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Raman Scattering by Lithium Niobate

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Polarized Raman scattering from a crystal of $LiNbO_3$ has been measured at room temperature using a continuous He-Ne gas laser as a source. The spectra and scattering efficiencies are discussed and frequency assignments are made for three transverse A_1 and one longitudinal and seven transverse E vibrations.

INTRODUCTION

RECENT studies have shown that lithium niobate, a uniaxial, piezoelectric crystal, possesses several interesting and useful physical properties. Whereas the ferroelectric properties of $LiNbO_3$ have been known[1] for some time, recent investigations have dealt with acoustic properties[2] where large electromechanical coupling and low transmission loss for elastic waves were found, nonlinear optical phenomena including phase-matched second-harmonic generation[3,4] and construction of a tunable optical parametric oscillator,[5] and measurements of electro-optic properties,[6,7] dielectric constants and loss tangents,[8] and photoelastic tensor components.[9] In view of the interest in this material, we have examined the polarized Raman-scattering spectra for $LiNbO_3$ using a laser source.

EXPERIMENTAL

A continuous 6328-Å He-Ne laser (Spectra-Physics Model 125) having an output power of $\sim$85 mW was used as the Raman source. Incident laser radiation was passed through a narrow-bandpass filter, chopped, and focused on the $LiNbO_3$ crystal. In all cases, the Raman-scattered radiation was observed at 90° from incidence and was focused on the entrance slit of a scanning double Czerny-Turner spectrometer (Spex Industries Model 1400). The output was detected using an S-20 photomultiplier (ITT FW 130 G), lock-in amplifier (PAR Model HR8), and chart recorder. Polarization measurements were made utilizing an adjustable half-wave plate to rotate the plane of the incident laser polarization and a calcite Ahrens prism to distinguish Raman bands polarized parallel and perpendicular to the scattering plane. In the wavelength region of interest, a factor of ≈ 2 was found to be necessary to correct for differences in the interaction between the measuring system and Raman radiation polarized parallel or perpendicular to the entrance aperture. In the present experiments, measurements were made to within 10 cm^{-1} of the laser frequency employing an experimental resolution of 5 cm^{-1}. Frequencies were determined by superposition of Ne emission lines; the estimated accuracies ranging from 0.4 cm^{-1} for sharp Raman bands to about 4 cm^{-1} for broad bands.

The $LiNbO_3$ crystal studied was grown by the Linde Company. It was x-ray oriented and cut in the form of a cube, approximately 4 mm on a side, with the faces perpendicular to the standard set[10] of orthogonal principal axes x, y, z for trigonal symmetry (z is a unique threefold axis and x is perpendicular to the glide plane). The orientation of the crystal during a measurement is given by the notation[11] $x(zz)y$, which denotes, from left to right, the direction of the incident radiation, its polarization, the polarization of the detected Raman-scattered radiation, and the direction of its observation, respectively, in terms of the above crystal principal axes. All spectra were recorded with the incident and scattered radiation directed along principal axes; the orientation accuracy was within $\pm 5°$. Raman spectra for $LiNbO_3$ at room temperature and for several different directions of polarization and propagation are shown in Fig. 1. In Fig. 2, $y(zy)x$ spectra recorded at room temperature and $\approx 100°K$ are compared.

THEORY

Lithium niobate belongs to the space group $R3c$[12] and has point group symmetry $3m$. There are two formula

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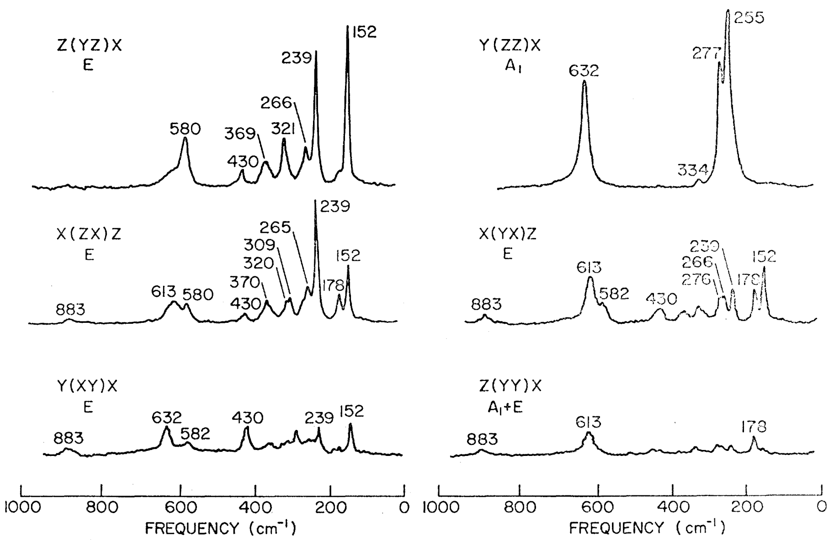

FIG. 1. Raman scattering by LiNbO$_3$ at room temperature for various directions of polarization and propagation.

units per unit cell and therefore 30 degrees of vibrational freedom. To a first approximation, vibrations with wave vector **k** near zero may be characterized group theoretically as $5A_1$, $5A_2$, and $10E$ phonon branches. Of these, one A_1 and one E are the three acoustic branches, the five A_2 fundamentals are Raman and infrared inactive, and the remaining $4A_1$ and $9E$ optical branches are both Raman and infrared active. For a general direction of phonon propagation, long-range electric fields associated with polar vibrations remove the degeneracy of the E branches at $\mathbf{k}=0$ and can admix phonons of different symmetries.

The theory of Raman scattering for uniaxial piezoelectric crystals has been reviewed recently by Loudon.[13] The intensity of Stokes-shifted Raman scattered radiation assuming a simple-harmonic-oscillator approximation is given by

$$I=C\nu_s^4[(n_p+1)/\Delta\nu_p]\{\sum_{\substack{\rho,\sigma,\tau\\=x,y,z}} e_i^\sigma R_{\sigma\rho}^\tau(\alpha\hat{\xi}^\tau+\beta\hat{k}^\tau)e_s^\rho\}^2, \qquad (1)$$

where C is a constant, ν_s is the frequency at which a phonon of frequency displacement $\Delta\nu_p$ is observed, n_p is the Bose-Einstein thermal population factor, e_i^σ and e_s^ρ are components of the polarization unit vectors for the incident and scattering light, respectively, along the principal axes σ and ρ, $\hat{\xi}$ and $\hat{k}$ are unit-vector components of the phonon polarization and propagation, α is a constant, and β is proportional to the magnitude of the electric field. The matrices for the components of the Raman tensor $R_{\sigma\rho}^\tau$ for the irreducible representations of the $3m$ point group are[13]

$$R[A_1(z)]=\begin{bmatrix} a & 0 & 0\\ 0 & a & 0\\ 0 & 0 & b\end{bmatrix},$$

$$R[E(y)]=\begin{bmatrix} c & 0 & 0\\ 0 & -c & d\\ 0 & d & 0\end{bmatrix}, \qquad (2)$$

$$R[E(-x)]=\begin{bmatrix} 0 & -c & -d\\ -c & 0 & 0\\ -d & 0 & 0\end{bmatrix},$$

where the x, y, or z in parentheses after the irreducible representation indicate the phonon polarization direction and is denoted by the index τ in Eq. (1).

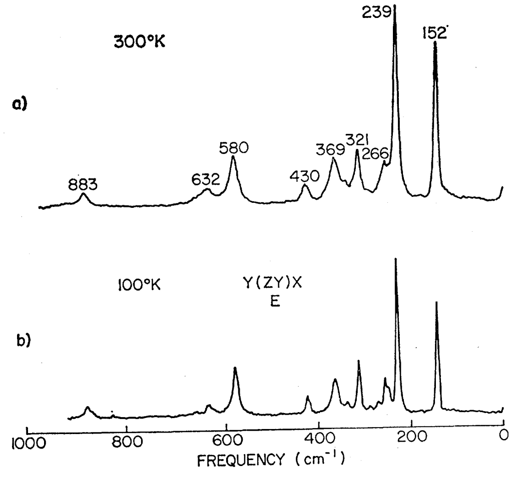

FIG. 2. Comparison of $y(zy)x$ Raman scattering by LiNbO$_3$ at (a) room temperature and (b) $\approx$100°K.

The properties of long-wavelength lattice vibrations in uniaxial crystals have been treated by Loudon.[14] In the limit $|\nu_t^{\parallel}-\nu_t^{\perp}|<|\nu_l^{\parallel}-\nu_t^{\parallel}|$ and $|\nu_l^{\perp}-\nu_t^{\perp}|$, the angular variations of the "quasitransverse" and "quasilongitudinal" Raman-active phonon frequencies

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are given by

$$\nu_t^2 = (\nu_t^{\parallel})^2 \sin^2\theta + (\nu_t^{\perp})^2 \cos^2\theta,$$

and (3)

$$\nu_l^2 = (\nu_l^{\parallel})^2 \cos^2\theta + (\nu_l^{\perp})^2 \sin^2\theta,$$

where t and l denote transverse and longitudinal optical modes propagating parallel ($\parallel$) or perpendicular ($\perp$) to the z axis, θ being the angle between the z axis and the phonon propagation vector. Whereas Eq. (3) was derived when only one group of three infrared-active lattice vibrations is present, several such groups of vibrations exist in $\mathrm{LiNbO_3}$ and therefore its validity for $\mathrm{LiNbO_3}$ is questionable, although Eq. (3) may be applicable for a group which is well separated from the other groups. A generalized Lyddane-Sachs-Teller relation[15] of the type

$$\prod_{j=1}^{N} \left[\frac{\nu_l(j)}{\nu_t(j)}\right]^2 = \frac{\epsilon_0}{\epsilon_\infty} \tag{4}$$

should apply, however, where ϵ_0 is the static and ϵ_∞ is the optical dielectric constant and the product is over the N infrared-active vibrations. Values of the static dielectric constants and the optical indices of refraction for $\mathrm{LiNbO_3}$ are given in Refs. 8 and 3, respectively, and yield $\epsilon_0/\epsilon_\infty \sim 5$–15.

DISCUSSION

Raman scattering efficiencies for piezoelectric crystals and their angular variations are dependent upon whether electrostatic forces predominate over anisotropy in the short-range interatomic forces or vice versa. The scattering efficiencies for the former case were calculated from Eqs. (1) and (2) for the crystal orientations used in Figs. 1 and 2 and the nonzero values are tabulated in Table I. From these results, only transverse A_1 symmetry branches should appear in the $y(zz)x$ spectrum. Similarly, only E branch phonons with polarization transverse to both the propagation direction and the z axis should appear in $z(yz)x$. Assignments of fundamental optical mode frequencies of $\mathrm{LiNbO_3}$ based upon the spectra observed for these orientations are given in Table II. The weak band which occurs in several spectra at $\approx 883\ \mathrm{cm^{-1}}$ is tentatively ascribed to a longitudinal E branch. Bands at 178 and 613 $\mathrm{cm^{-1}}$ have appreciable intensity only in orientations $z(yy)x$, $x(zx)z$, and $x(yz)z$, with additional structure at 276 and 309 $\mathrm{cm^{-1}}$ observed in the latter two cases. If $|\nu_t^{\parallel} - \nu_t^{\perp}|$ is small, as assumed in Eq. (3), these bands are more likely to be quasilongitudinal than quasitransverse. The small peak at 298 $\mathrm{cm^{-1}}$ appearing in $y(xy)x$ is also observed in $y(zy)x$ at 100°K.

Table I. Calculated Raman scattering efficiencies for $3m$ symmetry when electrostatic forces predominate over anisotropy. (o) and (e) denote ordinary and extraordinary phonons, respectively; θ is the angle between $\mathbf{k}$ and the z axis.

Orientation	Scattering efficiency	Character	θ
$z(yz)x$	$d^2\alpha^2$	E transverse (o)	45°
$x(zx)z$	$(d^2/2)(\alpha+\beta)^2$ $(d^2/2)\alpha^2$	E quasilongitudinal (e) E quasitransverse (e)	45°
$y(xy)x$	$(c^2/2)(\alpha+\beta)^2$ $(c^2/2)\alpha^2$	E longitudinal (e) E transverse (o)	90°
$y(zz)x$	$b^2\alpha^2$	A_1 transverse (e)	90°
$x(yx)z$	$(c^2/2)(\alpha+\beta)^2$ $(c^2/2)\alpha^2$	E quasilongitudinal E quasitransverse (e)	45°
$z(yy)x$	$(a^2/2)(\alpha+\beta)^2$ $(a^2/2)\alpha^2$ $c^2\alpha^2$	A_1 quasilongitudinal (e) A_1 quasitransverse (e) E transverse (o)	45°
$y(zy)x$	$(d^2/2)(\alpha+\beta)^2$ $(d^2/2)\alpha^2$	E longitudinal (e) E transverse (o)	90°
$z(yx)y$	$c^2\alpha^2$	E transverse (o)	45°

Table II. Symmetries and frequencies ($\mathrm{cm^{-1}}$) of several fundamental optical modes in $\mathrm{LiNbO_3}$ at room temperature.

A_1 transverse:	255, 277, 632
E transverse:	152, 239, 266, 321, 369, 430, 580
E longitudinal:	883

The temperature-dependent intensities of the above Raman bands were typical of those expected for one-phonon Stokes-shifted lines. As can be seen by comparison of the two $y(zy)x$ spectra in Fig. 2 taken at room temperature and $\approx$100°K, the lines narrow with decreasing temperature and additional structure is observed which may be indicative of small mode splittings. Any frequency shifts associated with the sharp 152 and 239 $\mathrm{cm^{-1}}$ peaks in going from $\approx$295 to $\approx$100°K are $\lesssim 1\ \mathrm{cm^{-1}}$; the linewidths decrease from 10 to 6 $\mathrm{cm^{-1}}$.

The scattering efficiencies in Table I for several spectra are the same except for d replaced by c, for example, $y(zy)x$—$y(xy)x$ and $x(zx)z$—$x(yx)z$. The relative intensities of these spectra in Fig. 1 suggest that $c < d$. The spectral intensity for $z(yx)y$, according to Table I, is proportional to c^2 and, while not shown, was found to be weak. No calculations or estimates of the constants of proportionality in the expressions for the Raman scattering efficiencies in uniaxial piezoelectric crystals have been reported to our knowledge; however, they would be of interest for the present $\mathrm{LiNbO_3}$ spectra.

The assignment of other fundamental optical-mode frequencies for $\mathrm{LiNbO_3}$ based upon the present data is hampered by uncertainties associated with (i) the expected angular dependence of the quasi-mode frequencies when there are several infrared-active lattice vibrations present, and (ii) the dominance of electrostatic forces over the anisotropy. Multiphonon proc-

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esses may also contribute to certain of the weaker unassigned bands. A $LiNbO_3$ crystal cut in another orientation, which from predicted scattering efficiencies could lead to an unambiguous determination of the longitudinal-branch frequencies and/or allow one to measure the frequency and intensity angular dependences, would obviously be desirable but unfortunately was not available. *Note added in proof.* The frequencies and strengths of infrared-active modes of $LiNbO_3$ have recently been determined from reflectivity measurements by J. D. Axe and D. F. O'Kane, Appl. Phys. Letters **9**, 58 (1966).

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Reformulation of the Dielectric Constant and of Ohm's Law in an Absorbing Medium*

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It is proposed that a fundamental revision of the formulation of the dielectric constant and of the conductivity of an absorbing and dispersive medium be considered. In the conventional formulation the dielectric constant ϵ of such a medium depends on the mechanism controlling the energy absorption, and therefore ϵ has the form $\epsilon\equiv\epsilon(\omega,\gamma)$, where ω is the frequency and γ is a "frictional" parameter representing the absorption process. Such a formulation, although widely accepted in the current literature and in the textbooks on electromagnetism, is not consistent with Maxwell's theory, and therefore is not adapted to the analysis of the energetic behavior of absorbing media. A different formulation is proposed in which the inconsistency with Maxwell's theory is removed. In the proposed formulation the dielectric constant of an absorbing medium is independent of the mechanism which controls the absorption process. The dielectric constant is of the type $\epsilon\equiv\epsilon(\omega)$ and not $\epsilon\equiv\epsilon(\omega,\gamma)$, i.e., it is the same as if the absorption mechanism did not exist at all. The mechanism of energy absorption is used to determine the conductivity of the medium but has no effect on the formulation of the dielectric constant. The novelty of the proposed formulation is based on the assumption which is used to arrive at a suitable definition of the driving force involved in the motion of a harmonic oscillator in the molecular model of an absorbing medium. In the conventional formulation the driving force $e\mathfrak{F}$ is assumed to be equal to $e\mathfrak{E}$ (where $\mathfrak{E}$ is the electric field intensity and e is the charge of an electron), whereas in the proposed formulation the assumption $e\mathfrak{F}=e\mathfrak{E}$ is replaced by the assumption $e\mathfrak{F}=e\mathfrak{E}+e\mathfrak{E}^{(\mathrm{extr})}$, where $e\mathfrak{E}^{(\mathrm{extr})}$ is an "extraneous" force. The extraneous force results from the conversion of the electrical field energy stored in the medium into "extraneous" energy (such as heat) which is removed from the medium during the interaction with an electric field. Therefore, $e\mathfrak{E}^{(\mathrm{extr})}$ acts as an energy sink. The distinction between the proposed formulation and the one used in the standard theory is based on a behavior of dispersive media which is physically different from the one customarily assumed, and therefore it does not represent merely a question of formalism. Using the concepts introduced in this analysis, Ohm's law is reformulated as representing a mechanism in which the rate of production of the dissipated energy is proportional to the mean energy stored in the medium. Such an interpretation of Ohm's law cannot be made in the framework of the standard theory, since the standard theory does not provide a procedure for determining the mean energy stored in an absorbing medium.

I. INTRODUCTION

WITHIN the last several decades and particularly in the first quarter of this century great advances have been made in the theory of dispersive media. As a result of the pioneer work of Sommerfeld and his associates[1] (particularly Brillouin), such concepts as the density energy stored by an alternating field in a dispersive medium, the velocity of energy transfer in an electric field interacting with a dispersive medium, have been clarified and formulated.

These pioneer investigations dealt, however, with dispersive media which are nonabsorbing. The results obtained have, therefore, a restricted applicability. No successful efforts have been made to date in extending these results to media in which a portion of the field energy is absorbed during the interaction process. Thus, some of the energetic aspects of the wave-matter interaction are very inadequately described at the present time. For instance, there is no adequate description of the process of building up of an electric field energy in an absorbing medium by means of a gradually increasing oscillating field, and therefore the concept of the energy stored by an oscillating field in an absorbing medium has not been formulated to date.

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