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Nonlinear Optical Coefficients and the Raman Scattering Efficiency of LO and TO Phonons in Acentric Insulating Crystals

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The relations between nonlinear optical coefficients and Raman scattering efficiencies of LO and TO phonons in crystals of arbitrary (acentric) structure are derived, under the adiabatic, electrostatic, and harmonic approximations usual to lattice dynamical theory. Expressions for the total electro-optic coefficients and the nonlinear optical coefficients are presented in terms of Raman efficiencies and the optic-mode frequencies. The use of the macroscopic field in computing the "electro-optic" contribution to LO scattering efficiencies is shown to be justified. The practical conditions under which these expressions may be solved are examined using scattering data for $LiNbO_3$, $LiTaO_3$, GaAs, BeO, ZnS, ZnO, and CdS. Theory and experiment are found to be in good agreement. It appears that for many materials nonlinear coefficients and electro-optic coefficients may be determined from Raman data with accuracy comparable to direct measurement in the traditional manner.

INTRODUCTION

It has been known for some time that the difference in Raman scattered intensity between transverse (TO) and longitudinal (LO) optic-phonon modes in piezoelectric crystals may be ascribed to an electro-optic effect arising from the electric field associated with the LO phonon.[1,2] Quantitative relations of a different sort between TO Raman scattering efficiencies and the lattice contributions to the electro-optic coefficient $(r_{ij,k})$[3] have been demonstrated for the ferroelectric insulators $LiNbO_3$ and $LiTaO_3$.[4] The various semiconductors with zinc-blende or wurtzite structure have particularly simple Raman spectra with only one optic phonon mode of given symmetry type, and for several of these materials[5–8] the LO as well as TO scattering data have been used to obtain values for the second-harmonic generation coefficient d_{kij}(SHG) as well as r_{ijk}. Burstein *et al.*[9] have presented a one-mode crystal analysis of polariton scattering efficiencies and a generalization thereof to describe polariton intensities in polyatomic crystals, and Scott and Ushioda[10] have applied their results, in a simplified form, to quartz. These analyses permit the calculation of d(SHG) from polariton scattering data. In this paper we shall restrict ourselves to TO and LO phonon scattering; i.e., we shall ignore the small-angle polariton scattering regime. To the author's knowledge, quantitative absolute relations between LO and TO phonon Raman scattering efficiencies and nonlinear optical coefficients for crystals of arbitrary symmetry having more than one simultaneously Raman and infrared (IR)-active mode of the same symmetry type have not been demon strated heretofore.

The "electro-optic" contribution to Raman scattering efficiencies is actually related quantitatively to d(SHG) rather than the electro-optic coefficient r. Aside from this confusion, a numerical factor-of-2 error has been made almost universally when the identification has been made, otherwise correctly, with d rather than r. A matter of more fundamental import is the confusion which has persisted in the literature regarding the matter of whether the macroscopic or local electric field should be used in computing the electro-optic contribution to LO scattering. Except for the early work of Poulet with local fields[1] the macroscopic field has been used in practice, but often with a disclaimer[2,9] indicating that this is an approximation expected to be valid for semiconductors with nonlocalized electrons. We do not consider the use of the macroscopic field to introduce any approximation whatsoever into the treatment of insulating and semi-insulating crystals to be presented here. These matters are discussed further in the Appendix, where the nomenclature of previous authors is correlated as well.

It is the purpose of this paper to present a complete description of the relations between r_{ijk}, d_{kij}, and the LO and TO Raman scattering efficiencies, valid for acentric, insulating crystals of arbitrary symmetry. [For brevity we shall call d(SHG) simply d in this paper.] The practical value of the relations derived lies in that accurate values of $|r|$ and $|d|$, and the sign of d/r, may be determined from Raman scattering data. Only the refractive index at the wavelength of the source used to excite the Raman spectrum, and the limiting dielectric constant ϵ_∞ at a frequency well above

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[1] H. Poulet, Ann. Phys. (Paris) **10**, 908 (1965).

[2] R. Loudon, Advan. Phys. **13**, 423 (1964); also, in *Proceedings of the International Conference On Light Scattering Spectra in Solids, New York University, 1968*, edited by G. B. Wright (Springer-Verlag, New York, 1969).

[3] I. P. Kaminow, in *Ferroelectricity*, edited by E. F. Weller (Elsevier Publishing Co., Amsterdam, 1967).

[4] I. P. Kaminow and W. D. Johnston, Jr., Phys. Rev. **160**, 519 (1967); **178**, 1528(E) (1969).

[5] A. Mooradian and A. L. McWhorter, in Ref. 2.

[6] W. D. Johnston, Jr., and I. P. Kaminow, Phys. Rev. (to be published).

[7] C. A. Arguello, D. L. Rousseau, and S. P. S. Porto, Phys. Rev. **181**, 1351 (1969).

[8] R. C. C. Leite, T. C. Damen, and J. F. Scott, in Ref. 2.

[9] E. Burstein, A. Pinczuk, and S. Iwasa, Phys. Rev. **157**, 611 (1967); E. Burstein, S. Ushioda, and A. Pinczuk, Solid State Commun. **6**, 407 (1968); E. Burstein, S. Ushioda, A. Pinczuk, and J. F. Scott, in Ref. 2.

[10] J. F. Scott and S. Ushioda, in LSSS (Ref. 2).

lattice, but well below electronic, resonances need be known in addition to the Raman data.

The optical and electrical requirements on a material for quantitative Raman data acquisition are often much less stringent than those for direct measurement of electro-optic or second-harmonic generation (SHG) coefficients. The method we describe thus may be an attractive alternative to direct measurement of such coefficients, particularly for new nonlinear materials, available samples of which are often unsatisfactory in size or quality for any but the crudest direct measurements of d and r. Practical examples indicate that, with reasonable care in taking the Raman data, the accuracy with which components of r and d may be determined can be comparable to or better than direct measurement, i.e., of the order of 10–20% on an absolute basis. We remark that, theoretically at least, the Raman measurement scheme is very similar to direct measurement of r or d, the difference being that the *thermal* motion of the atoms in the crystal, and the electric fields associated therewith, provide the "drive" for the "modulation" of Raman scattered light, rather than the external rf or optical fields used in direct measurement.

I. THEORY

We shall ignore phonon damping, polariton, and plasmon effects. The harmonic, electrostatic, and adiabatic approximations are assumed to be valid. The validity of these assumptions will be discussed in a practical context in the next section. In the meanwhile, we remind the reader that the harmonic approximation may not be valid near phase transitions. The electrostatic approximation requires that the phonons involved have wavelengths in the crystal short compared to electromagnetic radiation of the same frequency, which effectively eliminates polaritons[9] from consideration. We further assume that the density of free carriers is low enough that plasmon effects[5] may be ignored.

We first recall certain results from the theory of lattice dynamics, appropriate for a crystal of arbitrary symmetry with N atoms per unit cell. The equations of motion for the long-wavelength lattice vibrations, in matrix notation, are[11–13]

$$\ddot{\mathbf{w}}+\mathbf{N}\mathbf{w}=\mathbf{z}\mathbf{E}, \qquad (1.1)$$

$$\mathbf{P}=\mathbf{z}^T\mathbf{w}+\chi\mathbf{E}, \qquad (1.2)$$

where the three-dimensional vectors $\mathbf{P}$ and $\mathbf{E}$ are the polarization and macroscopic field, $4\pi\chi=\varepsilon_\infty-1$, and

$$w_\alpha(k)=[\rho(k)]^{1/2}u_\alpha(k), \quad \text{for} \quad \alpha=1\text{–}3 \quad \text{and} \quad k=1\text{–}N.$$

Also, ρ_k is the density of atoms of type k and the $u_\alpha(k)$ are the Cartesian-coordinate displacements along the α direction of the atoms of type k. $\mathbf{N}$ is a $3N\times3N$ matrix whose elements $N_{\alpha\beta}(kk')$ are the force constants between atoms of type k and k' encountered by displacements in the α and β directions, divided by $[\rho(k)\rho(k')]^{1/2}$, and $\mathbf{z}^T$ is the transpose of an effective charge parameter matrix, dimensioned $3N\times3$.

We now recall that the field associated with a phonon of wave vector $\mathbf{q}$ is given by[11]

$$E=-4\pi\left(\frac{\mathbf{q}}{q}\right)\left(\frac{\mathbf{q}\cdot\mathbf{P}}{q}\right). \qquad (1.3)$$

The eigenvalues of (1.1) with $E=0$ (denoted by ω_i) thus correspond to the squared frequencies of normal modes for which $\mathbf{q}_i\cdot\mathbf{P}_i/q_i=0$, where $\mathbf{q}_i$ is the wave vector and $\mathbf{P}_i$ the polarization of the ith mode. Thus, these eigenvalues correspond to either *transverse* ($\mathbf{q}_i\perp\mathbf{P}_i$) or *infrared-inactive* ($\mathbf{P}_i\equiv0$) modes. The *eigenvectors* of (1.1) with $\mathbf{E}=0$ we shall call the normal transverse mode coordinates W_i, and we define an effective *transverse* charge-parameter matrix Z_i^α by

$$\partial P^\alpha/\partial W_i=Z_i^\alpha. \qquad (1.4)$$

Z_α^i is related to the dielectric response function by[14]

$$\epsilon^{\alpha\beta}(\omega)=\epsilon_\infty^{\alpha\beta}+\sum_{i=1}^{3N}\frac{4\pi Z_i^\alpha Z_i^\beta}{\omega_i^2-\omega^2}. \qquad (1.5)$$

The IR-active normal modes are purely transverse or purely longitudinal only for phonon propagation along principal axes of the dielectric tensor. Accordingly the $\mathbf{W}_i$ for modes with $\mathbf{P}_i\neq0$ are the normal-mode coordinates only for modes with $\mathbf{q}$ along these directions. The propagation direction is of course immaterial for the modes with $\mathbf{P}_i\equiv0$, which include the three acoustic- ($\omega_i^2=0$) mode solutions to (1.1).

For convenience, we shall group the transverse normal-mode coordinates W_i separately as $Z_i^\alpha=0$ or not. If the crystal symmetry is orthorhombic or higher, the principal axes correspond to crystallographic axes and the modes with $Z_i^\alpha\neq0$ may be grouped by axis (α), since only one of the three Z_i^α components is $\neq0$ for each i; i.e., Z_i^α splits from a $3N\times3$ to three $N\times1$ matrices.

We need now consider the solutions to (1.1) when $\mathbf{q}\cdot\mathbf{P}=qP$ and the right-hand side of (1.1) is $-4\pi\mathbf{Z}\mathbf{P}$, to obtain the eigenfrequencies and normal coordinates for the longitudinal vibrations. These are conveniently expressed by writing (1.1) and (1.2) in terms of $\mathbf{W}$:

$$-\omega^2W_i+\omega_i^2W_i=-4\pi\sum_{\alpha=1}^{3}Z_i^\alpha P^\alpha, \quad i=1\text{–}3N \qquad (1.6)$$

$$P^\alpha=\sum_{i=1}^{3N}Z_i^\alpha W_i-\sum_{\beta=1}^{3}(\epsilon_\infty^{\alpha\beta}-\delta^{\alpha\beta})P^\beta. \qquad (1.7)$$

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[11] W. Cochran and R. A. Cowley, J. Phys. Chem. Solids **23**, 47 (1962).

[12] R. A. Cowley, Proc. Roy. Soc. (London) **A268**, 109 (1962).

[13] R. A. Cowley, Proc. Roy. Soc. (London) **A268**, 121 (1962).

[14] A. S. Barker, Jr., Phys. Rev. **145**, 391 (1966).

P^{α} may be eliminated from (1.6) and (1.7) to yield

$$-\omega^2\mathbf{W}+\mathbf{KW}=0\,, \tag{1.8}$$

where

$$K_{ij}=\omega_i^2\delta_{ij}+4\pi\sum_{\alpha=1}^{3}\sum_{\beta=1}^{3}Z_i^{\alpha}Z_j^{\beta}(\boldsymbol{\varepsilon}_\infty^{-1})^{\alpha\beta}\,,\qquad i,\ j=1\text{–}3N\,. \tag{1.9}$$

Note that (1.8) is thus not diagonal. We introduce new coordinates $\mathbf{W}'$ such that $\mathbf{UW}'=\mathbf{W}$, $\mathbf{U}^{-1}=\mathbf{U}^T$, and $\mathbf{U}^T\mathbf{KU}=\omega_i'^2\delta_{ij}$; i.e., $\mathbf{U}$ is a unitary matrix which diagonalizes $\mathbf{K}$. The ω_i' are the longitudinal mode eigenfrequencies, and $\mathbf{U}$ is a matrix whose columns are the normalized principal vectors of $\mathbf{K}$. Then (1.8) becomes

$$-\omega^2W_i'+\omega_i'^2W_i'=0\,. \tag{1.10}$$

Thus $\mathbf{W}'$ is the longitudinal normal-mode coordinate vector, and (1.7) becomes

$$P^{\beta}=\sum_{i=1}^{3N}\sum_{\gamma=1}^{3}Z_i'^{\gamma}W_i'(\epsilon_\infty^{-1})^{\gamma\beta}\,, \tag{1.11}$$

where

$$\mathbf{Z}'=\mathbf{ZU}\,. \tag{1.12}$$

We will require the relations

$$\partial P^{\alpha}/\partial W_i'=\sum_{\beta=1}^{3}Z_i'^{\beta}(\epsilon_\infty^{-1})^{\alpha\beta} \tag{1.13}$$

and

$$\partial W_i/\partial W_j=(U^T)_{ij}=U_{ji}\,. \tag{1.14}$$

Also, it can be shown[12] that the $3N\times3N$ matrix $\mathbf{U}$ consists of two or more matrices (depending on crystal symmetry) along the diagonal and zeros elsewhere, as follows: triclinic, $(3N-3)\times(3N-3)$ and 3×3; monoclinic, $(N-1)\times(N-1)$, $(2N-2)\times(2N-2)$ and 3×3; orthorhombic and higher, three $(N-1)\times(N-1)$ and 3×3. Thus, infrared-inactive modes do not "mix" to give the LO mode eigenvectors, and the various TO modes for which a given particular polarization "axis" may be identified mix *only with each other* to give the LO normal-mode coordinates appropriate to that particular axis.

We may now proceed to the relation of Raman scattering efficiency to nonlinear optical coefficients. The TO Stokes scattering efficiency within the medium is[2]

$$\frac{S(ij,k)}{l d\Omega}=\left\{\frac{h(\omega_0-\omega_k)^4(\bar{n}^k+1)}{2\omega_k c^4}\right\}\left|\frac{d\alpha_{ij}}{dW^k}\right|^2, \tag{1.15}$$

where $i,\ j=1$–3 and $k=1$–$3N$. A similar equation holds for LO modes, with ω'^k, n'^k, and W'^k replacing ω^k, n^k, and W^k. S is the ratio of scattered optical power with polarization along $\hat{\imath}$ to incident optical power with frequency ω_0 and polarization along $\hat{\jmath}$, for a collection solid angle $d\Omega$ and length of medium l, and $\bar{n}^k$ is the Bose factor for the frequency ω^k. Finally $d\alpha_{ij}/dW^k$ is the *total* derivative of the macroscopic optical polarizability α_{ij} with respect to normal-mode coordinate W^k (or W'^k for LO modes).

The polarizability may be regarded as a function of $\mathbf{W}$ (or $\mathbf{W}'$) and $\mathbf{E}$, the macroscopic field; *or* of $\mathbf{w}$ and $\boldsymbol{\mathcal{E}}$, the local "field" at each ion ($\boldsymbol{\mathcal{E}}$ is a $3\times3N$-dimensional matrix), which determine the microscopic polarizability. The macroscopic quantities are of course given by a sum of microscopic contributions over a unit cell. We shall use the macroscopic parameters since r_{ijk} and $d_{k,ij}$ are defined for macroscopic fields and polarizations.

From (1.3), (1.11), and (1.13), we obtain, for TO modes,

$$\frac{d\alpha_{ij}}{dW^k}=\frac{\partial\alpha_{ij}}{\partial W^k}\,, \tag{1.16}$$

and for LO modes,

$$\begin{aligned}\frac{\partial\alpha_{ij}}{dW'^k}&=\frac{\partial\alpha_{ij}}{\partial W'^k}+\sum_{\gamma}\frac{\partial\alpha_{ij}}{\partial E^{\gamma}}\frac{\partial E^{\gamma}}{\partial W'^k}\\&=\sum_{\gamma}\frac{\partial\alpha_{ij}}{\partial W^{\gamma}}U_{\gamma k}+\sum_{\gamma}\frac{\partial\alpha_{ij}}{\partial E^{\gamma}}\sum_{\beta}(-4\pi Z_k'^{\beta})\\&\qquad\times(\boldsymbol{\varepsilon}_\infty^{-1})^{\gamma\beta}\,,\end{aligned} \tag{1.17}$$

where $\boldsymbol{\varepsilon}_\infty^{-1}$ is the inverse to the dielectric tensor $\boldsymbol{\varepsilon}_\infty$. We now note that $\partial\alpha_{ij}/\partial E^k=4d_{kij}(\text{SHG})$,[15] where $d_{kij}(\text{SHG})$ is the second-harmonic generation coefficient.

It is worth emphasizing that (1.17) is properly expressed as written in terms of macroscopic quantities, regardless of the ionic or covalent, insulating or semiconducting, nature of the material. By analogy with the analysis made by Cowley,[12,13] an equivalent equation may be written in terms of microscopic (i.e., local) differential polarizabilities, microscopic coordinates, and the local field; and identification made with the desired macroscopic quantities ϵ, $d\alpha/dW$, and $\mathbf{d}$. Cowley shows that arbitrarily high multipole orders may be included in the microscopic treatment. It is easy to show (by an extension of Sec. 6 of Ref. 13) that $\mathbf{Z}$ and $\mathbf{K}$, if determined from (1.5) and (1.9) and the empirical mode frequencies, are the *effective* charge and force parameters including the contribution from *all* local polarization effects of whatever multipole order so that no additional "local-field" correction is needed.

Denoting $\partial\alpha_{ij}/\partial W^k$ by α_{ijk}, and the term in curly brackets in (1.15) by σ_k (or σ_k'), we have, from (1.15)–(1.17),

$$S_{ijk}{}^T/l d\Omega=\sigma_k(\alpha_{ijk})^2\,, \tag{1.18}$$

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[15] For the notation used and symmetry properties of r and d, see G. D. Boyd and D. A. Kleinman, J. Appl. Phys. **39**, 3597 (1968), Appendix 2.

$$S_{ijm}{}^{L}/l d\Omega=\sigma_{m}{}'\Big[\sum_{n=1}^{3N}\alpha_{ijn}U_{nm}-\sum_{\gamma,\beta}16\pi(\epsilon_{\infty}{}^{-1})^{\gamma\beta}\sum_{n=1}^{3N}Z_{n}{}^{\beta}U_{nm}d_{\gamma ij}\Big]^{2}. \quad (1.19)$$

A "sum rule" may be derived from (1.19) by dividing both sides by $\sigma_m{}'$ and summing on m. The right-hand side then is of the form $|\mathbf{A}\cdot\mathbf{U}|^2$, which equals $|\mathbf{A}|^2$ since U is a unitary matrix. Using (1.18) as well, we obtain

$$\sum_{m}(S_{ij,m}{}^{L}/\sigma_{m}{}'-S_{ijm}{}^{T}/\sigma_{m})=-32\pi\sum_{m,\gamma,\beta}(\epsilon_{\infty}{}^{-1})^{\gamma\beta}Z_{m}{}^{\beta}d_{\gamma,ij}\alpha_{ijm}+256\pi^{2}\sum_{m,\gamma,\beta}\big[(\epsilon_{\infty}{}^{-1})^{\gamma\beta}Z_{m}{}^{\beta}d_{\gamma,ij}\big]^{2}. \quad (1.20)$$

Finally, as shown in Ref. 3, the lattice contribution δr from the nth optic mode to the electro-optic coefficient, is given for crystals of orthorhombic or higher symmetry by

$$-\frac{n_i{}^2n_j{}^2}{4\pi}\delta r_{ij,k}=\alpha_{ij,k}Z_i{}^k/\omega_k{}^2 \quad \text{(no sum convention)} \quad (1.21)$$

so that

$$-\frac{n_i{}^2n_j{}^2}{4\pi}r_{ij,k}=\sum_{n=1}^{3N}\alpha_{ij,n}(Z_n{}^k/\omega_n{}^2)+4d_{kij}, \quad (1.22)$$

where n_i and n_j are refractive indices. More generally, for monoclinic or triclinic crystals,

$$\sum_{ij}r_{ij,k}\epsilon^{ij}=-4\pi\sum_{ij}(\boldsymbol{\varepsilon}^{-1})^{ij}\times\Big[\sum_{\gamma}\alpha_{ij,\gamma}Z_{\gamma}{}^{k}/\omega_{\gamma}{}^{2}+4d_{k,ij}\Big], \quad (1.23)$$

where $\boldsymbol{\varepsilon}$ is the dielectric tensor at the optical carrier frequency.

II. APPLICATION TO $LiNbO_3$ AND $LiTaO_3$

The only materials with more than one simultaneously Raman and IR-active mode of given symmetry type for which quantitative Raman efficiencies have been published, are the isomorphic ferroelectrics $LiNbO_3$ and $LiTaO_3$. Both these materials are of practical importance for nonlinear-optical-device applications, and values for the electro-optic and SHG coefficients have been determined by several workers. Below the Curie temperatures (1480 and 910°K, respectively) the crystals have the symmetry of point group $3m$ and space group $R3c$. There are two formula units per unit cell, allowing, as has been shown elsewhere,[16] nine long-wavelength optic modes of the doubly degenerate symmetry type E, four of type A_1 and five of type A_2, as well as the acoustic modes, one of type E and one of type A_1. The five A_2 modes are silent, and the E and A_1 modes are simultaneously Raman- and IR-active. The nine E and four A_1 optic modes may be considered in separate groups. The A_1 modes are related to the nonlinear coefficients r_{33} and r_{13}, d_{33} and d_{31}, and the E modes to r_{51} and r_{22}, d_{15} and d_{22} [4] (the usual compressed notation is used; thus $r_{ijk}\rightarrow r_{lk}$, but $d_{ijk}\rightarrow d_{il}$ where l ranges from 1 to 6).

The adiabatic approximation and, except for small-angle ($\lesssim 10°$) scattering, the electrostatic approximation are clearly justifiable for both materials. (The former requires that the optic-phonon frequencies be much less than frequencies of electronic resonances, and the latter requires that the wavelengths of the optic phonons be small compared to electromagnetic wavelengths for the same frequencies.) The harmonic approximation may be considered valid for a ferroelectric if the temperature is well removed from the Curie point and the effects associated with domain reversibility are relatively unimportant, i.e., the coercive field should be high and the domains "frozen" or nearly irreversible. Room-temperature reversal of the domains in $LiTaO_3$ and $LiNbO_3$ requires special techniques and has been reported only recently,[17] with coercive field values greater than 10^5 V/cm, so that, for our purposes, the reversible, ferroelectric nature of these materials may be ignored. The temperature dependence of the Raman spectra[18] provides the best indication of the relative importance of anharmonic effects. (The Raman spectra for an ideal harmonic crystal would, of course, show only the intensity variation with temperature due to the Bose population factor.) From the data of Ref. 18, it is estimated that anharmonic effects should be negligible below about 200°K for $LiTaO_3$ and below 400°K for $LiNbO_3$. At room temperature there is some evidence of anharmonic effects ("softening" of the soft-mode frequency, and violation of group-theoretical polarization selection rules) in the Raman spectrum of $LiTaO_3$, but the departure from ideal is still relatively small and may be considered as a perturbation to the normal-mode theory.

We have also ignored phonon damping, which might not seem justifiable *a priori* in terms of the reported linewidths,[4] which are themselves about 30% too small.[18] It is possible to include a first-order approximation of damping without sacrificing the normal-mode treatment; the same (nonzero) linewidth may be assumed for all optic phonons of given symmetry type, denoted by a common half-width at half-maximum Γ_0. Equation (1.8) may then be rewritten

$$-\omega^2W_i+\omega_i{}^2W_i+2i\Gamma_0\omega_iW_i=-4\pi\sum_{\alpha=1}^{3}Z_i{}^{\alpha}P^{\alpha}, \quad (2.1)$$

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[16] A. S. Barker, Jr., and R. Loudon, Phys. Rev. **158**, 433 (1967).

[17] S. H. Wemple, M. DiDomenico, and I. Camlibel, Appl. Phys. Letters **12**, 209 (1968); I. Camlibel, J. Appl. Phys. **40**, 1691 (1969).

[18] W. D. Johnston, Jr., and I. P. Kaminow, Phys. Rev. **168**, 1045 (1968).

TABLE I. Oscillator strengths $\Delta\kappa_i=4\pi Z_i^2/\omega_i^2$ and TO mode frequencies ω_i (cm^{-1}).

	Lithium niobate		
	A_1-type modes		
From Raman data[a]		From IR data[b]	
ω_i	Δk_i	ω_i	Δk_i
253	15.22	248	16.0
275	1.22	274	1.0
334	0.28	307	0.16
637	2.67	...	2.55
		+692	0.13
$\epsilon^{33}=28$,[c]	$\sum \Delta\kappa+\epsilon_\infty=23.99$,	$\sum \Delta\kappa+\epsilon_\infty=24.31$	
	E-symmetry-type modes		
92	3.7	...	...
152	21.6	152	22.0
238	1.7	236	0.8
262	5.1	265	5.5
322	1.8	322	2.2
368	1.9	363	2.3
436	0.1	431	0.2
582	3.0	586	3.3
630	0.6	...	[d]
		+670	0.2
$\epsilon^{11}=43$,[c]	$\epsilon_\infty+\sum \Delta\kappa=41.0$,	$\epsilon_\infty+\sum \Delta\kappa=41.3$	
	Lithium tantalate		
	A_1-type modes		
ω_i	$\Delta\kappa_i$	ω_i	$\Delta\kappa_i$
201	25.02	200	30
253	2.60	...	...
356	0.27	357	0.055
600	3.51	596	2.66
		(657 760)[e]	(0.36)
$\epsilon^{33}=43$,[c]	$\sum \Delta\kappa+\epsilon_\infty=36.4$		
	E-type modes		
74	7.08	...	...
140	12.76	142.5	24.1
206	9.12	215	0.36
251	0.28	253	2.4
316	0.13	316	2.5
383	3.74	375	2.0
462	0.09	462	0.013
596	2.45	593.5	2.33
662	0.53	673	0.05
		(165,175,238,405,750)	3.2[e]
$\epsilon^{11}=41$,[f]	$\sum \Delta\kappa+\epsilon_\infty=41.0$		

[a] Reference 18.
[b] Reference 15.
[c] Reference 21.
[d] Not reported.
[e] Additional modes.
[f] I. P. Kaminow and E. H. Turner, Appl. Opt. 5, 1612 (1966).

where i runs over the modes of given symmetry type corresponding to Γ_0. A unitary transformation still exists between the TO and LO normal-mode solutions (this would not be the case if Γ_0 were dependent on i) The eigenvalues for the normal-mode frequencies are of course complex but the observed TO and LO mode frequencies ($\bar{\omega}_i$ and $\bar{\omega}_i'$) as defined by the scattering peaks in the Raman spectra may be combined with the linewidth to yield ω_i^2 and $\omega_i'^2$, the TO and LO force constant parameters[19]:

$$\omega_i^2=\bar{\omega}_i^2+\Gamma_0^2, \quad \omega_i'^2=\bar{\omega}_i'^2+\Gamma_0^2. \tag{2.2}$$

The theory of Sec. I now applies with these values for ω_i and ω_i'. Unfortunately the optic-phonon linewidths in $LiTaO_3$ and $LiNbO_3$ vary by as much as a factor of 3 at room temperature for modes of either A_1 or E symmetry, so that the constant Γ_0 approximation is rather poor. Even taking the largest linewidths for Γ_0, corrections from (2.3) to the measured values of LO or TO frequencies do not exceed the precision ($\sim+2.5$ cm^{-1}) of the experimental data and accordingly the first-order linewidth correction is not considered significant. The variation among the linewidths is evidence that anharmonic coupling among the modes actually exists, but these higher-order effects will be assumed to be less important for Raman scattering computations than the first-order correction described above.

Finally, of course, allowance must be made for the variation of the Bose factor across the width of the Raman line. The published data[4] have taken this into account. While on the subject of the Raman data for $LiNbO_3$ and $LiTaO_3$, it should be pointed out that it now appears (as the result of a reexamination of the spectra by this author using a double-grating monochromator and improved electronics) that the lowest-frequency E-symmetry longitudinal phonon in $LiNbO_3$ was erroneously reported in Ref. 4 at 117 cm^{-1}, and that the correct value[20] should be 95 cm^{-1}. The linewidth and scattering efficiencies are unchanged. This makes the Raman data compatible with the IR data of Ref. 16. [The 117-cm^{-1} frequency assignment would imply that the 92-cm^{-1} E-type TO phonon had substantially greater oscillator strength ($\sim$30) than the IR data would allow.] With the exception of this change, all Raman data for $LiNbO_3$ and $LiTaO_3$ used in the calculations to follow are as reported in Ref. 4.

The IR reflectivity spectrum of $LiTaO_3$ at room temperature has been measured recently by Ditzenberger.[21] From these data, it would appear that a smaller splitting of the 74–80-cm^{-1} TO-LO E-symmetry-type mode in $LiTaO_3$ would be appropriate. A 75–78-cm^{-1} frequency assignment is certainly consistent with the accuracy of the Raman data and would apparently be more nearly consistent with the IR data. The comparison of Ditzenberger's data with those of Barker and Loudon[16] confirms that anharmonic effects are much more pronounced in $LiTaO_3$ than in $LiNbO_3$ at room temperature.

Comparison with Experiment

With the warning that the approximations of Sec. I are evidently less valid for $LiTaO_3$ than for $LiNbO_3$, we now turn to examine the predicted relations among the Raman data, IR data, and experimental values for dielectric constants and electro-optic and SHG coefficients. The calculations described below were all

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[19] A. S. Barker, Jr., in *Far Infrared Properties of Solids*, edited by S. S. Mitra and S. Nudelman (Plenum Press, Inc., New York, 1969).

[20] While this mode was not reported in Ref. 16, there is some evidence of its presence in Fig. 1 of that paper.

[21] J. A. Ditzenberger (unpublished).

carried out on a time-shared computer facility. Initially the linear dielectric properties of the lattice modes are determined. The equation system (1.5) is solved for the transverse charge parameters Z_i by requiring that $\epsilon(\omega_i')=0$ for all the LO frequencies ω_i'. (Actually $|Z_i^\alpha|^2$ is thus determined, but the phase of all Z_i may be chosen to be zero; this choice has the effect of fixing the sense of the TO normal-mode coordinates W_i.) The transverse charge parameters are related to the IR oscillator strengths ($\Delta\kappa_i^\alpha$) of the TO modes by

$$\Delta\kappa_i^{\alpha\beta}=4\pi Z_i^\alpha Z_i^\beta/\omega_i^2. \qquad (2.3)$$

The low-frequency (clamped) dielectric constant ϵ_0 is then given by

$$\epsilon_0^{\alpha\beta}=\epsilon_\infty^{\alpha\beta}+\sum_i \Delta\kappa_i^{\alpha\beta}. \qquad (2.4)$$

The values for $\Delta\kappa_i$ and ϵ_0 determined from the Raman data are compared in Table I with values from IR and microwave measurements.

The components of the unitary matrix relating TO and LO normal-mode coordinate vectors are then determined from components of the unit solution vectors $\mathbf{x}_i$ of the systems

$$[\mathbf{K}-\omega_i'\mathbf{I}]\mathbf{x}_i=0. \qquad (2.5)$$

In (2.4), (2.5) and (2.6) the index i runs over the number of normal modes of given symmetry type; thus for LiNbO$_3$ and LiTaO$_3$ i runs from 1 to 4 for A_1 modes, and from 1 to 9 for E modes. In Eqs. (2.4) and (2.5) i refers, of course, to TO modes, and in Eq. (2.6) i refers to LO modes.

The longitudinal charge parameters $Z_i'^\alpha$ may now be determined directly from Eq. (1.12). These last quantities are related to the polaron coupling coefficients,[14,22] α_j^β, which couple electrons and the jth LO phonon:

$$\alpha_j^\beta=\frac{2\pi e^2}{\hbar\omega_j'^3}\left(\frac{2m_\beta^*\omega_j'}{\hbar}\right)^{1/2}\sum_{\gamma=1}^{3} Z_j'^\gamma[\epsilon_\infty^{-1}]^{\beta\gamma}, \qquad (2.6)$$

where e is the charge, and m^* the bare mass (in the β direction), of the electron. For point group $3m$, (2.6) simplifies to

$$\alpha_j^\beta=\frac{2\pi e^2}{\hbar\omega_j'^3}\left(\frac{2m_\beta^*\omega_j'}{\hbar}\right)^{1/2}\left[\frac{Z_j'^\beta}{\epsilon_\infty^\beta}\right], \qquad (2.7)$$

with $\beta=3$, $j=1$–4 (A_1 modes), or $\beta=1$, $j=1$–9 (E modes). The values computed for the polaron coupling coefficients are given in Table II, where the bare mass has been set equal to the free-electron mass since this quantity is not known for LiNbO$_3$ nor LiTaO$_3$ as yet. The coupling coefficients are of the same magnitude as those reported by Barker[14] for SrTiO$_3$, BaTiO$_3$, and KTaO$_3$.

TABLE II. Polaron coupling coefficients (for free-electron mass) and LO frequencies[a] in cm^{-1}.

LiNbO$_3$		LiTaO$_3$	
ω_i' (cm^{-1})	α_i	ω_i'	α_i
A_1-symmetry-type modes			
273	0.003	245	0.027
331	0.019	347	0.14
428	0.84	399	0.68
874	1.38	864	1.39
E_L-symmetry-type modes			
95[b]	0.037	80	0.12
198	0.22	163	0.14
243	0.018	248	0.038
298	0.10	278	0.40
345	0.075	318	0.021
428	0.157	452	0.16
448	0.248	474	0.21
621	0.015	648	0.034
881	1.46	870	1.41

[a] Reference 4.
[b] See text.

We now consider the quadratic equation system (1.18) and (1.19). The validity of these relations is most easily tested by computing values for $\mathbf{S}^L$ and $\mathbf{r}$ from the measured values of $\mathbf{S}^T$, $\mathbf{d}$, ϵ_∞, and the other Raman spectral parameters. With N modes of given symmetry, there are 2^N separate sets of solutions for the N components of $\mathbf{S}^L$ of that symmetry, each such set corresponding to a different choice of signs among the components of $\boldsymbol{\alpha}$ [only the absolute value of the components of α_{ijk} are determined from (1.18)]. Thus for the A_1-symmetry longitudinal modes (1.18) predicts 16 possible four-component sets $\mathbf{S}^{Lp}$, which are to be compared to the experimental values $\mathbf{S}^{Le}$. For the E-symmetry modes there are 512 predicted nine-component sets.

For the purpose of comparing the experimental and predicted LO efficiencies we define a variance parameter by

$$V_p=\sum_{i=1}^{N}{}'\left(\frac{(S_i^{Lp}-S_i^{Le})}{S_i^{Le}}\right)^2+\left(\frac{\sum S_i^{Lp}-\sum S_i^{Le}}{\sum_i S_i^{Le}}\right)^2. \qquad (2.8)$$

The experimental values are all given the same *relative* weight by the first term. The prime on the summation indicates that only modes for which $S_i^{Le}\neq 0$ are included. The second term in (2.8) is the relative variance based on the "sum rule" given by Eq. (1.20). While the first term assumes a constant percentage accuracy for the S_i^{Le}, the second term has the effect of forcing the fit toward the stronger modes. A deviation parameter

$$v_p=(V_p/N')^{1/2} \qquad (2.9)$$

may also be defined, where N' is the number of terms contributing to the primed summation in (2.8). This last quantity may be interpreted as a mean percentage deviation between theoretical and experimental values for $\mathbf{S}^L$ for the pth set generated by (1.19).

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[22] C. Kittel, *Quantum Theory of Solids* (John Wiley & Sons, Inc., New York, 1963).

TABLE III. Experimental values of scattering efficiency for LO modes (ordered by increasing frequency), values calculated from TO efficiencies (Ref. 4), and measured values of d, variance parameter v (see text), and signs of lattice contributions α_{ijk} relative to d_{kij}. Units of S_L are 10^{-6} cm^{-1} sr^{-1}.

A_1 modes (113) coefficients				
LiNbO$_3$	$d_{31}=-6.25\times10^{-12}$ m/V[a]			
S_L(expt)$_{113}$	1.0	1.2	0.9	3.2
S_L(calc)$_{113}$	0.9	1.5	0.5	2.4
(α/d)	+	+	−	+
r_{13}(calc) $=12\times10^{-12}$ m/V			$v=30\%$	
r_{13}(expt) $=9\times10^{-12}$ m/V[b]				
LiTaO$_3$	$d_{31}=-1.5\times10^{-12}$ m/V[a]			
S_L(expt)	0.03	0.4	0.2	0.7
S_L(calc)	0.02	0.5	0.2	0.6
(α/d)	−	−	+	−
r(calc) $=-8\times10^{-12}$ m/V			$v=30\%$	
r_{13}(expt) $=9.5\times10^{-12}$ m/V[b]				

A_1 modes (333) coefficients				
LiNbO$_3$	$d_{33}=-37.5\times10^{-12}$ m/V[a]			
$S_{333}{}^L$(expt)	0.32	1.22	0.38	1.64
$S_{333}{}^L$(calc)	0.7	0.12	0.02	1.6
(α/d)	+	+	+	+
r_{33}(calc)	39			
r_{33}(calc)	39		$v=71\%$	
r_{33}(expt)[b]	31			
LiTaO$_3$	$d_{33}=-23\times10^{-12}$ m/V[a]			
$S_{333}{}^L$(expt)	0.03	0.3	0.17	0.69
L_{333}(calc)	0.09	0.003	0.001	0.26
(α/d)	+	+	+	+
r_{33}(calc)	40	$v=115\%$		
r_{33}(expt)	36			

E modes (131) coefficients									
LiNbO$_3$	$d_{15}=d_{31}=-6.75\times10^{-12}$ m/V[a]								
$S_{51}{}^L$(expt)	−	−	0.07	−	−	0.03	−	1.05	0.05
$S_{51}{}^L$(calc)	0.45	0.1	0.16	1.9	1.9	0.2	3.0	0.4	0.1
Sign (α/d)	−	−	+	−	+	+	+	+	−
r_{51}(calc)	19				$v=270\%$				
r_{51}(expt)[b]	28				(4 modes used)				
LiTaO$_3$	$d_{15}=d_{31}=1.5\times10^{-12}$ m/V[a]								
$S_{51}{}^L$(expt)	−	−	−	−	0.02	−	0.05	0.09	−
$S_{51}{}^L$(calc)	0.04	0.49	2.4	0.05	0.02	0.04	0.05	0.05	0.38
Sign (α/d)	−	−	+	+	−	+	−	−	−
r_{51}(calc)	1.6×10^{-12} m/V				$v=27\%$				
r_{51}(expt)[b]	20×10^{-12} m/V				(3 modes used)				

E modes (222) coefficients									
LiNbO$_3$	$d_{22}=3.6\times10^{-12}$ m/V[a]								
S_L(expt)222	0.005	0.05	0.04	0.03	0.05	0.04	0.09	1.1	0.07
$S_{222}{}^L$(calc)	0.02	0.2	0.01	0	0.04	0.16	0.2	0.72	0.08
Sign (α/d)	−	−	−	−	−	−	−	−	+
r_{22}(calc)	6×10^{-12} m/V						$v=154\%$		
r_{22}(expt)[b]	3.4×10^{-12} m/V								
LiTaO$_3$	$d_{22}=2.4\times10^{-12}$ m/V[a]								
$S_{222}{}^L$(expt)	0.1	0.08	0.06	0.09	0.02	0.24	0.06	0.04	0.04
$S_{222}{}^L$(calc)	0.001	0.05	0.1	0.09	0.02	0.34	10^{-6}	0.05	0.03
Sign (α/d)	+	+	+	−	+	+	+	−	+
r_{22}(calc)	9.6×10^{-12} m/V					$v=55\%$			
r_{22}(expt)[b]	1×10^{-12} m/V								

[a] R. C. Miller and A. Savage, Appl. Phys. Letters **9**, 169 (1966); J. E. Bjorkholm, IEEE J. Quantum Electron **QE-4**, 970 (1968); **QE-5**, 260 (1969).

[b] I. P. Kaminow and E. H. Turner, Appl. Opt. **5**, 1612 (1966).

The "best" set of $\mathbf{S}^L$ is determined as that set for which V_p is a minimum. A unique choice of signs for the components of $\boldsymbol{\alpha}_{ijk}$ relative to d_{kij} is thus determined, and a value for r_{ijk} may be determined from (1.24). The values so computed for r and the LO scattering efficiencies are compared with directly measured quantities in Table III. The values for the "deviation," v_p, and the signs of α_{ijk} for each mode relative to d_{kij}, are given as well. It should be emphasized that there are no free parameters whatsoever to be adjusted, and that *absolute* rather than relative theoretical and experimental values are compared; thus the possibility of systematic error in the determinations of experimental quantities may be important.

In the case of coefficients with index (51), only some of the LO scattering efficiencies are known, and only these have been fit, so that this comparison is less meaningful. The comparison of the index (13) coefficients should be more significant, since the LO efficiencies are known most accurately for that scattering geometry. Indeed, the agreement seems best for these scattering efficiencies and the electro-optic coefficients agree well with direct measurement. We note also that the signs of the $\boldsymbol{\alpha}_{13}$ components are (relative to d_{13}) exactly opposite for LiNbO$_3$ and LiTaO$_3$. The α_{33} components, however, are all the same in sign as d_{33} for both materials. There is an ambiguity in the determination of the experimental values of $S_{33}{}^L$ arising from the experimental geometry employed.[4] The results in the table were obtained as the best choice (minimum v_p) for any combination of $\mathbf{S}_{33}{}^L$ consistent with the published data.

The agreement for the quantities with index (13) is quite good, and is about the same for both materials. The 30% probable deviation is about what would be expected for ±10% uncertainty in the values of $\mathbf{S}^T$,

Table IV. Raman derived and direct experimental values of electro-optic and SHG coefficients (10^{-12} m/V).

Mat. 1	Coeff.	Calc	Expt
LiNbO$_3$[a]	r_{13}	12	8.6
	d_{31}	−6.5	−6.8
	r_{51}	23	28
	d_{15}	−32	($-6.8=d_{31}$)
	r_{33}	39	30.8
	d_{33}	−36	−37.5
	r_{22}	5.7	3.4
	d_{22}	17	3.6
LiTaO$_3$[a]	r_{13}	9.0	7.9
	d_{31}	−0.3	−1.5
	r_{51}	18	20
	d_{15}	−13	($-1.5=d_{31}$)
	r_{33}	44	35.8
	d_{33}	−49	−23
	r_{22}	−9.9	≈1
	d_{22}	3.9	2.4
GaAs[b]	r_{41}	−1.54	−1.5
	d_{14}	137	100–500
ZnS[c] (cubic)	r_{41}	$\begin{pmatrix}-0.81\\5.9\end{pmatrix}, \begin{pmatrix}0.28\\-3.3\end{pmatrix}$	1.2–2.1[a]
	d_{14}		30.5[d]
BeO[e,f]	r_{33}	$\begin{pmatrix}-3.9\\4.5\end{pmatrix}, \begin{pmatrix}-2.1\\5.9\end{pmatrix}$	…
	d_{33}		…
	r_{13}	$\begin{pmatrix}-2.1\\2.6\end{pmatrix}, \begin{pmatrix}-1.0\\0.1\end{pmatrix}$	…
	d_{31}		…
	r_{42}	$\begin{pmatrix}-1.3\\1.6\end{pmatrix}, \begin{pmatrix}-0.6\\0.2\end{pmatrix}$	…
	d_{24}		…
ZnO[e,g]	r_{33}	$\begin{pmatrix}2.3\\-7.6\end{pmatrix}, \begin{pmatrix}0.4\\-1.8\end{pmatrix}$	2.6
	d_{33}		−9.5
	r_{13}	$\begin{pmatrix}-1.4\\3.0\end{pmatrix}, \begin{pmatrix}-1.4\\3.0\end{pmatrix}$	−1.4
	d_{31}		2.8
	r_{42}	$\begin{pmatrix}-1.1\\3.4\end{pmatrix}, \begin{pmatrix}0.5\\0.6\end{pmatrix}$	…
	d_{24}		3.1
CdS[e,h]	r_{33}	$\begin{pmatrix}-1.5\\18.1\end{pmatrix}, \begin{pmatrix}+0.5\\-10.0\end{pmatrix}$	2.4
	d_{33}		42±13
	r_{13}	$\begin{pmatrix}-2.7\\3.0\end{pmatrix}, \begin{pmatrix}+0.1\\-8.6\end{pmatrix}$	1.1
	d_{31}		−26±5
	r_{42}	$\begin{pmatrix}-1.2\\14.2\end{pmatrix}, \begin{pmatrix}+0.27\\-6.2\end{pmatrix}$	…
	d_{24}		−29±8

[a] Values of r from I. P. Kaminow and E. H. Turner, Appl. Opt. **5**, 1612 (1966); values of d from R. C. Miller and A. Savage, Appl. Phys. Letters **9**, 169 (1966); J. E. Bjorkholm, IEEE J. Quantum. Electron. **QE-4**, 970 (1968); **QE-5**, 260 (1969).

[b] Reference 5.

[c] Scattering data from Ref. 24.

[d] C. K. N. Patel, Phys. Rev. Letters **16**, 613 (1966).

[e] Scattering data from Ref. 7, experimental values of r from Kaminow and Turner (footnote a).

[f] Experimental data not available presently.

[g] Experimental values of d from R. C. Miller, Appl. Phys. Letters **5**, 17 (1964).

[h] Experimental values of d from Patel (footnote d).

$\mathbf{S}^L$, and d_{13}. Geometrical requirements and the occurrence of optical index damage in LiNbO$_3$ and LiTaO$_3$ combine to reduce the signal-to-noise ratio for the $S_{33}{}^L$ measurements and these effects account qualitatively for the higher deviation. It is also likely that the values for d_{33} are not so accurate since phase-matched measurement of this quantity is not possible. For the E modes the agreement is less satisfactory, although the compounding of errors is much more severe with nine modes than with four as for the A_1 modes, and as the E-mode LO efficiencies are generally small, the measurements are prone to relatively greater experimental error as well. It is also possible that small uncertainties in the mode frequencies play a significant effect in calculating the LO efficiencies. The (22) results are considered to agree with the theory, in spite of the discrepancy between calculated and measured values of r_{22} for LiTaO$_3$. This coefficient is dominated by lattice contributions and a different choice of relative signs for these is required to produce agreement with the measured value of r_{22}. It is not surprising that in at least one instance the "noise" in the input data is sufficient to cause a minimum variance solution to correspond to an incorrect sign choice out of the 512 possibilities.

All in all, it is felt that the theory of Sec. I provides a quantitative description of the relations between electro-optic and SHG coefficients and Raman scattering efficiencies for LiNbO$_3$ and LiTaO$_3$ at room temperature, at least to the accuracy of the published data. Strong evidence is thus provided for the validity of using the macroscopic field in (1.17). Also, it appears that the influence of anharmonic effects on the LO scattering efficiencies of LiNbO$_3$ and LiTaO$_3$ are not significant in comparison to the present experimental error.

III. DISCUSSION

The relations given in Sec. I permit the determination of nonlinear optical coefficients from Raman scattering data, at least in principle. Practically, there is a "threshold" requirement on the accuracy of the Raman data which must be met for an unambiguous choice of the signs of the various lattice contributions to be made. In general, the more lattice modes contribute, the more accurately the Raman data must be known. In any given case the degree of precision required for an unambiguous determination depends on the particular combinations and magnitudes of frequencies and scattering efficiencies of the optic modes of the appropriate symmetry. It seems doubtful that determination of optical nonlinearity from Raman data for crystals having appreciably more complicated spectra than LiNbO$_3$ would be practical.

To determine the degree to which this method of measurement of nonlinear coefficients is practical, "best-fit" values of **d** and the resultant values of **r** are listed for LiNbO$_3$ and LiTaO$_3$ in Table IV, computed from the Raman data and refractive-index data alone. Values of **r** and **d** for GaAs[6] are included as well, as are values for ZnS, computed from Nilsen's scattering data,[23] and for ZnO, BeO, and CdS computed from the data of Arguello *et al.*[7]

As discussed elsewhere,[6] we consider the Raman determination of d_{41} and r_{41} for GaAs to be the best present value. Both possible solutions for ZnS from Nilsen's scattering data[23] and for BeO, ZnO, and CdS from the scattering efficiencies of Ref. 7 are listed. Both Nilsen and Arguello *et al.* confuse the electro-optic

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[23] W. G. Nilsen, Phys. Rev. **182**, 838 (1969).

coefficient with the purely electronic contribution thereto. Since they ignore the lattice contribution to the electro-optic coefficient, their comparison of calculated and experimental values would be appropriate only if the lattice contributions were small; which is not in fact the case. The confusion stems from application of equations from the earlier paper by Loudon cited above[2]; see Sec. 2 of the Appendix.

For $LiNbO_3$ and $LiTaO_3$ the quantities derived from the A_1-mode data are in fairly good agreement with the direct measurements. The values of d_{22} and d_{15} determined from the E modes do not agree so well. "Measured" values for d_{15} are actually the value for d_{31}, which we have assumed to be the same as d_{15} as required by Kleinman's proposed symmetry.[24] With the exception of r_{22} for $LiTaO_3$ the electro-optic coefficients calculated all agree with direct measurement to within 40% on an *absolute* basis. For ZnS only the constant-strain values for r_{41} are available, and our computed value should properly be compared to the constant-stress value.

The computed values for r and d for CdS and ZnO compare adequately with directly measured quantities. CdS exhibits considerable dispersion in the Raman scattered intensities in the visible transparency region[8] and values for r at 514.5 nm rather than 632.8 nm and for d(SHG) in the visible rather than at 10 600 nm, if available, would be more appropriate for comparison. The values for ZnO, which shows much less dispersion, are in excellent agreement.

We conclude that the determination of nonlinear optical coefficients from Raman data can indeed be practical, particularly as an alternative when direct measurement is impossible or inconvenient. This method could be particularly useful for the evaluation of new nonlinear optical materials, which are often not available with the optical or electrical quality required for quantitative direct measurement.

Finally, we wish to point out that Eq. (1.21) may be used as a test of the Kleinman symmetry proposal[23] mentioned earlier. Consider the case of quartz, which belongs to point group $D_3(32)$, wherein d_{14}(SHG) $=-d_{25}$(SHG) is required by the point symmetry. According to Kleinman's symmetry proposal (d_{ijk} invariant to any permutation of ijk), however, d_{14}(SHG) $=d_{25}$(SHG). Thus d_{14}(SHG) and d_{25}(SHG) must vanish for quartz; from (1.21), then,

$$\sum_i [S_{xyz}{}^L(i)/\sigma'(i)] = \sum_i [S_{xyz}{}^T(i)/\sigma(i)],$$

where the sum runs over the E-symmetry modes. While other aspects of the Raman spectrum of quartz have been studied extensively,[25] quantitative intensity data has not been published. Such a test of the Kleinman symmetry proposal should be at least as sensitive as test involving direct measurement of SHG coefficients.

IV. CONCLUSION

Equations have been derived relating the Raman scattering efficiencies for longitudinal and transverse optic-mode branches and nonlinear optical coefficients in acentric crystals of (otherwise) arbitrary symmetry. Within the limitations of the adiabatic and electrostatic approximations, and the harmonic approximation, the equations may be applied to the quantitative determination of nonlinear optical coefficients in terms of Raman data. The use of the macroscopic field, rather than the local field, in computing the electro-optic contribution to the LO scattering efficiency, has been justified, although either description will give correct results if used in a consistent way.

Evidence has been presented that the equations are indeed valid for $LiNbO_3$, and approximately valid for $LiTaO_3$, at room temperature. The results of computer analysis of the equations and the various published Raman and nonlinear optical data, indicate adequate agreement between theory and experiment on an absolute basis without any adjustable parameters.

Note added in proof. The absolute signs of all components of r are now known experimentally for $LiNbO_3$ [K. F. Hulme, P. H. Davies, and V. M. Cound, J. Phys. C **2**, 855 (1969)]. Also the absolute signs of the d components for ZnO, CdS, $LiNbO_3$, and $LiTaO_3$ are now known [R. C. Miller and W. A. Nordland, Appl. Phys. Letters **16**, 174 (1970); and (unpublished)]. These results have been included in Tables III and IV. A positive value for d_{31} ($LiTaO_3$) requires $r_{13}<0$, in conflict with Turner's measurement (footnote a, Table III), otherwise the sign relations are generally consistent with the Raman data.

APPENDIX

1. Macroscopic and Microscopic Fields

To some extent our difference with the authors who consider the local field to be the proper field for computation of the electro-optic contribution to LO Raman scattering efficiency is only semantic. We consider that the state of the crystal is completely described by giving the $3N$ coordinates of the N atoms in a unit cell, and the three components of the macroscopic electric field, including any externally applied electric field. It is clear that these $3N+3$ quantities suffice to cover all degree of freedom of the crystal plus external electric field. The local field at the lth atomic position may be written as[14,16]

$$\mathbf{E}_{\mathrm{loc}(l)} = \sum_m \beta(l,m)\mathbf{P}(m), \tag{A1}$$

where $\mathbf{P}(m)$ is the polarization due to atoms of type m and $\beta(l,m)$ is the Lorentz local-field factor. We may now consider that the macroscopic optical polarizability α_{ij} may be given as a sum over the microscopic polarizability contributions from each atom, which we

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[24] D. A. Kleinman, Phys. Rev. **126**, 1977 (1962).

[25] See, for example, J. F. Scott and S. P. S. Porto, Phys. Rev. **161**, 903 (1967).

call $\gamma_{(l)}$; thus,

$$\alpha_{ij}=\sum_l \gamma_{ij}{}^{(l)}.$$

We may now write for the differential of α_{ij}

$$d\alpha_{ij}=\sum_l d\gamma_{ij}{}^{(l)} \tag{A2}$$

and reexpress (1.16) or (1.17) with the local-field terms explicitly displayed:

$$d\alpha_{ij}=\sum_l\left(\frac{\partial\gamma_{ij}{}^{(l)}}{\partial W^\kappa}\bigg|_{E_{\mathrm{loc}(l)},\,E_{\mathrm{mac}}}+\frac{\partial\gamma_{ij}{}^{(l)}}{\partial E_{\mathrm{loc}(l)}{}^\kappa}\bigg|_{W,E_{\mathrm{mac}}}\frac{\partial E_{\mathrm{loc}(l)}}{\partial W^\kappa}\right.$$
$$\left.+\frac{\partial\gamma_{ij}{}^{(l)}}{\partial E_{\mathrm{mac}}}\bigg|_{W,E_{\mathrm{loc}}}\frac{\partial E_{\mathrm{mac}}}{\partial W^\kappa}\right)dW^k. \tag{A3}$$

The third sum on the right-hand side of (A3) contains $\partial\alpha/\partial E_{(\mathrm{mac})}$ which we will identify with $4d$(SHG). The first two terms were called simply $\partial\alpha/\partial W$ in Sec. I. Since the local fields are functions of the atom positions **W** only [from (A1) and (1.2)], it is immaterial whether (A3) or the forms of (1.16) and (1.17) are used. In either case, only the *macroscopic* field term contributes an additional amount to the LO scattering amplitude, above and beyond the TO amplitude. It is not possible to identify the microscopic quantities $\partial\gamma/\partial E_{\mathrm{loc}}$ with any of the nonlinear optical coefficients, which are defined so as to relate macroscopic fields.[15]

2. Identification of $\partial\alpha/\partial E$

It is easily seen that $(\partial\alpha/\partial E_{\mathrm{mac}})_W$ can correspond quantitatively only with a nonlinear optical coefficient determined with all three electromagnetic frequencies well above the lattice resonances so that the optic modes cannot contribute. Boyd and Kleinman[15] show that the proper relation to the SHG coefficient is

$$(\partial\alpha/\partial E_{\mathrm{mac}})_W=4d(\mathrm{SHG}). \tag{A4}$$

Burstein *et al.*[9] denote this quantity as b, and refer to it as the "electro-optic tensor," whereas it actually represents *only* the nonlattice contribution to the linear electro-optic (Pockels) tensor $r_{ij\kappa}$. Mooradian and McWhorter[5] correctly identify the quantity b with the SHG tensor rather than the electro-optic tensor, but are in error numerically by a factor of 2, i.e., they write $b=2d$. (Their numerical results for GaAs appear to be based on the correct relation, or to include a compensating factor-of-2 error, however.) Kaminow and Johnston[4] made a similar mistake, corrected in an erratum.

Loudon has referred to the additional LO scattering term as an electro-optic effect[26] and Poulet[1] also mistakenly identified this contribution with the Pockels coefficients. That the error persists is shown in the recent papers by Arguello, Rousseau, and Porto,[7] and Nilsen,[23] who continue to confuse the electro-optic contribution to LO scattering and the electro-optic coefficient appropriate to the Pockels effect. Their values for electro-optic coefficients computed from Raman data thus represent only the electronic contribution terms to the electro-optic coefficient. Since they have not included the lattice contribution, their quantitative comparison with directly measured electro-optic coefficients is not appropriate, particularly as the lattice contributions to the electro-optic coefficients in the materials they consider are of similar magnitude to the purely electronic terms.

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[26] Workers who wish to apply Eq. 52 of the first paper cited in Ref. 2 should be aware that Loudon has pointed out (second paper cited in Ref. 2) that Z_{41} in that equation represents only an electronic electro-optic contribution.