\hat{u}_{i,a}+\hat{u}_{i,j}u_{j,A}\ . \tag{E3}$$

Equation (E3) constitutes a matrix equation for the unknown $u_{j,A}$. This matrix equation can be rewritten in the form

$$(\delta_{ij}-\hat{u}_{i,j})u_{j,A}=\hat{u}_{i,a}\ . \tag{E4}$$

By inverting the left-hand matrix factor $(\delta_{ij}-\hat{u}_{i,j})\equiv(\overleftrightarrow{1}-\hat{\overleftrightarrow{u}})_{ij}$ we obtain an explicit solution

$$u_{i,A}=(\overleftrightarrow{1}-\hat{\overleftrightarrow{u}})^{-1}_{ij}\,\hat{u}_{j,a}=\hat{u}_{i,a}+\hat{u}_{i,j}\hat{u}_{j,a}+\hat{u}_{i,j}\hat{u}_{j,k}\hat{u}_{k,a}+\cdots\ . \tag{E5}$$

With the help of this solution, we can rewrite Eq. (E2) as an explicit transformation from a material to a spatial derivative:

$$\frac{\partial F}{\partial X_A}=\frac{\partial\hat{F}}{\partial x_a}+\frac{\partial\hat{F}}{\partial x_j}(\hat{u}_{j,a}+\hat{u}_{j,k}\hat{u}_{k,a}+\cdots)\ . \tag{E6}$$

An example of Eq. (E6) particularly useful to us is

$$y^{\mu}_{i,A}=\hat{y}^{\mu}_{i,a}+\hat{y}^{\mu}_{i,j}\hat{u}_{j,a}+\cdots\ . \tag{E7}$$

As a second example, we rewrite the Jacobian in the form

$$\begin{aligned}J&=\det(\delta_{iA}+u_{i,A})\\&=1+u_{i,I}+\tfrac{1}{2}(u_{i,I}u_{j,J}-u_{i,J}u_{j,I})+\det u_{i,A}\ ,\end{aligned} \tag{E8}$$

where

$$u_{i,J}\equiv\frac{\partial u_i}{\partial X_j}\ .$$

It is understood that for purposes of the summation convention $I=i$, $J=j$, e.g., $u_{i,I}\equiv u_{1,1}+u_{2,2}+u_{3,3}$. Equation (E5) permits J to be transformed to the purely spatial form

$$\hat{J}=1+\hat{u}_{i,i}+\tfrac{1}{2}(\hat{u}_{i,i}\hat{u}_{j,j}+\hat{u}_{i,j}\hat{u}_{j,i})+\cdots. \tag{E9}$$

Some additional kinematic corrections arise in an attempt to replace the accelerations by spatial rather than material second time derivatives. Indeed a general material time derivative can be expressed in terms of spatial time derivatives by means of

$$\frac{dF(\vec{X},t)}{dt}=\frac{\partial\hat{F}}{\partial t}+\dot{x}_i\frac{\partial\hat{F}}{\partial x_i}\ . \tag{E10}$$

Here again the hidden difficulty is that the right-hand side contains a velocity $\dot{x}_i$ which itself is a material time derivative. In order to evaluate this latter derivative we specialize Eq. (E10) by setting F equal to the variable X_A and make use of the fact that the material time derivative of a material coordinate vanishes:

$$\frac{dX_A}{dt}=0=\frac{\partial X_A(\vec{x},t)}{\partial t}+\frac{\partial X_A(\vec{x},t)}{\partial x_i}\,\dot{x}_i\ , \tag{E11}$$

which can be rewritten in the form

$$\dot{x}_i=-x_{i,A}\frac{\partial X_A(\vec{x},t)}{\partial t}\ . \tag{E12}$$

With the use of the displacement $\vec{u}$ defined in Eq. (5.15) we obtain

$$X_A=x_a-\hat{u}_a(\vec{x},t)\ ,\quad\frac{\partial X_A}{\partial t}=-\frac{\partial\hat{u}_a}{\partial t}\ . \tag{E13}$$

Equation (E12) then becomes

$$\dot{x}_i = (\delta_{iA} + u_{i,A})\frac{\partial \hat{u}_a}{\partial t}$$

$$= \frac{\partial \hat{u}_i}{\partial t} + (\hat{u}_{i,a} + \hat{u}_{i,b}\hat{u}_{b,a} + \cdots)\frac{\partial \hat{u}_a}{\partial t} . \tag{E14}$$

By choosing F in Eq. (E10) to be the velocity $\dot{x}_i$, we obtain

$$\ddot{x}_i = \frac{\partial}{\partial t}\left(\frac{\partial \hat{u}_i}{\partial t} + \hat{u}_{i,a}\frac{\partial \hat{u}_a}{\partial t}\right) + \dot{x}_j \frac{\partial}{\partial x_j}\left(\frac{\partial \hat{u}_i}{\partial t} + \hat{u}_{i,a}\frac{\partial \hat{u}_a}{\partial t}\right) + \cdots$$

$$= \frac{\partial^2 \hat{u}_i}{\partial t^2} + \hat{u}_{i,a}\frac{\partial^2 \hat{u}_a}{\partial t^2} + 2\frac{\partial \hat{u}_{i,a}}{\partial t}\frac{\partial \hat{u}_a}{\partial t} + \cdots \tag{E15}$$

after having made use of Eq. (E14). Similarly we obtain the acceleration of the internal coordinate in the form

$$\ddot{y}_i^{\mu} = \frac{\partial}{\partial t}\left(\frac{\partial \hat{y}_i^{\mu}}{\partial t} + \dot{x}_j \hat{y}^{\mu}_{i,j}\right) + \dot{x}_j \frac{\partial}{\partial x_j}\left(\frac{\partial \hat{y}_i^{\mu}}{\partial t} + \dot{x}_k \hat{y}^{\mu}_{i,k}\right)$$

$$= \frac{\partial^2 \hat{y}_i^{\mu}}{\partial t^2} + \frac{\partial^2 \hat{u}_j}{\partial t^2}\hat{y}^{\mu}_{i,j} + 2\frac{\partial \hat{u}_j}{\partial t}\frac{\partial \hat{y}^{\mu}_{i,j}}{\partial t} + \cdots . \tag{E16}$$

In Eqs. (E7), (E9), (E15), and (E16), only bilinear corrections have been displayed, but higher-order corrections are readily obtained by the above methods. These corrections generally decrease by a factor ku in each order where k is the appropriate propagation constant. In our macroscopic theory this factor is generally exceedingly small. Indeed it would not be consistent to retain corrections of higher order than displayed without including wave-vector dispersion whose effects are at least of the order ka (where a is a lattice constant).

APPENDIX F: MATRIX RECIPROCALS

The solution of Eq. (10.18) for the electromagnetic field requires us to calculate the reciprocals of the dyadic $\overleftrightarrow{\alpha}$ defined in Eq. (1.19). In other words, we must find the dyadic or matrix $\overleftrightarrow{\beta}$ that obeys the equation

$$\overleftrightarrow{\alpha} \cdot \overleftrightarrow{\beta} = (n^2 \overleftrightarrow{1} - \overleftrightarrow{\kappa} - n^2 \vec{s}\vec{s}) \cdot \overleftrightarrow{\beta} = \overleftrightarrow{1} . \tag{F1}$$

If we transfer the last term to the right-hand side, we obtain

$$\overleftrightarrow{\beta} = \overleftrightarrow{\Gamma} \cdot [\overleftrightarrow{1} + n^2 \vec{s}(\vec{s} \cdot \overleftrightarrow{\beta})], \quad \overleftrightarrow{\Gamma} \equiv (n^2 \overleftrightarrow{1} - \overleftrightarrow{\kappa})^{-1} . \tag{F2}$$

By taking the scalar product of this equation with the unit vector $\vec{s}$ we obtain

$$\vec{s} \cdot \overleftrightarrow{\beta} = \vec{s} \cdot \overleftrightarrow{\Gamma} + n^2(\vec{s} \cdot \overleftrightarrow{\Gamma} \cdot \vec{s})(\vec{s} \cdot \overleftrightarrow{\beta}) , \tag{F3}$$

which can be used to eliminate $\vec{s} \cdot \overleftrightarrow{\beta}$ with the result

$$\overleftrightarrow{\beta} = \overleftrightarrow{\alpha}^{1} = \overleftrightarrow{\Gamma} + n^2 \frac{\overleftrightarrow{\Gamma} \cdot \vec{s}\vec{s} \cdot \overleftrightarrow{\Gamma}}{1 - n^2 \vec{s} \cdot \overleftrightarrow{\Gamma} \cdot \vec{s}} . \tag{F4}$$

In Eq. (11.2), the term giving the piezoelectric correction to the elasticity tensor requires an evaluation of the inverse dyadic in the limit of large index of refraction. For large n, $\overleftrightarrow{\Gamma}$ takes the form

$$\overleftrightarrow{\Gamma} \approx \overleftrightarrow{1}/n^2 - \overleftrightarrow{\kappa}/n^4 . \tag{F5}$$

The first term in Eq. (F4) becomes negligible. Because of a fortuitous cancellation in the denominator of Eq. (F4) the numerator and denominator of the second term in Eq. (F4) both behave as $1/n^2$. Hence, with error of order $1/n^2$, we obtain

$$\overleftrightarrow{\alpha}^{-1} \approx -\vec{s}\vec{s}/(\vec{s} \cdot \overleftrightarrow{\kappa} \cdot \vec{s}) . \tag{F6}$$

We often desire to invert the matrix $\overleftrightarrow{\alpha}$ to calculate the response of the electromagnetic field to a nonlinear polarization, and we wish to decompose the solution into the two propagating and one nonpropagating waves. Rather than using the formal solution (F4) and then performing a decomposition into eigenvectors it is more appropriate to take the reciprocal of $\overleftrightarrow{\alpha}$ directly by making use of its eigenvectors. The method is a fairly general one. If we have a pair of Hermitian matrices or operators A and B whose eigenfunctions obey

$$A\Psi_j = \lambda_j B\Psi_j , \tag{F7}$$

then $0 = (\Psi_j, A\Psi_i) - (A\Psi_j, \Psi_i) = (\lambda_i - \lambda_j^*)(\Psi_i, B\Psi_j)$ implies as in the usual Hermitian case that the eigenvectors Ψ_i can be chosen to obey the weighted orthonormality condition

$$(\Psi_i, B\Psi_j) = \delta_{ij} , \tag{F8}$$

a biorthogonality condition between the set of vectors $\{\Psi_i\}$, and the set $\{B\Psi_i\}$. Reality of λ_i follows directly from $\lambda_j = (\Psi_j, A\Psi_j)/(\Psi_j, B\Psi_j)$ and the fact that the diagonal elements of a Hermitian operator or matrix are real. We now seek a solution of the inhomogeneous equation

$$(A - \lambda B)\Psi = \Phi \tag{F9}$$

through the use of an eigenvector expansion

$$\Psi = \textstyle\sum_j \Psi_j C_j . \tag{F10}$$

It is then possible to solve for the expansion coefficients:

$$C_i = (\lambda_i - \lambda)^{-1}(\Psi_i, B\Psi_i)^{-1}(\Psi_i, \Phi) . \tag{F11}$$

Thus the total state vector takes the form

$$\Psi = (A - \lambda B)^{-1}\Phi = \textstyle\sum_i \Psi_i(\lambda_i - \lambda)^{-1}(\Psi_i, B\Psi_i)^{-1}(\Psi_i, \Phi) , \tag{F12}$$

from which the form of the inverse operator can be seen. For the special case in which the symbols take the meaning

$$A=(\overleftrightarrow{1}-\vec{s}\vec{s})\ ,\quad B=\overleftrightarrow{\kappa}\ ,\quad \lambda=1/n^2\ , \tag{F13}$$

the eigenfunction equation takes the form

$$(\overleftrightarrow{1}-\vec{s}\vec{s})\cdot\vec{\mathcal{E}}^{\varphi}=(1/n^{\varphi})^2\,\overleftrightarrow{\kappa}\cdot\vec{\mathcal{E}}^{\varphi}\ . \tag{F14}$$

The biorthogonality condition Eq. (F8) then states the orthogonality of the three field eigenvectors $\vec{\mathcal{E}}^{\varphi}$ with the corresponding electric displacement eigenvectors $\vec{\mathfrak{D}}^{\varphi}\equiv\overleftrightarrow{\kappa}\cdot\vec{\mathcal{E}}^{\varphi}$

$$\vec{\mathcal{E}}^{\varphi}\cdot\vec{\mathfrak{D}}^{\theta}\equiv\vec{\mathcal{E}}^{\varphi}\cdot\overleftrightarrow{\kappa}\cdot\vec{\mathcal{E}}^{\theta}=\delta^{\varphi\theta}\ . \tag{F15}$$

Equation (F14) is Eq. (12.3) that appears in the discussion of the crystal optics of an anisotropic medium. For this case, the inverse operator can be written in the form

$$\lambda^{-1}(A-\lambda B)^{-1}=\overleftrightarrow{\alpha}^{-1}=\sum_{\varphi}\frac{\vec{\mathcal{E}}^{\varphi}\vec{\mathcal{E}}^{\varphi}}{[(n/n^{\varphi})^2-1](\vec{\mathcal{E}}^{\varphi}\cdot\vec{\mathfrak{D}}^{\varphi})}\ , \tag{F16}$$

or more explicitly in terms of the three eigenvectors in the form

$$\overleftrightarrow{\alpha}^{-1}=\frac{\vec{\mathcal{E}}^{1}\vec{\mathcal{E}}^{1}}{[(n/n^{1})^2-1](\vec{\mathcal{E}}^{1}\cdot\vec{\mathfrak{D}}^{1})}+\frac{\vec{\mathcal{E}}^{2}\vec{\mathcal{E}}^{2}}{[(n/n^{2})^2-1](\vec{\mathcal{E}}^{2}\cdot\vec{\mathfrak{D}}^{2})}-\frac{\vec{s}\vec{s}}{(\vec{s}\cdot\overleftrightarrow{\kappa}\cdot\vec{s})}\ . \tag{F17}$$

The fact that one eigenvector is always longitudinal as shown in Eq. (12.6) was used to obtain the last term of Eq. (F17). For a uniaxial crystal, the indices 1 and 2 can be understood to refer to the ordinary o and extraordinary e eigenvectors.

---

[1] G. D. Boyd, F. R. Nash, and D. F. Nelson, Phys. Rev. Letters 24, 1298 (1970).

[2] D. F. Nelson and M. Lax, Phys. Rev. B 3, 2778 (1971).

[3] D. F. Nelson and M. Lax, Phys. Rev. B 3, 2795 (1971).

[4] R. A. Toupin, J. Ratl. Mech. Anal. 5, 849 (1956).

[5] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford U. P., London, 1954), Chap. VI.

[6] H. A. Lorentz, *The Theory of Electrons* (Stechert, New York, 1916), Chap. IV.

[7] J. J. Hopfield, Phys. Rev. 112, 1555 (1958).

[8] J. J. Hopfield and D. G. Thomas, Phys. Rev. 132, 563 (1963).

[9] A. S. Barker and R. Loudon (unpublished).

[10] D. F. Nelson and M. Lax, Phys. Rev. Letters 24, 379 (1970).

[11] F. Pockels, Ann. Phys. Chem. Ser. III 37, 144 (1889); 37, 269 (1889); 37, 372 (1889); and 39, 440 (1890).

[12] D. F. Nelson and P. D. Lazay, Phys. Rev. Letters 25, 1187 (1970).

[13] R. A. Toupin, Intern. J. Eng. Sci. 1, 101 (1963).

[14] See, however, Toupin's criticism of Born and Huang, Ref. 13, pp. 123 and 124.

[15] P. Penfield, Jr. and H. A. Haus, *Electrodynamics of Moving Media* (MIT Press, Cambridge, Mass., 1967).

[16] S. R. DeGroot, *The Maxwell Equations* (North-Holland, Amsterdam, 1969).

[17] E. I. Blount (unpublished).

[18] N. Bloembergen, *Nonlinear Optics* (Benjamin, New York, 1965), p. 5.

[19] C. G. B. Garrett and F. N. H. Robinson, IEEE J. Quantum Electron. QE2, 328 (1966).

[20] C. G. B. Garrett, IEEE J. Quantum Electron. QE4, 70 (1968).

[21] F. N. H. Robinson, Bell System Tech. J. 46, 913 (1967).

[22] S. K. Kurtz and F. N. H. Robinson, Appl. Phys. Letters 10, 62 (1967).

[23] P. N. Butcher, *Nonlinear Optical Phenomena* (Ohio State University Engineering Publications, Columbus, Ohio, 1965).

[24] R. W. Terhune and P. D. Maker, in *Lasers*, edited by A. K. Levine (Dekker, New York, 1968), p. 295.

[25] D. A. Kleinman, in *Laser Handbook*, edited by F. T. Arecchi and E. Schultz-Dubois (North-Holland, Amsterdam, to be published).

[26] J. A. Armstrong, N. Bloembergen, J. Ducuing, and P. S. Pershan, Phys. Rev. 127, 1918 (1962).

[27] P. S. Pershan, Phys. Rev. 130, 919 (1963).

[28] R. H. Lyddane, R. G. Sachs, and E. Teller, Phys. Rev. 59, 673 (1941).

[29] W. Cochran and R. A. Cowley, J. Phys. Chem. Solids 23, 447 (1962).

[30] H. Goldstein, *Classical Mechanics* (Addison-Wesley, Cambridge, Mass., 1951), p. 366.

[31] F. D. Murnaghan, Am. J. Math. 59, 235 (1937).

[32] In fluid dynamics, the corresponding representations are called Eulerian and Lagrangian, respectively. See, for example, R. Courant, *Differential and Integral Calculus* (Nordermann, New York, 1936), Vol. II, p. 212.

[33] C. Truesdell, J. Ratl. Mech. Anal. 1, 125 (1952). (1952).

[34] C. A. Truesdell and R. A. Toupin, in *Handbuch der Physik*, edited by S. Flüge (Springer, Berlin, 1960), Vol. III/1.

[35] C. E. Shannon, Proc. IRE 37, 10 (1949); J. M. Whittaker, *Interpolatory Function Theory* (Cambridge U. P., Cambridge, England, 1935), Chap. IV.

[36] Of course, parity conservation has been shown to be violated in the weak interactions. What is of interest here, however, is parity conservation in the electromagnetic interactions that govern the atomic bonding forces in crystals. Tests of this principle have been performed on atoms and molecules with rather small upper limits resulting for the parameter measuring the parity-violating interaction [see G. Feinberg, in *Atomic Physics*, edited by B. Bederson, V. W. Cohen, and F. M. J. Pichanick (Plenum, New York, 1969), p. 1]. No sensitive tests of parity conservation in crystals have been performed to our knowledge.

[37] H. Weyl, *Classical Groups* (Princeton U.P., Princeton, N. J., 1946), Chap. 2.

[38] F. D. Murnaghan, *Finite Deformations of an Elastic Solid* (Wiley, New York, 1951).

[39] Reference 34, Sec. 31, p. 266.

[40] Reference 34, Sec. 37, p. 279.

[41] If derivatives $E_{AB,C}$ are included, the phenomenon of

acoustic rotation (activity) will be obtained as proposed by R. A. Toupin, Arch. Ratl. Mech. Anal. 11, 385 (1962); G. Klugê and G. Schuly, Acoustica 16, 60 (1965); and by D. L. Portigal and E. Burstein, Phys. Rev. 170, 673 (1968); and observed by D. L. Portigal, thesis (University of Pennsylvania, 1967) (unpublished); by A. S. Pine, Phys. Rev. B 2, 2049 (1970); and by J. Joffrin and A. Levelut, Solid State Commun. 8, 1573 (1970). Of course, $E_{AB,C}$ involves second derivatives of the original variables, and is neglected along with other second derivatives of variables in the stored energy in this paper.

[42] W. K. H. Panofsky and M. Phillips, *Classical Electricity and Magnetism*, 2nd ed. (Addison-Wesley, Cambridge, Mass., 1962), p. 163.

[43] Reference 15, p. 217.

[44] Reference 13, Eqs. (5.2) and (5.14)–(5.18).

[45] R. C. Miller, Appl. Phys. Letters 5, 17 (1964).

[46] M. Lax, J. Phys. Chem. Solids Suppl. I, 179 (1965).

[47] See A. W. Warner, M. Onoe, and G. A. Coquin, J. Acoust. Soc. Am. 42, 1223 (1967) for the importance of this term in $LiNbO_3$ and $LiTaO_3$.

[48] M. Born and E. Wolf, *Principles of Optics*, 2nd ed. (MacMillan, New York, 1964), Chap. 14.

[49] D. A. Kleinman, Phys. Rev. 128, 1761 (1962).

[50] K. Huang, Proc. Roy. Soc. (London) A208, 352 (1951).

[51] A. E. H. Love, *Mathematical Theory of Elasticity*, 4th ed. (Cambridge U. P., Cambridge, England, 1927), Chap. VII.

[52] W. W. Cady, *Piezoelectricity* (Dover, New York, 1964), Vol. 1, p. 267.

[53] J. A. Giordmaine, Phys. Rev. 138, A1599 (1965).

[54] D. A. Kleinman, Phys. Rev. 126, 1977 (1962).

[55] G. D. Boyd, T. J. Bridges, M. A. Pollack, and E. H. Turner, Phys. Rev. Letters 26, 387 (1971).

[56] B. F. Levine, Phys. Rev. Letters 22, 787 (1969); 25, 440 (1970).

[57] W. L. Faust and C. H. Henry, Phys. Rev. Letters 17, 1265 (1966); W. L. Faust, C. H. Henry, and R. H. Eick, Phys. Rev. 173, 781 (1968).

[58] D. F. Nelson and E. H. Turner, J. Appl. Phys. 39, 3337 (1968).

[59] J. Chapelle and L. Taurel, Compt. Rend. 240, 743 (1955).

[60] An essentially equivalent Green's function modified to produce a vanishing field on a plane boundary, and specialized to the vicinity of phase match, has been used by D. A. Kleinman, A. Ashkin, and G. D. Boyd [Phys. Rev. 145, 338 (1966)] to obtain extraordinarily detailed understanding of the intensity pattern associated with second-harmonic generation from a focused laser beam.

[61] C. Eckart, Rev. Mod. Phys. 20, 390 (1948).

[62] J. A. Stratton, *Electromagnetic Theory* (McGraw-Hill, New York, 1941), Sec. 8.5.

[63] See, for example, Ref. 42, p. 18, and C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (McGraw-Hill, New York, 1955), p. 133.

PHYSICAL REVIEW B VOLUME 4, NUMBER 10 15 NOVEMBER 1971

Investigation of the *A*, *B*, and *C* Bands in KBr: In by Means of Electromodulated Optical Absorption

V. Grasso, P. Perillo, and G. Vermiglio
Istituto di Fisica dell'Università di Messina, Messina, Italy
and Gruppo Nazionale di Struttura della Materia del Consiglio Nazionale delle Ricerche,
Messina, Italy

(Received 8 March 1971)

The effect of an electric field ($\sim 10^4$ V/cm, rms) on the *A*, *B*, and *C* absorption bands of potassium bromide–indium phosphors has been studied. The *A* and *C* bands are composed of three subbands, while the *B* band exhibits a doublet structure. A correlation has also been found between the absorption intensities of these bands, the decrease in the *A* and *B* bands being compensated by the increase in the *C* band. A perturbative treatment has been used to explain the observed variation of the zeroth-order moments of *A*, *B*, and *C* bands.

INTRODUCTION

Single crystals of alkali halides containing metal impurity ions with $(ns)^2$ outermost electron configuration exhibit three absorption bands, called *A*, *B*, and *C* in order of increasing energy, in spectral regions where the host medium is normally transparent.[1,2] These absorption bands have been associated with the transition between molecular orbitals $(a_{1g})^2 \rightarrow (a_{1g})(t_{1u})$ and assigned to $^1A_{1g}(^1S_0) \rightarrow {}^3T_{1u}(^3P_1)$, $^1A_{1g}(^1S_0) \rightarrow {}^3E_u$, $^3T_{2u}(^3P_2)$, and $^1A_{1g}(^1S_0) \rightarrow {}^1T_{1u}(^1P_1)$, respectively.[3,4] Transitions from the ground state to $^3T_{1u}$ and to $^1T_{1u}$ are allowed, owing to their spin-orbit mixing. Transitions to ^3E_u, $^3T_{2u}$ are partially allowed because of vibrational perturbation, as supported by the strong temperature dependence of the oscillator strength.[5]

Fukuda *et al.*,[6] studying absorption spectra of KCl:In at various temperatures, found that the *A* band has a doublet structure and the *C* band a triplet structure. According to Toyozawa and Inoue,[7] these structures are explained in terms of the dynamical Jahn-Teller effect with linear electron-lattice interaction which splits these bands into