Nonlinear Optical Properties of Solids: Energy Considerations*

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It is shown that the interaction between macroscopic, nondissipative media, and time-varying electromagnetic fields can be described by a time-averaged potential function. From this function it is possible to derive phenomenologically the tensors that describe any of the usual electro- and magneto-optic effects for electric and magnetic fields of any frequency. In addition, these same potential functions describe the various optical nonlinearities like harmonic generation in potassium dihydrogen phosphate, and harmonic generation by electric quadrupole and magnetic dipole nonlinearities.

The symmetry relations first derived by Armstrong, Bloembergen, Ducuing, and Pershan for electric dipole nonlinearities follow directly from the methods presented here. In addition, one can derive analogous relations for electric quadrupole and magnetic dipole nonlinearities. These relations also demonstrate the reciprocal nature of the linear electro-optic effect and rectification of light. The Faraday effect and the production of a dc magnetization due to incident circularly polarized light are also reciprocal effects.

I. INTRODUCTION

THE nonlinear responses of macroscopic media to applied electric and magnetic fields at lower than optical frequencies are well known. Crystal rectifiers and harmonic generators, magnetic amplifiers, saturable reactors, etc., are just a few of many examples.

Until recently, the only available electromagnetic (EM) fields at optical frequencies were so feeble that one could linearize the response of any material body to them with no appreciable error. With the development of optical lasers, this is no longer true and recent experiments[1–6] have clearly demonstrated nonlinear responses to optical frequency fields.

Theoretically, these optical phenomena have been considered from both a quantum mechanical, or first principle, approach as well as phenomenologically.[7–13]

It is the purpose of this paper to show that energy considerations first suggested by Armstrong, Bloembergen, Ducuing, and Pershan (ABDP) can be generalized to include all nonlinear electromagnetic processes in which the medium is nonabsorptive. In particular, in addition to the ones first obtained by ABDP for electric dipole nonlinearities, it is possible to derive dispersion symmetry relations, for electric quadrupole and magnetic dipole optical nonlinearities, solely from macroscopic arguments. The method to be presented is so general that it will be possible to use one form of tensor to describe all nonlinear effects of the same type regardless of the frequencies involved. For example, the dc magnetic Voigt effect, microwave modulation of light by magnetic techniques, and magnetic optical nonlinearities are all described by different Fourier components of the same tensor. With the aid of these dispersion symmetry relations, it will be possible to estimate the order of magnitude of some of the, as yet, unobserved optical nonlinearities.

The thermodynamic, or energy, arguments will be developed in Sec. II. Sections III through V will be concerned with the various specific types of nonlinearities.

II. MAXWELL'S EQUATIONS—ENERGY CONSIDERATIONS

The starting point from which one derives the EM wave equations for macroscopic media is Maxwell's equations in vacuum and a distribution of charges and currents.[14,15]

$$\begin{aligned}\nabla\times\mathbf{e}&=-(1/c)\partial\mathbf{b}/\partial t,\\ \nabla\times\mathbf{b}&=(1/c)\partial\mathbf{e}/\partial t+(4\pi/c)\mathbf{j}.\end{aligned}\tag{2.1}$$

Taking a suitably defined average, one obtains

$$\begin{aligned}\nabla\times\mathbf{E}&=-(1/c)\partial\mathbf{B}/\partial t,\\ \nabla\times\mathbf{B}&=(1/c)\partial\mathbf{E}/\partial t+(4\pi/c)\mathbf{J},\end{aligned}\tag{2.2}$$

where[16]

$$\mathbf{J}=\partial\mathbf{P}/\partial t+c\nabla\times\mathbf{M}-\partial(\nabla\cdot\mathbf{Q})/\partial t+\cdots.\tag{2.3}$$

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[1] P. Franken, A. E. Hill, C. W. Peters, and G. Weinreich, Phys. Rev. Letters **7**, 118 (1961).
[2] M. Bass, P. A. Franken, A. E. Hill, C. W. Peters, and G. Weinreich, Phys. Rev. Letters **8**, 18 (1962).
[3] J. A. Giordmaine, Phys. Rev. Letters **8**, 19 (1962).
[4] P. D. Maker, R. W. Terhune, M. Nisenoff, and C. M. Savage, Phys. Rev. Letters **8**, 21 (1962).
[5] R. W. Terhune, P. D. Maker, and C. M. Savage, Phys. Rev. Letters **8**, 404 (1962).
[6] M. Bass, P. A. Franken, J. F. Ward, and G. Weinreich, Phys. Rev. Letters **9**, 446 (1962).
[7] T. Neugebauer, Acta. Phys. Acad. Sci. Hung. **10**, 221 (1959).
[8] D. A. Kleinman, Phys. Rev. **125**, 87 (1962).
[9] R. Braunstein, Phys. Rev. **125**, 475 (1962).
[10] W. C. Hennenberger, Bull. Am. Phys. Soc. **7**, 14 (1962).
[11] J. A. Armstrong, N. Bloembergen, J. Ducuing, and P. S. Pershan, Phys. Rev. **127**, 1918 (1962).
[12] N. Bloembergen and P. S. Pershan, Phys. Rev. **128**, 606 (1962).
[13] D. A. Kleinman, Phys. Rev. **126**, 1977 (1962).
[14] H. A. Lorentz, *The Theory of Electrons* (B. G. Teubner, Leipzig, 1909).
[15] J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibility* (Clarendon Press, Oxford, 1932).
[16] L. Rosenfeld, *Theory of Electrons* (Interscience Publishers, Inc., New York, 1951). The partition of currents into terms originating in electric dipole, magnetic dipole and electric quadrupole moments is useful for the discussion of volume elements small compared to the wavelengths involved. It is by no means a necessary step and for infinite media equivalent physical results are often obtained from different assignments of J to P, M, or Q. See L. D. Landau and E. M. Lifshitz, *Electrodynamics of Continuous Media* (Pergamon Press, Inc., New York, 1960), p. 252.

P is the electric dipole moment per unit volume, **M** is the magnetic dipole moment per unit volume, and **Q** is the electric quadrupole moment per unit volume. It is well known that the dipole moment per unit volume is uniquely defined only when the net charge density per unit volume is zero. Similarly, **M** and **Q** are not uniquely defined when $\partial\mathbf{P}/\partial t$ and **P**, respectively, are nonzero. It is possible, however, to define **M** and **Q** in a meaningful manner.

In the usual manner one obtains the following form of the energy conservation equation:

$$(c/4\pi)\nabla\cdot(\mathbf{E}\times\mathbf{B})+(1/4\pi)\mathbf{B}\cdot\partial\mathbf{B}/\partial t+(1/4\pi)\mathbf{E}\cdot\partial\mathbf{E}/\partial t+\mathbf{E}\cdot\mathbf{J}=0. \quad (2.4)$$

For a vacuum, i.e., $\mathbf{J}=0$, the first term is the power flow, and the second and third terms are the time derivative of the energy density per unit volume. The interaction between material and EM field is thus represented by the last term. It is important to realize that the last term is not simply the contribution of the material to the energy density per unit volume. Only when **M** and **Q** vanish can we regard $\mathbf{E}\cdot\mathbf{J}=\mathbf{E}\cdot\partial\mathbf{P}/\partial t$ as the time derivative of an energy density. This was the case, for example, in ABDP where only the electric dipole nonlinearity was treated. In general, one must do a partial integration to obtain

$$(c/4\pi)\nabla\cdot(\mathbf{E}\times\mathbf{H}-4\pi c^{-1}\mathbf{E}\cdot\partial\mathbf{Q}/\partial t)+(1/4\pi)\mathbf{H}\cdot\partial\mathbf{B}/\partial t+(1/4\pi)\mathbf{E}\cdot\partial\mathbf{D}/\partial t+\nabla\mathbf{E}:\partial\mathbf{Q}/\partial t=0, \quad (2.5)$$

where $\mathbf{H}=\mathbf{B}-4\pi\mathbf{M}$ and $\mathbf{D}=\mathbf{E}+4\pi\mathbf{P}$. Note that the above definition of **D** implies

$$\nabla\cdot\mathbf{D}-4\pi\nabla\nabla:\mathbf{Q}=4\pi\rho.$$

For the purposes of this paper, it is not important whether this definition or one in which $\nabla\cdot\mathbf{D}=4\pi\rho$ is given. The terms $-c\nabla\cdot(\mathbf{E}\times\mathbf{M})$ and $-\nabla\cdot(\mathbf{E}\cdot\partial\mathbf{Q}/\partial t)$ represent divergences of an energy flow through the material medium. This is demonstrated in Fig. 1 for the $\mathbf{E}\times\mathbf{M}$ term. The circular current corresponds to a magnetization out of the page. The charge gains energy from the **E** field at z_2 and gives it to the **E** field at z_1; there is a net transfer of energy from right to left opposite to the vector cross product $\mathbf{E}\times\mathbf{M}$. Similar considerations will demonstrate the power flow for the quadrupole term.

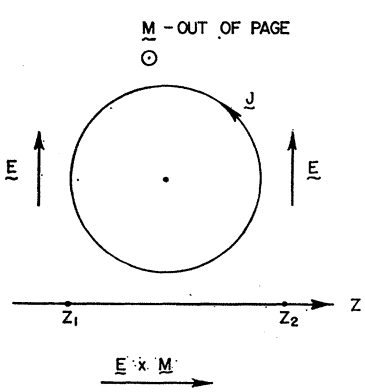

FIG. 1. Schematic demonstration of power flow proportional to $-(\mathbf{E}\times\mathbf{M})$. The counterclockwise current **J** is equivalent to a magnetization out of the page.

If the material energy density per unit volume is U,

$$\partial U/\partial t=\mathbf{H}\cdot\partial\mathbf{M}/\partial t+\mathbf{E}\cdot\partial\mathbf{P}/\partial t+\nabla\mathbf{E}:(\partial\mathbf{Q}/\partial t), \quad (2.6)$$

so that Eq. (2.5) becomes

$$\nabla\cdot\mathbf{S}+(1/4\pi)\mathbf{H}\cdot\partial\mathbf{H}/\partial t+(1/4\pi)\mathbf{E}\cdot\partial\mathbf{E}/\partial t+\partial U/\partial t=0, \quad (2.7)$$

where **S** is Poynting's vector generalized to include quadrupole effects. Equation (2.7) says that the rate at which energy flows out of a volume element is equal to the rate at which the energy stored in the EM field is decreasing {i.e., $-(1/4\pi)[\mathbf{H}\cdot\partial\mathbf{H}/\partial t+\mathbf{E}\cdot\partial\mathbf{E}/\partial t]$} plus the rate at which the material is doing work on the EM field (i.e., $-\partial U/\partial t$). Equation (2.6) can be recognized as the usual expression for the *work done on a system* by the external fields.[17]

Restricting our attention to nondissipative media, it is clear that in the steady state the average work done on (or by) the material must be zero. In the linear problem, for example, **E** and $\partial\mathbf{P}/\partial t$ are 90 deg out of phase and the average of their products vanishes. This is not to say, however, that the average energy stored in the medium by virtue of its polarization is zero. When the fields are initially turned on, work is done on (or by) the material to establish what is eventually termed the "steady state" amplitudes of **P**, **M**, **Q**, etc. It is most reasonable to assume that the net work done in producing the steady-state amplitudes is independent of the manner in which they were established. Equivalently, the final "steady-state" energy density only depends on the "steady-state" fields and polarizations, not on how they were produced.

In order to make these statements more quantitative, consider

$$\mathcal{E}(\omega,t)=\frac{1}{T}\int_{t-T/2}^{t+T/2}\mathbf{E}(t)\exp(-i\omega t)dt, \quad (2.8)$$

where T is a time long enough so that $\omega T\gg 1$, but still short enough that $\mathcal{E}(\omega,t)$ is independent of T. If we were only concerned with linear problems, this last point would mean that T is much less than the time in which the fields go from zero to their "steady-state" values. Actually, we are primarily interested in nonlinear problems so that T must be small compared to the time in which the nonlinear interactions will significantly change the Fourier distribution of any of the field variables. This means that we are restricted to weak nonlinearities. Fortunately, this is not a serious restriction since the nonlinearities in which we will be interested are weak enough that there is no difficulty in picking a time T. The Fourier distribution of all

[17] Mark W. Zemansky, *Heat and Thermodynamics* (McGraw-Hill Book Company, Inc., New York, 1961), pp. 60–65.

variables are defined similarly to Eq. (2.8) and will be indicated by script capitals. If there are n interacting waves,

$$E(t)=2\,\mathrm{Re}\sum_{\nu=1}^{n}\mathcal{E}(\omega_\nu,t)\exp(i\omega_\nu t) \tag{2.9}$$

and Eq. (2.6) becomes

$$\begin{aligned}\partial U/\partial t=2\,\mathrm{Re}\sum_{\nu=1}^{n}&[\mathcal{H}^*(\omega_\nu,t)\cdot\partial\mathfrak{M}(\omega_\nu,t)/\partial t\\&+i\omega_\nu\mathcal{H}^*(\omega_\nu,t)\cdot\mathfrak{M}(\omega_\nu,t)]\\&+2\,\mathrm{Re}\sum_{\nu=1}^{n}[\mathcal{E}^*(\omega_\nu,t)\cdot\partial\mathfrak{P}(\omega_\nu,t)/\partial t\\&+i\omega_\nu\mathcal{E}^*(\omega_\nu,t)\cdot\mathfrak{P}(\omega_\nu,t)]\\&+2\,\mathrm{Re}\sum_{\nu=1}^{n}[\nabla\mathcal{E}^*(\omega_\nu,t):\partial\mathfrak{Q}(\omega_\nu,t)/\partial t\\&+i\omega_\nu\nabla\mathcal{E}^*(\omega_\nu,t):\mathfrak{Q}(\omega_\nu,t)]\\&+\text{high-frequency terms.}\end{aligned} \tag{2.10}$$

The physical statements we have been able to make about the energy only pertained to the time average values. Averaging over T causes the high-frequency terms in Eq. (2.10) to vanish.

Under steady-state conditions $\partial\mathfrak{M}(\omega_\nu,t)/\partial t=0$, $\partial\mathfrak{P}(\omega_\nu,t)/\partial t=0$, $\partial\mathfrak{Q}(\omega_\nu,t)/\partial t=0$ and since one requires that $\langle\partial U/\partial t\rangle_T=0$

$$\begin{aligned}0=2\,\mathrm{Re}\sum_{\nu=1}^{n}i\omega_\nu[&\mathcal{H}^*(\omega_\nu,t)\cdot\mathfrak{M}(\omega_\nu,t)+\mathcal{E}^*(\omega_\nu,t)\cdot\mathfrak{P}(\omega_\nu,t)\\&+\nabla\mathcal{E}^*(\omega_\nu,t):\mathfrak{Q}(\omega_\nu,t)].\end{aligned} \tag{2.11}$$

Equation (2.11) is one way of saying that the total power flow is a constant even though it can redistribute itself amongst the several frequencies. ABDP demonstrated that for the $\mathcal{E}^*\cdot\mathfrak{P}$ term Eq. (2.11) followed from the symmetry relations. The argument cannot be reversed, however.

The physical argument that the steady-state energy density only depends on the final state and not on the path by which it was attained is equivalent to requiring $\langle\partial U/\partial t\rangle_T$ be an exact differential; i.e., $\langle\partial U/\partial t\rangle_T=d\Phi/dt$, or

$$\begin{aligned}d\Phi=2\,\mathrm{Re}\sum_{\nu=1}^{n}&[\mathcal{H}^*(\omega_\nu,t)\cdot d\mathfrak{M}(\omega_\nu,t)\\&+\mathcal{E}^*(\omega_\nu,t)\cdot d\mathfrak{P}(\omega_\nu,t)+\nabla\mathcal{E}^*:d\mathfrak{Q}(\omega_\nu,t)].\end{aligned} \tag{2.12}$$

One can define a second potential

$$\begin{aligned}F=\Phi-2\,\mathrm{Re}\sum_{\nu=1}^{n}&[\mathcal{H}^*(\omega_\nu,t)\cdot\mathfrak{M}(\omega_\nu,t)\\&+\mathcal{E}^*(\omega_\nu,t)\cdot\mathfrak{P}(\omega_\nu,t)+\nabla\mathcal{E}^*(\omega_\nu,t):\mathfrak{Q}(\omega_\nu,t)],\end{aligned} \tag{2.13}$$

so that

$$\mathfrak{P}(\omega_\nu,t)=-\partial F/\partial\mathcal{E}^*(\omega_\nu,t), \tag{2.14a}$$

$$\mathfrak{M}(\omega_\nu,t)=-\partial F/\partial\mathcal{H}^*(\omega_\nu,t), \tag{2.14b}$$

$$\mathfrak{Q}(\omega_\nu,t)=-\partial F/\partial[\nabla\mathcal{E}^*(\omega_\nu,t)]. \tag{2.14c}$$

From the existence of a "time-averaged free energy" and the relations (2.14a, b, c) one can describe all of the conventional electro- and magneto-optical effects as well as all of the phenomena by which one obtains parametric amplification with nondissipative media. Many of the dispersive effects in magnetic double resonance experiments also follow. In the subsequent sections we will consider several forms for F and the phenomena which they lead to.

For weak nonlinearities, by the methods of ABDP, macroscopic current density $\mathbf{J}$ in Eq. (2.2) and Eq. (2.3) can be partitioned into linear and nonlinear parts. At the frequency ω_ν one can write

$$\begin{aligned}\nabla\times\mathcal{E}(\omega_\nu)&=-i(\omega_\nu/c)\mathcal{H}(\omega_\nu),\\\nabla\times\mathcal{H}(\omega_\nu)&=i(\omega_\nu/c)\boldsymbol{\varepsilon}(\omega_\nu)\cdot\mathcal{E}(\omega_\nu)\\&\quad+(4\pi/c)\mathfrak{J}(\omega_\nu)^{\mathrm{NLS}},\end{aligned} \tag{2.15}$$

where it has been assumed that the linear material is nonmagnetic: i.e., $\boldsymbol{\mu}(\omega_\nu)=1$ so that $\mathcal{H}(\omega_\nu)=\mathfrak{B}(\omega_\nu)$, and $\mathfrak{J}(\omega_\nu)^{\mathrm{NLS}}$ is given by the ω_νth Fourier component of the nonlinear part of Eq. (2.3) where the superscript NLS means nonlinear source. The linear dielectric constant at ω_ν is given by $\boldsymbol{\varepsilon}(\omega_\nu)$. An equivalent form of Eq. (2.15) would be

$$\begin{aligned}\nabla\times\mathcal{E}(\omega_\nu)&=-i(\omega_\nu/c)[\mathcal{H}(\omega_\nu)+4\pi\mathfrak{M}(\omega_\nu)^{\mathrm{NLS}}],\\\nabla\times\mathcal{H}(\omega_\nu)&=i(\omega_\nu/c)[\boldsymbol{\varepsilon}(\omega_\nu)\cdot\mathcal{E}(\omega_\nu)+4\pi\mathfrak{P}(\omega_\nu)^{\mathrm{NLS}}\\&\quad-4\pi\nabla\cdot\mathfrak{Q}(\omega_\nu)^{\mathrm{NLS}}],\end{aligned} \tag{2.16}$$

where

$$\mathcal{H}(\omega_\nu)=\mathfrak{B}(\omega_\nu)-4\pi\mathfrak{M}(\omega_\nu)^{\mathrm{NLS}}.$$

The difference between Eqs. (2.15) and (2.16) is the difference in the meaning of $\mathcal{H}(\omega_\nu)$. The two different definitions of $\mathcal{H}(\omega_\nu)$ will lead to different boundary conditions and slightly different, although equivalent, forms for the energy density and power flow. Equation (2.15) with correct boundary conditions proves most straightforward to use in the approximation that $|\mathfrak{J}^{\mathrm{NLS}}(\omega_\nu)|$ is a constant. This is the approach used by Bloembergen and Pershan[12] in the treatment of boundary harmonics. The interpretation of the exact nonlinear coupled amplitude equations of ABDP will be somewhat more direct for magnetic nonlinearities when Eq. (2.16) is used.

III. ELECTRIC DIPOLE EFFECTS

We will consider all effects that can be derived from a free energy of the form $\boldsymbol{\chi}:\mathcal{E}\mathcal{E}$, $\boldsymbol{\chi}:\mathcal{E}\mathcal{E}\mathcal{E}$, etc., as electric dipole effects. The first term is, of course, the free energy for a linear medium, but it proves illustrative to treat it by the methods we use for the more complicated phenomena.

Consider the free energy

$$F=-\tfrac{1}{2}[\chi_{ij}(\omega)\mathcal{E}_i^*(\omega)\mathcal{E}_j(\omega)+\chi_{ij}^*(\omega)\mathcal{E}_i(\omega)\mathcal{E}_j^*(\omega)], \quad (3.1)$$

where it is understood that repeated indices are to be summed over. Since there are only nine independent products $\mathcal{E}_i^*(\omega)\mathcal{E}_j(\omega)$, there can be only nine independent tensor components, i.e., $\chi(\omega)$ is Hermitian:

$$\chi_{ij}(\omega)=\chi_{ji}^*(\omega). \quad (3.2)$$

From Eq. (2.14a)

$$\mathfrak{P}_i(\omega)=-\partial F/\partial\mathcal{E}_i^*(\omega)=\chi_{ij}(\omega)\mathcal{E}_j(\omega),$$

and the dielectric tensor ϵ

$$\epsilon_{ij}(\omega)=1+4\pi\chi_{ij}(\omega) \quad (3.3)$$

is also Hermitian. If the crystal is nonmagnetic, it is invariant under time reversal and the tensor χ must also be invariant under time reversal. From Eq. (A7) of the Appendix one obtains

$$\chi_{ij}(\omega)=\chi_{ij}^*(\omega), \quad (3.4)$$

so that χ and $\boldsymbol{\varepsilon}$ are real symmetric tensors, as is well known. Note, however, that for magnetic crystals the off-diagonal elements are imaginary and one obtains the well-known Faraday rotation. This is discussed at greater length in Sec. V when magnetic nonlinearities are considered. A second point worth noting, however, is that optical activity is not an electric dipole effect, since this requires imaginary off-diagonal elements of $\boldsymbol{\varepsilon}$ for a crystal invariant under time reversal.[18] In Sec. V it is shown that optical activity follows from a free energy of the form $\chi:\mathcal{E}\mathcal{H}$.

The linear electro-optic,[19] or Pockels, effect and the largest of the optical nonlinearities can be obtained from a free energy of the form

$$F=-[\chi_{ijk}(\omega_3,\omega_2,\omega_1)\mathcal{E}_i^*(\omega_3)\mathcal{E}_j(\omega_2)\mathcal{E}_k(\omega_1) +\chi_{ijk}^*(\omega_3,\omega_2,\omega_1)\mathcal{E}_i(\omega_3)\mathcal{E}_j^*(\omega_2)\mathcal{E}_k^*(\omega_1)], \quad (3.5)$$

where $\omega_3=\omega_1+\omega_2$.

Since there is only one way to form the product of the ith component of $\boldsymbol{\mathcal{E}}^*(\omega_3)$, the jth component of $\boldsymbol{\mathcal{E}}(\omega_2)$, and the kth component of $\boldsymbol{\mathcal{E}}(\omega_1)$, there is only one quantity $\chi_{ijk}(\omega_3,\omega_2,\omega_1)$ and any permutation of frequencies and indices must be equal, i.e., $\chi_{ijk}(\omega_3,\omega_2,\omega_1)=\chi_{jik}(\omega_2,\omega_3,\omega_1)$, etc. This is not yet the symmetry obtained by ABDP which are relations between the nonlinear polarizability tensors.

From Eq. (2.14a) we have

$$\begin{aligned}\mathfrak{P}_i(\omega_3)&=\chi_{ijk}(\omega_3,\omega_2,\omega_1)\mathcal{E}_j(\omega_2)\mathcal{E}_k(\omega_1),\\ \mathfrak{P}_j(\omega_2)&=\chi_{ijk}^*(\omega_3,\omega_2,\omega_1)\mathcal{E}_i(\omega_3)\mathcal{E}_k^*(\omega_1),\\ \mathfrak{P}_k(\omega_1)&=\chi_{ijk}^*(\omega_3,\omega_2,\omega_1)\mathcal{E}_i(\omega_3)\mathcal{E}_j^*(\omega_2).\end{aligned} \quad (3.6)$$

The tensors of ABDP, ${}^0\chi$, were defined initially from the following relations:

$$\begin{aligned}\mathfrak{P}_i(\omega_3)&={}^0\chi_{ijk}(\omega_3,\omega_2,\omega_1)\mathcal{E}_j(\omega_2)\mathcal{E}_k(\omega_1),\\ \mathfrak{P}_j(\omega_2)&={}^0\chi_{jik}(\omega_2,\omega_3,\omega_1)\mathcal{E}_i(\omega_3)\mathcal{E}_k^*(\omega_1),\\ \mathfrak{P}_k(\omega_1)&={}^0\chi_{kij}(\omega_1,\omega_3,\omega_2)\mathcal{E}_i(\omega_3)\mathcal{E}_j^*(\omega_2).\end{aligned} \quad (3.7)$$

From Eqs. (3.6) and (3.7) we have

$$\begin{aligned}\chi_{ijk}(\omega_3,\omega_2,\omega_1)={}^0\chi_{ijk}(\omega_3,\omega_2,\omega_1)&=[{}^0\chi_{jik}(\omega_2,\omega_3,\omega_1)]^*\\ &=[{}^0\chi_{kij}(\omega_1,\omega_3,\omega_2)]^*.\end{aligned} \quad (3.8)$$

For crystals invariant under time reversal, Eq. (A7) of the Appendix shows

$$\chi_{ijk}(\omega_3,\omega_2,\omega_1)=\chi_{ijk}^*(\omega_3,\omega_2,\omega_1),$$

and Eq. (3.8) is equivalent to the relations obtained by ABDP. For crystals which lack time-inversion symmetry, Eq. (3.8) is a generalization of those relations.

For the particular case of second-harmonic generation it is simplest to start from the free energy rather than to take the limits of Eqs. (3.6) as $\omega_1\to\omega_2$. In the limiting procedure it is difficult to keep track of factors of 2.

The physical effects resulting from these types of nonlinearities at optical frequencies have been thoroughly treated by ABDP and others.[12]

To obtain the low-frequency linear electro-optic effect, one must take the limit as $\omega_1\to 0$. The free energy, Eq. (3.5), must be extended to include the case when $\omega_3=\omega_2-\omega_1$. If ω_1 is small, one should expect

$$\chi_{ijk}(\omega_2+\omega_1,\omega_2,\omega_1)=\chi_{ijk}(\omega_2,\omega_2-\omega_1,\omega_1),$$

so that

$$F=-2\,\mathrm{Re}\chi_{ijk}(\omega_2+\omega_1,\omega_2,\omega_1)[\mathcal{E}_i^*(\omega_2+\omega_1)\mathcal{E}_j(\omega_2)\mathcal{E}_k(\omega_1) +\mathcal{E}_i^*(\omega_2)\mathcal{E}_j(\omega_2-\omega_1)\mathcal{E}_k(\omega_1)]. \quad (3.9)$$

If the nonlinearity is large enough so that the amplitudes of the side bands, i.e., $\omega_2\pm\omega_1$, become comparable to the amplitude at ω_2, the free energy must be extended further to include the other side bands; i.e., $\omega_2\pm 2\omega_1$, $\omega_2\pm 3\omega_1$, $\cdots$, etc.

IV. ELECTRIC QUADRUPOLE EFFECTS

All effects that are derivable from a free energy of the form $\chi:\mathcal{E}\nabla\mathcal{E}$, $\chi\vdots\mathcal{E}\mathcal{E}\nabla\mathcal{E}$, etc., will be considered electric quadrupole effects. This does not imply neglecting electric dipole moments of the form $\chi:\nabla\mathcal{E}$ and $\chi:\mathcal{E}\nabla\mathcal{E}$ but rather that these effects have their origin in a quadrupole-type interaction. Restricting attention, at this time, to tensors χ symmetric in the last two indices; i.e., if

$$\chi(\omega_3,\omega_2,\omega_1)\vdots\mathcal{E}^*(\omega_3)\mathcal{E}(\omega_2)\nabla\mathcal{E}(\omega_1) \equiv\chi_{ijkl}(\omega_3,\omega_2,\omega_1)\mathcal{E}_i^*(\omega_3)\mathcal{E}_j(\omega_2)\partial_k\mathcal{E}_l(\omega_1),$$

it is assumed that

$$\chi_{ijkl}(\omega_3,\omega_2,\omega_1)=\chi_{ijlk}(\omega_3,\omega_2,\omega_1). \quad (4.1)$$

[18] E. U. Condon, Rev. Mod. Phys. **9**, 432 (1937).

[19] *American Institute of Physics Handbook*, edited by Dwight E. Gray (McGraw-Hill Book Company, Inc., New York, 1957).

That part of χ antisymmetric in the last two indices will multiply $\partial_k \mathcal{E}_l(\omega_1) - \partial_l \mathcal{E}_k(\omega_1)$ and this is equal to $-i(4\pi\omega_1/c)\epsilon^{kln}\mathcal{H}_n(\omega_1)$, where ϵ^{kln} is the unit antisymmetric tensor of the third rank. If kln is a cyclic permutation of x, y, z, $\epsilon^{kln}=+1$; if it is an antisymmetric permutation, $\epsilon^{kln}=-1$. Thus, the part of χ antisymmetric in the last two indices can be written as $\chi:\mathcal{E}\mathcal{H}$, $\chi\vdots\mathcal{E}\mathcal{E}\mathcal{H}$, etc. Terms of this type will be discussed in detail in Sec. V.

A free energy of the form $\chi\vdots\mathcal{E}\nabla\mathcal{E}$, symmetric in the last two indices, corresponds to a quadrupole correction to the linear dielectric constant. The third rank tensor χ reverses sign on inversion of the spatial coordinates: i.e., $x\to -x$, $y\to -y$, $z\to -z$, and thus vanishes for all crystals invariant under spatial inversion. For the remaining crystals this correction has been treated in detail by Satten[20] and will not be discussed here. Terms of the form $F=-\chi\vdots(\nabla\mathcal{E})(\nabla\mathcal{E})$ are of higher order and are neglected here.

The lowest order nonlinear quadrupole term has a free energy of the form

$$\begin{aligned}F=-2\,\mathrm{Re}[&\chi_{ijkl}(\omega_3,\omega_2,\omega_1)\mathcal{E}_i^*(\omega_3)\mathcal{E}_j(\omega_2)\partial_k\mathcal{E}_l(\omega_1)\\&+\chi_{likj}(\omega_1,\omega_3,\omega_2)\mathcal{E}_l(\omega_1)\mathcal{E}_i^*(\omega_3)\partial_k\mathcal{E}_j(\omega_2)\\&+\chi_{jlki}(\omega_2,\omega_1,\omega_3)\mathcal{E}_j(\omega_2)\mathcal{E}_l(\omega_1)\partial_k\mathcal{E}_i^*(\omega_3)]\end{aligned}\tag{4.2}$$

for $\omega_3=\omega_1+\omega_2$.

In addition to the symmetry of Eq. (4.1), one requires the dispersion, or permutation symmetry relations between the first two indices of the type

$$\begin{aligned}&\chi_{ijkl}(\omega_3,\omega_2,\omega_1)=\chi_{jikl}(\omega_2,\omega_3,\omega_1),\\&\chi_{likj}(\omega_1,\omega_3,\omega_2)=\chi_{ilkj}(\omega_3,\omega_1,\omega_2),\\&\text{etc.}\end{aligned}\tag{4.3}$$

The reasoning behind Eq. (4.3) is the same as was used to justify the symmetry of the tensor in Eq. (3.5). The importance of a free energy of this type derives from the fact that for crystals invariant under space inversion it represents the largest nonmagnetic mechanism for producing second harmonic.

From Eqs. (2.14a, c) and (4.2) one obtains

$$\begin{aligned}\mathfrak{P}_i(\omega_3)&=\chi_{ijkl}(\omega_3,\omega_2,\omega_1)\mathcal{E}_j(\omega_2)\partial_k\mathcal{E}_l(\omega_1)\\&\quad+\chi_{likj}(\omega_1,\omega_3,\omega_2)\mathcal{E}_l(\omega_1)\partial_k\mathcal{E}_j(\omega_2),\\\mathfrak{Q}_{ki}(\omega_3)&=\chi_{jlki}(\omega_2,\omega_1,\omega_3)\mathcal{E}_j(\omega_2)\mathcal{E}_l(\omega_1),\end{aligned}\tag{4.4a}$$

$$\begin{aligned}\mathfrak{P}_j(\omega_2)&=\chi_{ijkl}^*(\omega_3,\omega_2,\omega_1)\mathcal{E}_i(\omega_3)\partial_k\mathcal{E}_l^*(\omega_1)\\&\quad+\chi_{jlki}^*(\omega_2,\omega_1,\omega_3)\mathcal{E}_l^*(\omega_1)\partial_k\mathcal{E}_i(\omega_3),\\\mathfrak{Q}_{kj}(\omega_2)&=\chi_{likj}^*(\omega_1,\omega_3,\omega_2)\mathcal{E}_l^*(\omega_1)\mathcal{E}_i(\omega_3),\end{aligned}\tag{4.4b}$$

and

$$\begin{aligned}\mathfrak{P}_l(\omega_1)&=\chi_{likj}^*(\omega_1,\omega_3,\omega_2)\mathcal{E}_i(\omega_3)\partial_k\mathcal{E}_j^*(\omega_2)\\&\quad+\chi_{jlki}^*(\omega_2,\omega_1,\omega_3)\mathcal{E}_j^*(\omega_2)\partial_k\mathcal{E}_i(\omega_3),\\\mathfrak{Q}_{kl}(\omega_1)&=\chi_{ijkl}^*(\omega_3,\omega_2,\omega_1)\mathcal{E}_i(\omega_3)\mathcal{E}_j^*(\omega_2).\end{aligned}\tag{4.4c}$$

[20] Robert A. Satten, J. Chem. Phys. **26**, 766 (1956).

It is a rather trivial loss of generality to restrict attention here to crystals invariant under time reversal. From Eq. (A7) of the Appendix, all the χ's are real and, henceforth, the stars can be neglected. The nonlinear source currents $\mathfrak{J}^{\mathrm{NLS}}$, to be inserted into Eqs. (2.15) are of the form

$$\mathfrak{J}_i(\omega_\nu)^{\mathrm{NLS}}=i\omega_\nu[\mathfrak{P}_i(\omega_\nu)^{\mathrm{NLS}}-\partial_k\mathfrak{Q}_{ki}(\omega_\nu)^{\mathrm{NLS}}],\tag{4.5}$$

$$\begin{aligned}\mathfrak{J}_i(\omega_3)^{\mathrm{NLS}}=i\omega_3[&\chi_{ijkl}(\omega_3,\omega_2,\omega_1)\\&-\chi_{jlki}(\omega_2,\omega_1,\omega_3)]\mathcal{E}_j(\omega_2)\partial_k\mathcal{E}_l(\omega_1)\\&+i\omega_3[\chi_{likj}(\omega_1,\omega_3,\omega_2)-\chi_{jlki}(\omega_2,\omega_1,\omega_3)]\\&\times\mathcal{E}_l(\omega_1)\partial_k\mathcal{E}_j(\omega_2),\end{aligned}\tag{4.6a}$$

$$\begin{aligned}\mathfrak{J}_j(\omega_2)^{\mathrm{NLS}}=i\omega_2[&\chi_{ijkl}(\omega_3,\omega_2,\omega_1)-\chi_{likj}(\omega_1,\omega_3,\omega_2)]\\&\times\mathcal{E}_i(\omega_3)\partial_k\mathcal{E}_l^*(\omega_1)\\&+i\omega_2[\chi_{jlki}(\omega_2,\omega_1,\omega_3)-\chi_{likj}(\omega_1,\omega_3,\omega_2)]\\&\times\mathcal{E}_l^*(\omega_1)\partial_k\mathcal{E}_i(\omega_3),\end{aligned}\tag{4.6b}$$

$$\begin{aligned}\mathfrak{J}_l(\omega_1)^{\mathrm{NLS}}=i\omega_1[&\chi_{likj}(\omega_1,\omega_3,\omega_2)-\chi_{ijkl}(\omega_3,\omega_2,\omega_1)]\\&\times\mathcal{E}_i(\omega_3)\partial_k\mathcal{E}_j^*(\omega_2)\\&+i\omega_1[\chi_{jlki}(\omega_2,\omega_1,\omega_3)-\chi_{ijkl}(\omega_3,\omega_2,\omega_1)]\\&\times\mathcal{E}_j^*(\omega_2)\partial_k\mathcal{E}_i(\omega_3).\end{aligned}\tag{4.6c}$$

Defining tensors χ^{eff} such that

$$\begin{aligned}\mathfrak{J}(\omega_3)^{\mathrm{NLS}}&=i\omega_3\chi^{\mathrm{eff}}(\omega_3,\omega_2,\omega_1):\mathcal{E}(\omega_2)\mathcal{E}(\omega_1),\\\mathfrak{J}(\omega_2)^{\mathrm{NLS}}&=i\omega_2\chi^{\mathrm{eff}}(\omega_2,\omega_1,\omega_3):\mathcal{E}^*(\omega_1)\mathcal{E}(\omega_3),\\\mathfrak{J}(\omega_1)^{\mathrm{NLS}}&=i\omega_1\chi^{\mathrm{eff}}(\omega_1,\omega_3,\omega_2):\mathcal{E}(\omega_3)\mathcal{E}^*(\omega_2),\end{aligned}\tag{4.7}$$

one can see that the permutation symmetry relations of ABDP [i.e., Eqs. (3.8)] do not hold exactly for χ^{eff}. For example, if $\mathbf{k}_3=\mathbf{k}_1+\mathbf{k}_2+\Delta\mathbf{k}$, from Eq. (4.3)

$$\begin{aligned}&[\chi_{ijl}^{\mathrm{eff}}(\omega_3,\omega_2,\omega_1)]^*-\chi_{lji}^{\mathrm{eff}}(\omega_1,\omega_2,\omega_3)\\&\quad=i[\chi_{ijkl}(\omega_3,\omega_2,\omega_1)-\chi_{ljki}(\omega_1,\omega_2,\omega_3)](\Delta\mathbf{k})_k.\end{aligned}\tag{4.8}$$

Only for the case of exact phase matching, i.e., $\Delta\mathbf{k}=0$, can one treat the current elements of Eqs. (4.6) as effective dipole moments per unit volume. The right-hand side of Eq. (4.8) is related to the transport of energy by the quadrupole interactions as discussed in relation to Eq. (2.5). Since χ^{eff} is imaginary, and $\omega_3=\omega_1+\omega_2$,

$$\begin{aligned}&\langle\mathbf{E}(t)\cdot\mathbf{J}(t)^{\mathrm{NLS}}\rangle\\&\quad=2\,\mathrm{Re}[i\omega_2\{\chi_{jli}^{\mathrm{eff}}(\omega_2,\omega_1,\omega_3)-[\chi_{ijl}^{\mathrm{eff}}(\omega_3,\omega_2,\omega_1)]^*\}\\&\qquad+i\omega_1\{\chi_{lij}^{\mathrm{eff}}(\omega_1,\omega_3,\omega_2)-[\chi_{ijl}^{\mathrm{eff}}(\omega_3,\omega_2,\omega_1)]^*\}]\\&\qquad\times\mathcal{E}_l^*(\omega_1)\mathcal{E}_j^*(\omega_2)\mathcal{E}_i(\omega_3).\end{aligned}$$

Applying Eqs. (4.3) and (4.8)

$$\begin{aligned}&\langle\mathbf{E}(t)\cdot\mathbf{J}(t)^{\mathrm{NLS}}\rangle\\&\quad=2\,\mathrm{Re}\{[i\omega_1\chi_{ijkl}(\omega_3,\omega_2,\omega_1)+i\omega_2\chi_{likj}(\omega_1,\omega_3,\omega_2)\\&\qquad-i\omega_3\chi_{jlki}(\omega_2,\omega_1,\omega_3)]\\&\qquad\times[(-i\Delta\mathbf{k})_k\mathcal{E}_l^*(\omega_1)\mathcal{E}_j^*(\omega_2)\mathcal{E}_i(\omega_3)]\},\end{aligned}\tag{4.9}$$

and this can be recognized as the time average of $\nabla\cdot[\mathbf{E}(t)\cdot\partial\mathfrak{Q}/\partial t]$.

The coupled amplitude equations developed by

ABDP [i.e., Eqs. (4.9) of ABDP] can be generalized to include quadrupole nonlinearities by replacing $i\omega_\nu \mathfrak{P}(\omega_\nu)^{\mathrm{NLS}}$ with $\mathfrak{J}(\omega_\nu)^{\mathrm{NLS}}$. The exact solutions will follow in the same manner as the dipole nonlinearity except that the integration constant corresponding to the time average Poynting's vector will not be simply $\langle \mathbf{E}\times\mathbf{H}\rangle_T$, but it will have an additional term corresponding to the transport of energy by the quadrupole interaction shown in Eq. (4.9).

The currents given by Eqs. (4.6) can be seen to be invariant if one adds to the free energy [Eq. (4.2)] a term that would correspond to a surface-energy density, $F'=F+\nabla\cdot\mathbf{G}$

$$\nabla\cdot\mathbf{G}=\partial_k[\mathcal{Y}_{kijl}(\omega_3,\omega_2,\omega_1)\mathcal{E}_i^*(\omega_3)\mathcal{E}_j(\omega_2)\mathcal{E}_l(\omega_1)]. \quad (4.10)$$

If $\chi_{ijkl}(\omega_3,\omega_2,\omega_1)=\chi_{jlki}(\omega_2,\omega_1,\omega_3)=\chi_{likj}(\omega_1,\omega_3,\omega_2)$, Eq. (4.2) reduces to a surface-energy density, and Eqs. (4.6) all yield zero currents. It may often prove convenient to define new tensors χ' by a suitable definition of $\mathcal{Y}$ such that F' is given by Eq. (4.2) with χ' replacing χ and

$$\chi_{ijkl}'(\omega_3,\omega_2,\omega_1)+\chi_{jlki}'(\omega_2,\omega_1,\omega_3)+\chi_{likj}'(\omega_1,\omega_3,\omega_2)=0. \quad (4.11)$$

Alternatively, one could set one of the tensors, for example, $\chi'(\omega_3,\omega_2,\omega_1)=0$, with no loss of generality.

For second harmonic generation there are only two tensors, $\chi(\omega,\omega,2\omega)$ and $\chi(2\omega,\omega,\omega)$. With no loss of generality one could set $\chi(2\omega,\omega,\omega)=0$ and obtain

$$F=-2\,\mathrm{Re}\chi(\omega,\omega,2\omega)\vdots\boldsymbol{\mathcal{E}}(\omega)\boldsymbol{\mathcal{E}}(\omega)\nabla\boldsymbol{\mathcal{E}}^*(2\omega), \quad (4.12)$$

so that

$$\mathfrak{J}^{\mathrm{NLS}}(2\omega)=-\frac{\partial}{\partial t}\nabla\cdot\mathfrak{Q}(2\omega)$$
$$=-2i\omega\nabla\cdot[\chi(\omega,\omega,2\omega):\boldsymbol{\mathcal{E}}(\omega)\boldsymbol{\mathcal{E}}(\omega)]. \quad (4.13)$$

For an isotropic material, the form of $\chi(\omega,\omega,2\omega)$ is given by Table I. It is straightforward to demonstrate that for a plane wave at frequency ω moving with wave vector $\mathbf{k}(\omega)$ such that $\mathbf{k}(\omega)\cdot\boldsymbol{\mathcal{E}}(\omega)=0$ the current given by Eq. (4.13) is parallel to $\mathbf{k}(\omega)$. Neglecting surface harmonics[12] this current cannot generate a second harmonic.

TABLE I. The form of the tensor $\chi(\omega,\omega,2\omega)$ to be used in Eqs. (4.12) and (4.13) for isotropic materials.[a]

$ij \backslash kl$	$\chi_{ijkl}(\omega,\omega,2\omega)$								
	xx	yy	zz	yz	zy	zx	xz	xy	yx
xx	$\chi_{1,1}$	$\chi_{1,2}$	$\chi_{1,2}$						
yy	$\chi_{1,2}$	$\chi_{1,1}$	$\chi_{1,2}$						
zz	$\chi_{1,2}$	$\chi_{1,2}$	$\chi_{1,1}$						
yz				$\chi_{6,6}$	$\chi_{6,6}$				
zy				$\chi_{6,6}$	$\chi_{6,6}$				
zx						$\chi_{6,6}$	$\chi_{6,6}$		
xz						$\chi_{6,6}$	$\chi_{6,6}$		
xy								$\chi_{6,6}$	$\chi_{6,6}$
yx								$\chi_{6,6}$	$\chi_{6,6}$

[a] $\chi_{6,6}=\frac{1}{2}(\chi_{1,1}-\chi_{1,2})$.

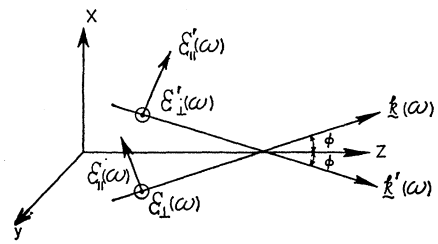

FIG. 2. A possible geometry for generating second harmonic radiation in an isotropic material with anomalous dispersion.

If the field $\mathcal{E}(\omega)$ is not a simple plane wave, but two plane waves as shown in Fig. 2, it is possible to match phase velocities in the z direction, if the isotropic material exhibits anomalous dispersion. The sum of $\boldsymbol{\mathcal{E}}(\omega)$ and $\boldsymbol{\mathcal{E}}'(\omega)$ has components

$$\begin{aligned}\mathcal{E}_x(\omega)&=[(\mathcal{E}_{\parallel}+\mathcal{E}_{\parallel}')\cos\phi\cos k_x x\\&\quad-i(\mathcal{E}_{\parallel}-\mathcal{E}_{\parallel}')\cos\phi\sin k_x x]\exp(-ik_z z),\\ \mathcal{E}_y(\omega)&=[(\mathcal{E}_{\perp}+\mathcal{E}_{\perp}')\cos k_x x-i(\mathcal{E}_{\perp}-\mathcal{E}_{\perp}')\sin k_x x]\\&\quad\times\exp(-ik_z z), \quad (4.14)\\ \mathcal{E}_z(\omega)&=[(\mathcal{E}_{\parallel}'-\mathcal{E}_{\parallel})\sin\phi\cos k_x x+i(\mathcal{E}_{\parallel}'+\mathcal{E}_{\parallel})\\&\quad\times\sin\phi\sin k_x x]\exp(-ik_z z).\end{aligned}$$

The quadrupole moments and the currents can be obtained by direct substitution of Eqs. (4.14) into Eq. (4.13) where χ is given in Table I. The only terms that will couple to a plane wave at 2ω propagating in the z direction are the parts of $\mathfrak{Q}_{xz}$ and $\mathfrak{Q}_{yz}$ that do not have an x-spatial dependence. The term $\mathfrak{Q}_{xz}(2\omega)$ vanishes identically, however,

$$\begin{aligned}\mathfrak{Q}_{yz}(2\omega)&=\chi_{6,6}(\mathcal{E}_{\parallel}'\mathcal{E}_{\perp}-\mathcal{E}_{\parallel}\mathcal{E}_{\perp}')\sin\phi\exp(-i2k_z z),\\ \mathfrak{J}_y^{\mathrm{NLS}}(2\omega)&=-4\omega k_z\chi_{6,6}(\mathcal{E}_{\parallel}'\mathcal{E}_{\perp}-\mathcal{E}_{\parallel}\mathcal{E}_{\perp}')\\&\quad\times\sin\phi\exp(-i2k_z z). \quad (4.15)\end{aligned}$$

Observe that if there is symmetry between $\boldsymbol{\mathcal{E}}$ and $\boldsymbol{\mathcal{E}}'$ such that $\mathcal{E}_{\parallel}'=\mathcal{E}_{\parallel}$ and $\mathcal{E}_{\perp}=\mathcal{E}_{\perp}'$, there is no second harmonic generation. This effect can be large only for large anomalous dispersion since

$$\sin\phi=\{1-[n(2\omega)/n(\omega)]^2\}^{1/2}.$$

Second harmonic generation by means of a quadrupole nonlinearity will thus be a very weak effect in all isotropic media.

Anisotropic media, on the other hand, can have observable second harmonic generation by a quadrupole nonlinearity. Consider the tensor $\chi(\omega,\omega,2\omega)$ for calcite given in Table II. There are several differences between this and the fourth rank elastic tensors. For example, $\chi_{xxzz}(\omega,\omega,2\omega)\neq\chi_{zzxx}(\omega,\omega,2\omega)$, $\chi_{xxyz}(\omega,\omega,2\omega)\neq\chi_{yzxx}(\omega,\omega,2\omega)$ because there are no operations that will transform z into x or y and leave the crystal invariant. The identity $\chi_{xxyy}(\omega,\omega,2\omega)=\chi_{yyxx}(\omega,\omega,2\omega)$ follows from the operations of a trigonal axis in calcite.

TABLE II. The form of the tensor $\chi(\omega,\omega,2\omega)$ to be used in Eqs. (4.12) and (4.13) for calcite.[a]

$ij \backslash kl$	xx	yy	zz	yz	zy	xz	zx	xy	yx
xx	$\chi_{1,1}$	$\chi_{1,2}$	$\chi_{1,3}$	$\chi_{1,4}$	$\chi_{1,4}$				
yy	$\chi_{1,2}$	$\chi_{1,1}$	$\chi_{1,3}$	$-\chi_{1,4}$	$-\chi_{1,4}$				
zz	$\chi_{3,1}$	$\chi_{3,1}$	$\chi_{3,3}$						
yz	$\chi_{4,1}$	$-\chi_{4,1}$		$\chi_{4,4}$	$\chi_{4,4}$				
zy	$\chi_{4,1}$	$-\chi_{4,1}$		$\chi_{4,4}$	$\chi_{4,4}$				
xz						$\chi_{4,4}$	$\chi_{4,4}$	$\chi_{4,1}$	$\chi_{4,1}$
zx						$\chi_{4,4}$	$\chi_{4,4}$	$\chi_{4,1}$	$\chi_{4,1}$
xy						$\chi_{1,4}$	$\chi_{1,4}$	$\chi_{6,6}$	$\chi_{6,6}$
yx						$\chi_{1,4}$	$\chi_{1,4}$	$\chi_{6,6}$	$\chi_{6,6}$

[a] $\chi_{6,6}=\frac{1}{2}[\chi_{1,1}-\chi_{1,2}]$.

One can match the phase velocity of an ordinary ray at the fundamental frequency to an extraordinary ray at the second harmonic[3,4] as shown in Fig. 3. As discussed in ABDP [Eq. (4.8)], harmonic generation is due to the component of $\mathfrak{J}^{\mathrm{NLS}}(2\omega)$ parallel to $\hat{e}_2$; i.e.,

$$|\mathfrak{J}^{\mathrm{NLS}}(2\omega)|_{\mathrm{useful}}=-(4\omega^2\epsilon^{1/2}(\omega)/c)\mathcal{E}^2(\omega)\times[(\hat{e}_2)_x\chi_{y'y'z'x'}(\omega,\omega,2\omega)+(\hat{e}_2)_z\chi_{y'y'z'z'}(\omega,\omega,2\omega)]. \quad (4.16)$$

Although the linear optical properties of a uniaxial crystal are constant for all rays on a cone forming a given angle θ with the crystal axis, this is not true for the nonlinear properties. The most general form of the tensor components in Eq. (4.16) can be obtained from Table II by a rotation through an angle ϕ about the z axis (i.e., crystal axis) so that the new y' axis is parallel to $\mathbf{E}(\omega)$ and then a rotation by θ about $\mathbf{E}(\omega)$ so that z' is the direction of $\mathbf{k}(\omega)$.

$$\hat{e}_2\cdot\mathfrak{J}^{\mathrm{NLS}}(2\omega)=-2\omega^2\epsilon^{1/2}(\omega)c^{-1}\mathcal{E}^2(\omega)\times[(\chi_{1,2}+\chi_{1,3})\sin\alpha+(\chi_{1,3}-\chi_{1,2})\sin(2\theta+\alpha)+2\chi_{1,4}\sin3\phi\cos(2\theta-\alpha)]. \quad (4.17)$$

The fact that Eq. (4.17) is nonzero is due to the crystal anisotropy since for isotropic crystals the primary wave is a transverse wave and $\alpha=0$. From Table I isotropic crystals have $\chi_{1,2}=\chi_{1,3}$ and $\chi_{1,4}=0$.

The experiments of Terhune *et al.*,[5] detected quadrupole second harmonic in calcite for one particular geometry. They calculate for their orientation of crystal, the bracketed term in Eq. (4.17) was of the order of 10^{-18} esu units. This sets a lower limit on the three constants $\chi_{1,2}$, $\chi_{1,3}$, and $\chi_{1,4}$ since ϕ might have been set near 0, $\pi/3$, $2\pi/3$, etc.; the real χ's may be larger by approximately $(1/\sin\alpha)\approx20$. It would be interesting to see if an angular dependence corresponding to the last term is observable. This would give a direct measure of $\chi_{1,4}$ independent of $\chi_{1,2}$ and $\chi_{1,3}$.

Although in isotropic material there is no second harmonic generation per unit volume, due to the quadrupole nonlinearity there can be generation at the surface.[12] The quadrupole term in the current density, i.e., Eq. (4.5) changes the boundary condition that the tangential component of $\mathcal{H}$ is continuous across the surface of a nonlinear dielectric. One can show from Eq. (2.15) that if $\hat{n}_{1,2}$ is a unit vector, normal to the surface between medium 1 and medium 2, directed from 1 into 2; and if $\hat{\sigma}$ is a unit vector parallel to the surface, such that $\hat{n}_{1,2}\cdot\hat{\sigma}=0$, the boundary condition on $\mathcal{H}(\omega)$ can be written as

$$(\mathcal{H}_2(\omega)-\mathcal{H}_1(\omega))\cdot\hat{\sigma}=-(4\pi i\omega/c)[\mathfrak{Q}_2(\omega)-\mathfrak{Q}_1(\omega)]:\hat{n}_{1,2}(\hat{n}_{1,2}\times\hat{\sigma}). \quad (4.18)$$

If the fundamental is polarized perpendicular to the plane formed by the normal to the interface and the direction of wave propagation, Eq. (4.18) reduces to the usual condition that the tangential component of $\mathcal{H}$ is continuous. In this case, the quadrupole surface harmonic is obtained by substituting for $\mathfrak{P}^{\mathrm{NLS}}(\omega)$ of Eq. (4.12) of reference 12, the quantity $(i\omega)^{-1}\mathfrak{J}^{\mathrm{NLS}}(\omega)$ as given by Eq. (4.13) of this paper. The tensor χ is given in Table I.

For other polarizations of the fundamental, the right-hand side of Eq. (4.18) does not reduce to zero and to calculate the boundary harmonics it must be used instead of Eq. (4.11) of reference 12.

V. MAGNETIC DIPOLE EFFECTS

All effects which can be derived from a free-energy proportional to one or more powers of the magnetic field will be considered magnetic dipole effects. Higher magnetic multipoles are explicitly neglected since free energies proportional to gradients of the magnetic field are not treated. The simplest magnetic free energy describes the linear phenomena of optical activity,[18]

$$F=-\{\chi_{ij}(\omega)\mathcal{E}_i^*(\omega)\mathcal{H}_j(\omega)+\chi_{ij}^*(\omega)\mathcal{E}_i(\omega)\mathcal{H}_j^*(\omega)\}. \quad (5.1)$$

Assuming a crystal invariant under time reversal, Eq. (A7) of the Appendix requires $\chi_{ij}(\omega)=-\chi_{ij}^*(\omega)$; i.e., χ is pure imaginary. The forms of χ for quartz and $NaClO_3$, both optically active, are given in Table III. The dielectric currents are obtained from $\mathfrak{J}(\omega)=\partial\mathfrak{P}$

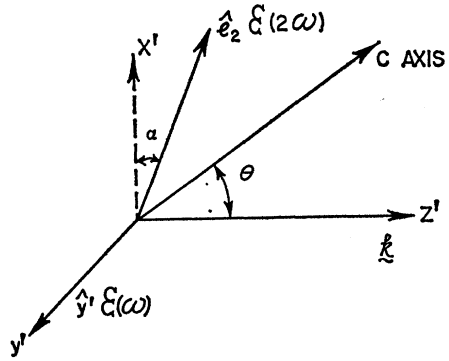

FIG. 3. Geometry for matching an ordinary wave at ω to an extraordinary wave at 2ω in a uniaxial crystal. The second harmonic $\mathcal{E}$ field is directed along the unit vector $\hat{e}_2$.

TABLE III. The form of the pseudotensor $\chi(\omega)$ to be used in Eq. (5.1) to describe optical activity in quartz and $NaClO_3$. For $NaClO_3$ $\chi_{1,1}=\chi_{3,3}$. The symbol $|\chi_{1,1}|$ should be taken to mean the imaginary part of $\chi_{1,1}$ and is thus a real number that can be either positive or negative.

	x	y	z
x	$i\|\chi_{1,1}\|$		
y		$i\|\chi_{1,1}\|$	
z			$i\|\chi_{3,3}\|$

$\times(\omega)/\partial t+c\nabla\times\mathfrak{M}(\omega)$ and one can write the part of the dielectric constant due to Eq. (5.1) in the form

$$\Delta\epsilon_{il}=i4\pi(ck_n/\omega)(|\chi_{ii}|+|\chi_{ll}|)\epsilon^{lin}, \tag{5.2}$$

where $\mathbf{k}$ is the propagation vector for the wave and ϵ^{lin} is the antisymmetric third rank tensor introduced in Sec. IV. The second rank pseudotensor χ will vanish if the crystal has inversion symmetry since the second index transforms like $\mathcal{H}$ and keeps its sign under inversion. The somewhat weaker condition of the presence of a mirror plane, however, can make individual terms in χ vanish. For example, if the crystal is invariant under reflection in the x-y plane, the only nonvanishing elements of χ are χ_{xz}, χ_{yz}, χ_{zx}, and χ_{zy}. This has the physical significance that if light is propagating parallel to a crystal mirror plane, the crystal must have the same effect on right and left circular polarization and there can be no optical activity. Note that the sign of the effective dielectric constant in Eq. (5.2) depends on the sign of k_n. This has the important consequence that light going forward and backward through an optically active material will emerge with no net rotation of the plane of polarization. This should be distinguished from the Faraday effect which doubles the rotation on passing the same crystal backward and forward.

The form of free energy leading to the Faraday effect represents the simplest type of magnetic nonlinearity,

$$\begin{aligned}F=-2\,\mathrm{Re}[&\chi_{ijk}(\omega_3,\omega_2,\omega_1)\mathcal{E}_i^*(\omega_3)\mathcal{E}_j(\omega_2)\mathcal{H}_k(\omega_1)\\&+\chi_{jki}(\omega_2,\omega_1,\omega_3)\mathcal{E}_j(\omega_2)\mathcal{E}_k(\omega_1)\mathcal{H}_i^*(\omega_3)\\&+\chi_{kij}(\omega_1,\omega_3,\omega_2)\mathcal{E}_k(\omega_1)\mathcal{E}_i^*(\omega_3)\mathcal{H}_j(\omega_2)],\end{aligned} \tag{5.3}$$

where $\omega_3=\omega_1+\omega_2$. Considering, for the moment, only crystals invariant under time reversal, Eq. (A7) of the Appendix requires these χ's to be pure imaginary. From arguments used in both Secs. III and IV, there is a permutation symmetry between the first two indices

$$\chi_{ijk}(\omega_3,\omega_2,\omega_1)=\chi_{jik}(\omega_2,\omega_3,\omega_1),\quad\text{etc.} \tag{5.4}$$

If $\omega_1\ll\omega_2$, ω_3, one must also include the free energy for $\omega_3'=\omega_2-\omega_1$ in the same manner as was discussed in Sec. III for the linear electro-optic effect. Let ω_1 correspond to a low frequency (i.e., $\omega_1/2\pi<10^9$ cps) while ω_2 and ω_3 are optical frequencies. From the normal dispersion of magnetic phenomena,[21] it follows that $\chi(\omega_2\pm\omega_1,\omega_2,\omega_1)$ is much larger than the other four tensors and one can simplify the free energy by taking $\chi_{ijk}(\omega_2+\omega_1,\omega_2,\omega_1)\approx\chi_{ijk}(\omega_2,\omega_2-\omega_1,\omega_1)\equiv\chi_{ijk}$,

$$\begin{aligned}F=-2\,\mathrm{Re}\chi_{ijk}[&\mathcal{E}_i^*(\omega_2+\omega_1)\mathcal{E}_j(\omega_2)\mathcal{H}_k(\omega_1)\\&+\mathcal{E}_i^*(\omega_2)\mathcal{E}_j(\omega_2-\omega_1)\mathcal{H}_k(\omega_1)].\end{aligned} \tag{5.5}$$

One obtains

$$\mathfrak{P}_i(\omega_2+\omega_1)=\chi_{ijk}\mathcal{E}_j(\omega_2)\mathcal{H}_k(\omega_1), \tag{5.6a}$$

$$\mathfrak{P}_i(\omega_2-\omega_1)=\chi_{jik}^*\mathcal{E}_j(\omega_2)\mathcal{H}_k^*(\omega_1), \tag{5.6b}$$

$$\begin{aligned}\mathfrak{M}_k(\omega_1)=\chi_{ijk}^*[&\mathcal{E}_i(\omega_2+\omega_1)\mathcal{E}_j^*(\omega_2)\\&+\mathcal{E}_i(\omega_2)\mathcal{E}_j^*(\omega_2-\omega_1)].\end{aligned} \tag{5.6c}$$

In the limit that $\omega_1\to 0$, Eqs. (5.6a) and (5.6b) will describe the dc Faraday effect. One must use caution in taking the limit as $\omega_1\to 0$ to combine the upper and lower sidebands, Eqs. (5.6a) and (5.6b), in the proper way. The correct results are most easily obtained if one starts from the free energy for a dc magnetic field, but it is possible to obtain them from the limit of Eq. (5.5) as $\omega_1\to 0$, if one is careful to keep track of $\chi_{ijk}(\omega_2+\omega_1,\omega_2,\omega_1)$ and $\chi_{ijk}(\omega_2-\omega_1,\omega_2,\omega_1)$ in the limiting processes.

For an isotropic material, invariant under time reversal, one can show the only nonzero elements of χ are

$$\begin{aligned}\chi_{xyz}=\chi_{yzx}=\chi_{zxy}=-\chi_{xzy}=-\chi_{zyx}=-\chi_{yxz}\\=i|\chi_{1,2,3}|,\end{aligned} \tag{5.7}$$

and one can write Eqs. (5.6a, b) as

$$\mathfrak{P}(\omega_2)=i|\chi_{1,2,3}|\,\mathcal{E}(\omega_2)\times[\mathcal{H}(\omega_1)+\mathcal{H}^*(\omega_1)]. \tag{5.8}$$

The change in the effective dielectric constant, thus, has the usual form

$$\Delta\epsilon_{ij}=i4\pi|\chi_{1,2,3}|\,\epsilon^{ijk}h_k(t), \tag{5.9}$$

where $h_k(t)$ is the real value of the kth component of the magnetic field at ω_1. The form of Eq. (5.9) is identical to the form of Eq. (5.2) except that the latter changes sign with reversal of the direction of propagation.

If one initially has a circularly polarized optical $\mathcal{E}$ field propagating in the z direction, Eq. (5.6c) shows there will be a z component of magnetization at zero frequency.[22]

$$\mathfrak{M}_z(0)=\pm 2|\chi_{1,2,3}|\,|\mathcal{E}|^2. \tag{5.10}$$

In concentrated neodymium ethylsulfate $|\chi_{1,2,3}|$ is known from Faraday measurements to be approximately 10^{-9} cgs unit at 4.2°K.[23] A 1-MW laser pulse will thus produce a total flux $\phi=\oint 4\pi M\cdot d\mathbf{A}=10^{-4}$ cgs unit. If the optical pulse is 10^{-6} sec long and is detected by a 1000 turn coil, the pickup voltage should be 1 mV. This is independent of the cross-section area

[21] L. D. Landau and E. M. Lifshitz, *Electrodynamics of Continuous Media* (Pergamon Press, Inc., New York, 1960).

[22] R. W. Terhune, in *Proceedings of the Ohio State Symposium on Lasers and Applications, Columbus, Ohio, November 1962* (to be published).

[23] J. Becquerel, W. J. de Haas, and J. van den Handel, Physica 5, 753 (1938).

TABLE IV. The form of the pseudotensor $\chi(\omega_3,\omega_2,\omega_1)$ to be used in Eq. (5.3) for a cubic crystal that lacks time-reversal symmetry because of a dc magnetization in the [001] direction.[a]

$ij \backslash k$	$\chi_{ijk}(\omega_3,\omega_2,\omega_1)$ x	y	z
xx			$\lvert\chi_{1,3}\rvert$
yy			$\lvert\chi_{1,3}\rvert$
zz			$\lvert\chi_{3,3}\rvert$
yz	$i\lvert\chi_{4,1}\rvert$	$\lvert\chi_{4,2}\rvert$	
zy	$i\lvert\chi_{4,1}'\rvert$	$\lvert\chi_{4,2}'\rvert$	
zx	$\lvert\chi_{4,2}'\rvert$	$-i\lvert\chi_{4,1}'\rvert$	
xz	$\lvert\chi_{4,2}\rvert$	$-i\lvert\chi_{4,1}\rvert$	
xy			$i\lvert\chi_{6,3}\rvert$
yx			$-i\lvert\chi_{6,3}\rvert$

[a] Note that the $\lvert\chi_{i,j}\rvert$ can be either positive or negative.

of the laser pulse so long as the volume over which M is produced is large enough that the flux does not close on itself completely within the pickup coil.

When all frequencies are optical frequencies, for media invariant under time reversal, the nonlinearity described by Eq. (5.3) is equivalent to the quadrupole nonlinearity described by Eq. (4.2).[16] The order of magnitude of this term corresponds to the Faraday rotation of a diamagnet and might possibly be detectable only because the dispersion of this effect takes place at optical frequencies.

Materials which lack time-reversal symmetry, either because they are subjected to an external dc magnetic field or because they are ferromagnetic, can have detectable nonlinear effects even when ω_1 is an optical frequency. Consider a cubic crystal, class O_h, that lacks time-inversion symmetry because it has a dc magnetization in the [001] direction. The point group operations under which this crystal is invariant are shown in Fig. 4. The form of $\chi(\omega_3,\omega_2,\omega_1)$ is given in Table IV. If the crystal were invariant under time-reversal symmetry, the real parts of the tensor given by Table IV would vanish and $\lvert\chi_{4,1}\rvert$ would equal $\lvert\chi_{6,3}\rvert$ as for the dc Faraday effect described by Eq. (5.7). The real terms can be seen to come from the dc magnetization in the [001] direction by considering a cubic crystal, invariant under time reversal, but subjected to a dc magnetic field in the [001] direction. The free energy will have terms of the form

$$F=-2\,\mathrm{Re}\chi_{ijk}(\omega_3,\omega_2,\omega_1)\mathcal{E}_i^*(\omega_3)\mathcal{E}_j(\omega_2)\mathcal{H}_k(\omega_1) -2\,\mathrm{Re}\chi_{ijkl}(\omega_3,\omega_2,\omega_1,0)\mathcal{E}_i^*(\omega_3)\mathcal{E}_j(\omega_2) \times\mathcal{H}_k(\omega_1)\mathcal{H}_l(0). \quad (5.11)$$

Since the crystal is invariant under time reversal, Eq. (A7) of the Appendix requires $\chi_{ijk}(\omega_3,\omega_2,\omega_1)$ to be pure imaginary and of the form of Eq. (5.7). The components $\chi_{ijkl}(\omega_3,\omega_2,\omega_1,0)$ are real and have the same form as the tensor given by Table I except that due to dispersion $\chi_{yzzy}=\chi_{zyyz}=\chi_{6,6}\neq\chi_{zyzy}=\chi_{yzyz}=\chi_{6,6}'$. Similar relations hold for the other terms. The free energy in Eq. (5.11) can be put in the form of Eq. (5.3) by contracting on the index l. The third rank tensor will thus have the form in Table V. If $\lvert\chi_{4,1}\rvert=\lvert\chi_{6,3}\rvert=-\lvert\chi_{4,1}'\rvert=\chi_{1,2,3}^{(3)}$ Tables IV and V have identical forms. The Voigt effect,[24] microwave modulation by the Faraday effect,[25,26] and the nonlinear optical effects correspond to the tensors in Tables IV and V for $\omega_1=0$, ω_1 near a microwave resonance frequency, and ω_1 an optical frequency, respectively.

Consider the case where $\mathcal{H}(0)$ is a dc field along the z axis, $\mathcal{H}_k(\omega_1)$ is a circularly polarized microwave field in the x-y plane, ω_1 is near a magnetic resonance, and light is propagating in the x direction. Analogous to Eq. (5.9) one obtains

$$\Delta\epsilon_{yz}=4\pi i\lvert\chi_{1,2,3}^{(3)}\rvert h_x(t)+4\pi\lvert\chi_{6,6}^{(4)}\rvert\mathcal{H}_z(0)h_y(t). \quad (5.12)$$

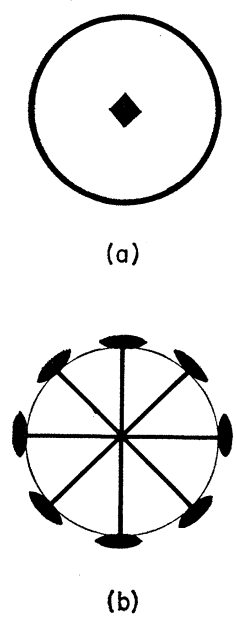

FIG. 4. The point-group symmetries of a cubic crystal, O_h, which has a dc magnetization along the [001] axis. Figure 4(a) shows the pure spatial operations under which the crystal is invariant. Figure 4(b) shows those spatial operations which when coupled with time reversal will leave the crystal invariant.

TABLE V. The form of the pseudotensor that results from contracting the free energy of Eq. (5.11) on the index l. The superscripts 3 and 4 refer to terms that originate from the third rank tensor and fourth rank tensor, respectively.[a]

$ij \backslash k$	x	y	z
xx			$\lvert\chi_{1,2}^{(4)}\rvert\mathcal{H}_z(0)$
yy			$\lvert\chi_{1,2}^{(4)}\rvert\mathcal{H}_z(0)$
zz			$\lvert\chi_{1,1}^{(4)}\rvert\mathcal{H}_z(0)$
yz	$i\lvert\chi_{1,2,3}^{(3)}\rvert$	$\lvert\chi_{6,6}^{(4)}\rvert\mathcal{H}_z(0)$	
zy	$-i\lvert\chi_{1,2,3}^{(3)}\rvert$	$\lvert\chi_{6,6}^{(4)\prime}\rvert\mathcal{H}_z(0)$	
zx	$\lvert\chi_{6,6}^{(4)\prime}\rvert\mathcal{H}_z(0)$	$i\lvert\chi_{1,2,3}^{(3)}\rvert$	
xz	$\lvert\chi_{6,6}^{(4)}\rvert\mathcal{H}_z(0)$	$-i\lvert\chi_{1,2,3}^{(3)}\rvert$	
xy			$i\lvert\chi_{1,2,3}^{(3)}\rvert$
yx			$-i\lvert\chi_{1,2,3}^{(3)}\rvert$

[a] Note that $\lvert\chi_{i,j}^{(4)}\rvert$ and $\lvert\chi_{1,2,3}^{(3)}\rvert$ can be either positive or negative.

[24] Francis A. Jenkins and Harvey E. White, *Fundamentals of Optics* (McGraw-Hill Book Company, Inc., New York, 1960).
[25] N. Bloembergen, P. S. Pershan, and L. R. Wilcox, Phys. Rev. **120**, 2014 (1960).
[26] L. K. Anderson, Appl. Phys. Letters **1**, 44 (1962).

Bloembergen, Pershan, and Wilcox[25] have shown that for light propagating parallel to the magnetization of a sample there is a Faraday rotation proportional to the instantaneous magnetization, even if that magnetization is rotating at a microwave frequency. Mathematically, a magnetization in the x direction will produce a change in $\Delta\epsilon_{yz}=iKM_x$ where K is a function of the material and the wavelength of the light. Neglecting damping, the Bloch equations can be solved for

$$\mathfrak{M}_x=\gamma\mathfrak{M}_0(\omega_0^2-\omega_1^2)^{-1}(\omega_0 h_x-i\omega_1 h_y),$$

and

$$\Delta\epsilon_{yx}=K\gamma\mathfrak{M}_0(\omega_0^2-\omega_1^2)^{-1}[\omega_0 ih_x+\omega_1 h_y]. \quad (5.13)$$

Comparing Eqs. (5.12) and (5.13), we have

$$4\pi|\chi_{1,2,3}^{(3)}|=K\gamma^2\mathfrak{M}_0\mathfrak{H}_z(0)(\omega_0^2-\omega_1^2)^{-1}, \quad (5.14a)$$

$$4\pi|\chi_{6,6}^{(4)}|=K\gamma\chi_{\mathrm{dc}}\omega_1(\omega_0^2-\omega_1^2)^{-1}, \quad (5.14b)$$

where $\mathfrak{M}_0$ is the steady-state dc magnetization, ω_0 is the microwave resonance frequency $\gamma\mathfrak{H}_z(0)$, and χ_{dc} is the static susceptibility $\mathfrak{M}_0/\mathfrak{H}_z(0)$.

In the limit $\omega_1\rightarrow 0$, Eq. (5.14a) approaches $4\pi\times|\chi_{1,2,3}^{(3)}|=K\chi_{\mathrm{dc}}\approx 1.3\times 10^{-8}$ cgs unit in concentrated neodymium ethylsulfate at 4.2°K, this being known from Faraday effect measurements. For $\omega_1\approx\omega_0$, $|\chi_{1,2,3}^{(3)}|\approx|\chi_{6,6}^{(4)}|$ and the discussions of Bloembergen *et al.* on modulation of light follow. The nonlinear optical problem is obtained for $\omega_1\gg\omega_0$, $4\pi|\chi_{1,2,3}^{(3)}|\propto\omega^{-2}\approx 0$, $4\pi\times|\chi_{6,6}^{(4)}|\approx\gamma K\chi_{\mathrm{dc}}\omega_1^{-1}$. At the ruby laser line $\gamma/\omega_1\approx 7\times 10^{-9}$ cgs unit and $4\pi|\chi_{6,6}^{(4)}|\approx 9\times 10^{-17}$ cgs unit. In an external dc field of 10^4 G, the nonlinear polarization at ω_3 will be given by

$$\mathfrak{P}_y(\omega_3)=\chi_{yzy}^{\mathrm{eff}}(\omega_3,\omega_2,\omega_1)\mathcal{E}_z(\omega_2)\mathfrak{H}_y(\omega_1),$$

where $\chi^{\mathrm{eff}}\sim 0.7\times 10^{-13}$ cgs units in concentrated neodymium ethylsulfate at 4.2°K. This should be compared with $\chi'\sim 3\times 10^{-11}$ in potassium dihydrogen phosphate[5] (KDP) for the electric dipole nonlinearity at room temperature. Neodymium ethylsulfate is not an isotropic crystal, but the essential features of the nonlinear effect and the estimate of its size are not affected by this.

The coupled amplitude equations of ABDP can be obtained by replacing $i\omega_\nu\mathfrak{P}^{\mathrm{NLS}}(\omega_\nu)$ with $\mathfrak{J}^{\mathrm{NLS}}(\omega_\nu)=i\omega_\nu\mathfrak{P}^{\mathrm{NLS}}(\omega_\nu)+c\nabla\times\mathfrak{M}^{\mathrm{NLS}}(\omega_\nu)$, $\mathfrak{P}^{\mathrm{NLS}}$ and $\mathfrak{M}^{\mathrm{NLS}}$ following directly from Eqs. (2.14) and the assumed form of the free energy. In this case, the boundary conditions[12] at the surface of the nonlinear dielectric are changed to the tangential component of $\mathfrak{H}-4\pi\mathfrak{M}^{\mathrm{NLS}}$ is continuous rather than just the tangential component of $\mathfrak{H}$.

An alternative, but completely equivalent, procedure would be to redefine the quantities in Eq. (2.15) so that $\mathfrak{H}'(\omega_\nu)=\mathfrak{H}(\omega_\nu)-4\pi\mathfrak{M}^{\mathrm{NLS}}(\omega_\nu)$. Neglecting the quadrupole terms, Eq. (2.15) becomes

$$\nabla\times\mathcal{E}(\omega_\nu)=-i(\omega_\nu/c)\partial\mathfrak{H}'(\omega_\nu)-4\pi(i\omega_\nu/c)\mathfrak{M}^{\mathrm{NLS}}(\omega_\nu),$$
$$\nabla\times\mathfrak{H}'(\omega_\nu)=i(\omega_\nu/c)\boldsymbol{\epsilon}(\omega_\nu)\cdot\mathcal{E}(\omega_\nu)+4\pi(i\omega_\nu/c)\mathfrak{P}^{\mathrm{NLS}}(\omega_\nu). \quad (5.15)$$

In this form the tangential component of $\mathfrak{H}'(\omega_\nu)$ is continuous.

For the exact solutions to the nonlinear coupled amplitude equations, one of the integration constants corresponds to the power flow being constant. The proper form of this term will automatically follow from the equations; however, one should note that this constant will correspond to $2\,\mathrm{Re}\sum_\nu\mathcal{E}^*(\omega_\nu)\times\mathfrak{H}'(\omega_\nu)$ using $\mathfrak{H}'$ rather than $\mathfrak{H}$. This has been pointed out in Sec. II and is analogous to the considerations in Sec. IV for the power flow by means of a quadrupole nonlinearity.

VI. CONCLUSION

The main purpose of this paper has been to show that for nondissipative media, there exists a function F, the time-average free energy, from which one can derive all the constitutive equations involved in the electromagnetic theory of macroscopic media. This includes linear as well as nonlinear relations. Linear and quadratic electro-optic effects, Faraday and magnetic Kerr effects, optical activity, as well as the new nonlinear optical phenomena of harmonic generation, mixing, electric rectification and magnetic rectification have all been derived phenomenologically from several of the simplest possible forms for F. In addition, several of the phenomena in different frequency ranges have been shown to be related. It has, thus, been possible to predict the order of magnitude of several, as yet, unobserved effects.

In principle, there is no reason why these methods cannot also be used to define free energies that are functions of acoustic fields as well as the products of acoustic fields and electromagnetic fields. In this way, one can also obtain the linear and nonlinear electro-elastic and magneto-elastic effects. One should also be able to obtain information on dissipative effects by introducing several general types of phenomenological loss terms.

APPENDIX: TIME-REVERSAL TRANSFORMATION

Consider a vector or pseudovector quantity $\mathbf{A}(t)$ and its Fourier transform $\mathfrak{A}(\omega)$:

$$\mathbf{A}(t)=\int_{-\infty}^{\infty}\mathfrak{A}(\omega)\exp(i\omega t)d\omega,$$
$$\mathfrak{A}(\omega)=\int_{-\infty}^{\infty}\mathfrak{A}(t)\exp(-i\omega t)dt/2\pi. \quad (A1)$$

If $\mathbf{A}(t)$ is real, $\mathfrak{A}(\omega)=\mathfrak{A}^*(-\omega)$. Under time reversal, t goes into $-t$ and ω goes into $-\omega$ so that, if T_R is the time-reversal operator,

$$T_R\mathfrak{A}(\omega)=\int_{-\infty}^{\infty}[T_R\mathbf{A}(t)]\exp(-i\omega t)dt/2\pi. \quad (A2)$$

If $T_R\mathbf{A}(t)=\mathbf{A}(-t)$ as it does for $\mathbf{E}(t)$, then

$$T_R\mathfrak{A}(\omega)=\int_{-\infty}^{\infty}\mathbf{A}(-t)\exp(-i\omega t)dt/2\pi=\mathfrak{A}^*(\omega). \quad \text{(A3)}$$

If $T_R\mathbf{A}(t)=-\mathbf{A}(-t)$ as it does for $\mathbf{H}(t)$, then

$$T_R\mathfrak{A}(\omega)=-\int_{-\infty}^{\infty}\mathbf{A}(-t)\exp(-i\omega t)dt/2\pi = -\mathfrak{A}^*(\omega). \quad \text{(A4)}$$

Consider a real scalar quantity Φ:

$$\Phi=2\,\mathrm{Re}[\chi(\omega_a,\omega_b,\omega_c,\cdots)_{ijk\cdots} \times\mathfrak{A}(\omega_a)_i\mathfrak{B}(\omega_b)_j\mathfrak{C}(\omega_c)_k\cdots], \quad \text{(A5)}$$

where each of the quantities **A**, **B**, **C** is either a vector or a pseudovector. Under time reversal A will transform like $T_R\mathfrak{A}(\omega_a)_i=t_A\mathfrak{A}^*(\omega_a)_i$, where t_A is either $+1$ if **A** transforms like **E** or -1 if **A** transforms like **H**. Similar transformations hold for **B**, **C**, etc. Then, under time reversal

$$T_R\Phi=\Phi=(-1)^n 2\,\mathrm{Re}[T_R\chi(\omega_a,\omega_b,\omega_c,\cdots)_{ijk\cdots} \times\mathfrak{A}^*(\omega_a)_i\mathfrak{B}^*(\omega_b)_j\mathfrak{C}^*(\omega_c)_k\cdots], \quad \text{(A6)}$$

where n is the number of quantities **A**, **B**, **C**, etc., that transform like **H**. If Φ is to be a real scalar, χ must transform as

$$T_R\chi(\omega_a,\omega_b,\omega_c,\cdots)=(-1)^n\chi^*(\omega_a,\omega_b,\omega_c,\cdots), \quad \text{(A7)}$$

where the tensor χ has n indices that transform like **H** on time reversal.

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Influence of the Spin of the Electron on the Quantum Magnetoacoustic Effect in Metals*

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A discussion is given of the influence of the orientation of the electron spins on the quantum oscillations of the ultrasonic attenuation in metals. This effect occurs for the situation in which a longitudinal acoustic wave propagates along the direction of an applied magnetic field in a sufficiently pure crystal and at low temperatures. It is shown that the attenuation consists of two series of spikes which occur periodically as a function of the reciprocal of the intensity of the magnetic field. The period of either series is related to an extremal cross-sectional area of the Fermi surface of the material and the shift between the two series is proportional to the cyclotron effective mass of the electrons.

WITHIN the framework of the semiclassical theory of ultrasonic absorption by metals,[1] the attenuation of a longitudinal acoustic wave propagating parallel to the direction of an applied dc magnetic field $\mathbf{B}_0$ is independent of the magnitude B_0 of $\mathbf{B}_0$. However, Gurevich *et al.*[2] have shown that, if quantum effects are taken into account, the coefficient of ultrasonic attenuation γ experiences large oscillations as a function of B_0. These oscillations have been observed by Korolyuk and Prushack[3] in Zn at liquid-helium temperatures.

The mechanism responsible for ultrasonic attenuation is absorption of phonons by the conduction electrons of the metal. In the simplest model of electrons having a spherical effective mass m^*, the stationary states of an electron in the magnetic field $\mathbf{B}_0$ are described by the wave functions[4]

$$|nk_yk_z\rangle=L_0^{-1}\exp(ik_yy+ik_zz)u_n(x+\hbar k_y/m^*\omega_c), \quad (1)$$

and their corresponding eigenvalues

$$E_n(k_z)=\hbar\omega_c(n+\tfrac{1}{2})+\hbar^2k_z^2/2m^*. \quad (2)$$

Here we have taken $\mathbf{B}_0$ parallel to the z axis of a Cartesian coordinate system (x,y,z). The length L_0 is the dimension of a cubic box of volume $V=L_0^3$ which contains the electrons, $\omega_c=eB_0/m^*c$ is the cyclotron frequency, e is the charge on a proton, and c is the speed of light in empty space. The wave numbers k_y and k_z can take any values consistent with periodic boundary conditions with the fundamental period taken as the volume V. The functions $u_n(x)$ are normalized harmonic

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[1] M. H. Cohen, M. J. Harrison, and W. A. Harrison, Phys. Rev. **117**, 937 (1960).
[2] V. L. Gurevich, V. G. Skobov, and Yu. A. Firsov, Soviet Phys.—JETP **13**, 552 (1961).
[3] A. P. Korolyuk and T. A. Prushack, Soviet Phys.—JETP **14**, 1201 (1962).
[4] L. D. Landau, Z. Physik **64**, 629 (1930). The energy levels defined by the different values of n in Eq. (2) are called Landau levels.