

Quantitatively, all these results are, of course, strictly valid for the chosen model only. It is felt, however, that in a qualitative sense the observations described in this section will have a more general validity, irrespective of the model. The model chosen here is a rather severe test of the method, as real metals, especially those of cubic symmetry, are often considerably less anisotropic, so a better reproduction of the actual probability distribution may be expected. The next step therefore ought to be a real, high-accuracy experiment on a metal with a well-known Fermi surface in order to see how well the shape of the Fermi surface can be derived from positron annihilation measurements. Such an experiment is presently being set up at this institute.

5. SUMMARY

In the present paper, a method has been developed to reconstruct the two-quantum momentum distribution from a number of angular correlations, measured for various orientations of a single crystal. In order to obtain a reliable picture of the momentum distribution, a considerably larger than usual number of correlations may be required. Moreover, if only a few correlations

are measured, the common practice of choosing p_z along axes of highest symmetry is unfavorable for an accurate determination of the momentum distribution. Distributions with a smoothly varying angular dependence are expected to be reproduced rather well, but difficulties may be experienced with distributions showing sharp peaks in certain directions. If the total measuring time is kept fixed, there exists an optimum between the effects of systematic and statistical errors. The position of this optimum depends on the choice of the set of crystal orientations for which the angular correlations are determined.

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Quantitative Determination of Sources of the Electro-Optic Effect in LiNbO_3 and LiTaO_3

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The electro-optic effect in crystals can be separated into two types of microscopic interaction: an electron-lattice contribution in which the applied field produces a lattice displacement, which in turn modifies the electronic polarizability (or refractive index), and a direct electron-field contribution in which the applied field modifies the electronic polarizability in the absence of lattice displacements. The latter contribution in LiNbO_3 and LiTaO_3 can be estimated from second-harmonic-generation experiments by Miller and Savage, and accounts for less than 10% of the refractive-index change. Each polar-lattice optic mode in LiNbO_3 and LiTaO_3 ($4A_1+9E$) contributes separately to the electro-optic effect an amount proportional to the product of its Raman-scattering efficiency and infrared oscillator strength. We have measured the absolute scattering efficiencies for LiNbO_3 and LiTaO_3 . The oscillator strengths for LiNbO_3 have been measured by Barker and Loudon. We find that the dominant contribution to the electro-optic coefficients r_{33} and r_{13} comes from the lowest-frequency A_1 mode; and to r_{42} and r_{22} from the next lowest E mode. These same modes dominate the low-frequency dielectric constant. The absolute values of r_{13} , r_{33} , r_{42} , and r_{22} calculated from the combined Raman, infrared, and second-harmonic-generation data are in excellent agreement with the electro-optic coefficients measured directly by Turner. In addition to the absolute scattering efficiencies for all the transverse and longitudinal modes in LiTaO_3 and LiNbO_3 , we have also determined the mode frequencies and linewidths, which are important in calculating Raman gain.

SPONTANEOUS Raman scattering is a form of light modulation that is produced by thermally excited lattice modes. In a piezoelectric crystal, some of these same modes can be excited by an externally applied electric field to produce light modulation by means of

the linear electro-optic effect. We derive¹ a simple relationship between an electro-optic coefficient measured at

¹I. P. Kaminow, in *Ferroelectricity: Proceedings of the Symposium on Ferroelectricity, General Motors Research Laboratories, Warren, Michigan, 1966* (Elsevier Publishing Company, Inc., Houston, Texas, to be published).

radio-frequencies and the corresponding Raman-scattering efficiencies, and confirm its validity on an absolute basis for both LiNbO_3 and LiTaO_3 . We find that the electro-optic effect is due primarily to the lowest-frequency A_1 -type optic mode and the next lowest E mode, with only a small pure electronic contribution.

Poulet² and, later, Loudon³ considered the influence of an electronic electro-optic effect on the Raman spectra of piezoelectric crystals as a means for explaining observed differences in transverse and longitudinal mode scattering efficiencies. In that case, the modulating electric field is produced by the thermally excited lattice polarization at the optic-mode frequencies. In a recent experiment using far-infrared lasers, Faust and Henry⁴ were able to apply modulating fields at frequencies near the optic modes of GaP and make a relative correlation between Raman efficiency and effective electro-optic coefficient in the dispersion region. They find the electronic contribution to the low-frequency electro-optic effect to be about double the lattice contribution for GaP.

The correspondence between observed electro-optic and Raman effects can be shown as follows. Take Q_k^m as the instantaneous amplitude of a polar mode with angular frequency ω_m and lattice displacements along k , where displacements along z and normal to z correspond to A_1 and E modes, respectively. Define the scattering efficiency⁵ $S_{ij,k}^m$ as the total optical power scattered with polarization i into solid angle $d\Omega$ from a length of crystal l , divided by the total incident power with polarization j . The only nonvanishing elements in a third-rank tensor with symmetry C_{3v} are $S_{xx,z}^m = S_{yy,z}^m = S_{13}^m$, $S_{zz,z}^m = S_{33}^m$ for A_1 modes; and $S_{xx,y}^m = S_{yy,y}^m = S_{xy,x}^m = S_{22}^m$, $S_{yz,y}^m = S_{xz,x}^m = S_{42}^m$ for E modes, where we have introduced a reduced notation for the interchangeable indices (ij). In terms of the differential polarizability $\alpha_{ij,k}^m$, the scattering efficiency (inside the medium) for a Stokes line is given in mks units by^{5,6}

$$S_{ij,k}^m = \left(\frac{\hbar\omega_m\omega_s^4(n_0^m+1)ld\Omega}{64\pi^2\epsilon_0^2c^4} \right) \left(\frac{v|\alpha_{ij,k}^m|^2}{K_k^m} \right), \quad (1)$$

where ω_s is the angular frequency of scattered light, n_0^m the Bose population factor, ϵ_0 the permittivity, c the velocity of light in vacuum, v the unit cell volume, and K_k^m the spring constant for the m mode. We will abbreviate the first factor in (1) by σ_m . By the definition of $\alpha_{ij,k}^m$, the change in i component of optical polarization per unit volume due to lattice displacements is $\alpha_{ij,k}^m Q_k^m E_j$, where summation over repeated indices is

understood, and E_j is the real instantaneous amplitude of the incident optical field.

According to the definition of clamped linear electro-optic coefficient⁷ $r_{ij,k}$, a modulating electric field E_k applied to a piezoelectric crystal at frequencies well above sample acoustic resonances, but well below lattice optic-mode frequencies, gives a differential optical polarization $\epsilon_0 n_i^2 r_{ij,k} n_j^2 E_k E_j$, where n_i and n_j are principal refractive indices at the optical frequencies. Physically, the electro-optic effect may be regarded as follows. The modulating field E_k induces proportional lattice displacements $Q_k^m = \beta_k^m E_k$ in the various polar modes. These displacements in turn cause a perturbation via an electron-lattice interaction in the optical polarization induced by the optical field E_j . An additional perturbation on the polarization is introduced by a direct electron-modulating field interaction in which the lattice remains rigid, as in the case of optical second harmonic generation (SHG). The value of this latter contribution, $\xi_{ijk} E_k E_j$, can be calculated from SHG measurements. The lattice contribution $\alpha_{ij,k}^m \beta_k^m E_k E_j$ can be determined from a combination of Raman-scattering and infrared-absorption measurements.

Equating the electro-optic polarization to the sum of lattice and electronic contributions, we have the desired relationship¹ between electro-optic and Raman parameters,

$$\epsilon_0 n_i^2 r_{ij,k} n_j^2 = \alpha_{ij,k}^m \beta_k^m + \xi_{ijk}, \quad (2)$$

summed over m . Equation (2) holds for lattice-mode frequencies well below electronic transition frequencies. The parameters in (2) are insensitive to variations in optical frequency far from electronic and lattice resonances. The dependence of $r_{ij,k}$ on modulating frequency⁴ results from the dispersion in β_k^m near ω_m (transverse).

In electro-optic measurements, E_k is produced by a low-impedance voltage source connected to electrodes on the crystal. Since the depolarizing field is effectively short-circuited, the local field is that for a transverse mode⁶ and the transverse value of $\alpha_{ij,k}^m$ must be employed in (2). At frequencies well below ω_m , β_k^m is given by⁶ $[\epsilon_0 \Delta\kappa_k^m v / K_k^m]^{1/2}$ or, alternatively, by $\epsilon_0 \Delta\kappa_k^m v / Z_k^m$, where $\Delta\kappa_k^m$ is the contribution of the m mode to κ_k , the low-frequency dielectric constant, and Z_k^m is the effective charge in a unit cell of volume v . Then, using (1) and the first form of β_k^m for now, we have (compare Ref. 3)

$$r_{ij,k} = (\epsilon_0 n_i^2 n_j^2)^{-1} \{ \pm [\epsilon_0 \Delta\kappa_k^m S_{ij,k}^m / \sigma_m]^{1/2} + \xi_{ijk} \}, \quad (3)$$

in which the summation is over m and the ambiguities in sign arise from taking the square root of the absolute value in (1).

We have examined the Raman spectra of both LiNbO_3 and LiTaO_3 and have found all the allowed ($4A_1 + 9E$) frequencies for both transverse (T) and

² H. Poulet, Ann. Phys. (Paris) **12**, 908 (1955).

³ R. Loudon, Proc. Roy. Soc. (London) **A275**, 223 (1963).

⁴ W. L. Faust and C. H. Henry, Phys. Rev. Letters **17**, 1265 (1966).

⁵ R. Loudon [Advan. Phys. **13**, 423 (1964)] defines efficiency in terms of photon fluxes.

⁶ M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, London, 1956).

⁷ I. P. Kaminow and E. H. Turner, Proc. IEEE **54**, 1374 (1966).

TABLE I. Observed parameters of Raman spectra.

E Modes					A ₁ Modes				
$\omega_m/2\pi c$ (cm ⁻¹)	$(S_{22}^m)/ld\Omega$ 10 ⁻⁶ cm ⁻¹ sr ⁻¹	$(S_{42}^m)/ld\Omega$ 10 ⁻⁶ cm ⁻¹ sr ⁻¹	$\frac{\alpha_{42}}{\alpha_{22}}$	2 Γ (cm ⁻¹)	$\omega_m/2\pi c$ (cm ⁻¹)	$(S_{13}^m)/ld\Omega$ 10 ⁻⁶ cm ⁻¹ sr ⁻¹	$(S_{33}^m)/ld\Omega$ 10 ⁻⁶ cm ⁻¹ sr ⁻¹	$\frac{\alpha_{35}}{\alpha_{13}}$	2 Γ (cm ⁻¹)
(A) LiNbO ₃									
92 T	~0.004	~0.006	a	8	253 T	1.76	16.0	+	15
117 L	~0.005	a	b	8	273 L	1.05	(0.32,2.2)	-	8
152 T	0.39	3.8	(±)	8	275 T	1.86	4.0	+	8
198 L	0.04	0.07	b	8	331 L	1.22	(1.22,1.22)	+	6
238 T	0.11	2.9	(±)	8	334 T	0.94	0.95	+	6
243 L	0.05	a	b	8	428 L	0.95	(0.38,1.78)	+	10
262 T	0.11	0.54	(±)	6	637 T	4.65	10.2	+	15
298 L	0.09	a	b	7	874 L	3.18	(1.64,5.4)	+	20
322 T	0.16	0.96	(∓)	6					
345 L	0.07	0.05	b	6					
368 T	0.01	0.94	(±)	15					
428 L	0.51	a	b	12					
436 T	0.15	0.39	(∓)	8					
448 L	0.03	a	b	11					
582 T	0.30	2.2	(∓)	15					
621 L	0.04	0.03	b	17					
630 T	0.54	0.04	(∓)	8					
881 L	1.1	1.05	b	20					
(B) LiTaO ₃									
74 T	0.09	~0.003	(±)	19	201 T	0.49	10.4	+	15
80 L	0.10	a	b	12	~245 L	~0.03	~0.03	+	8
140 T	0.45	1.43	(±)	6	253 T	0.16	0.64	+	15
163 L	0.06	a	b	6	347 L	0.35	(0.44,0.28)	+	8
206 T	0.04	0.59	(±)	6	356 T	0.44	0.18	+	8
~248 L	0.02	0.02	b	8	399 L	0.18	(0.19,0.17)	+	10
251 T	0.03	0.03	(±)	10	600 T	0.75	3.2	+	8
278 L	0.06	0.05	b	6	864 L	0.72	(0.73,0.69)	+	14
316 T	0.05	0.54	(∓)	6					
318 L	0.04	a	b	12					
383 T	0.06	0.48	(±)	12					
452 L	0.08	a	b	6					
462 T	0.09	0.09	(±)	6					
474 L	0.08	a	b	6					
596 T	0.40	0.03	(±)	11					
648 L	0.24	a	b	17					
662 T	0.10	0.04	(∓)	15					
870 L	0.04	0.09	b	15					

* Insufficient intensity or interference with other modes.

^b Indeterminate by symmetry for 90°.

longitudinal (L) optic modes, and most of the corresponding scattering efficiencies. The observations were made with 90° scattering using the 4880 Å line of an argon laser. Crystals were oriented so that the observed phonon Q_k^m traveled either along z or in a plane normal to z . The observed frequencies are listed in Table I. The large number of modes present make it difficult to decide which longitudinal and transverse modes are partners. With the exception of the 92- and 630-cm⁻¹ lines, which have not been reported previously, the LiNbO₃ results agree with earlier infrared and Raman observations.⁸⁻¹⁰ The LiTaO₃ spectrum has not been examined before. The linewidth 2 Γ ranges between 6 and 20 cm⁻¹. As indicated in Table I, the generalized

Lyddane-Sachs-Teller relations,¹¹ with κ_k the dielectric constant¹² and κ_k^∞ the pure electronic contribution¹³ to κ_k extrapolated to low frequency, are well satisfied.

The scattering efficiencies listed in Table I were obtained by comparison with scattering from the 992-cm⁻¹ benzene line, whose peak scattering efficiency at 4880 Å, 0.264×10^{-6} cm⁻¹sr⁻¹ per angstrom bandwidth, and linewidth, 2.3 cm⁻¹, were measured recently.¹⁴ The unknown efficiency is found by multiplying the integrated benzene efficiency, assuming a Lorentzian line shape, by the ratio of areas of the unknown and benzene

¹¹ W. Cochran and R. A. Cowley, J. Phys. Chem. Solids **23**, 447 (1962).

¹² A. W. Warner, M. Onroe, and G. A. Coquin, J. Acoust. Soc. Am. (to be published).

¹³ W. L. Bond, J. Appl. Phys. **36**, 1674 (1965); A. D. Boyd, R. C. Miller, K. Nassau, W. L. Bond, and A. Savage, Appl. Phys. Letters **5**, 234 (1964).

¹⁴ J. G. Skinner and W. G. Nilsen, J. Opt. Soc. Am. (to be published).

⁸ A. S. Barker, Jr., and R. Loudon, Phys. Rev. (to be published).

⁹ J. D. Axe and D. F. O'Kane, Appl. Phys. Letters **9**, 58 (1966); **9**, 253 (1966).

¹⁰ R. F. Schaufele and M. J. Weber, Phys. Rev. **152**, 705 (1966).

lines as observed with a scanning spectrometer system having a particular setting of all parameters. Corrections are made for polarization and spectral sensitivity of the system using a calibration obtained with a standard tungsten-iodine lamp. The external incident and scattered powers are corrected for reflections at the crystal surfaces, and the effect of refractive index on solid angle is taken into account. Including the uncertainty in the benzene calibration, the error in efficiency measurements is probably within the range 10–20%, depending upon mode strength and interference with nearby lines. From Table I, we make the observation that efficiencies are generally weaker for longitudinal than for transverse modes.^{2,3}

For particular combinations of incident and scattered directions and polarizations, α_{13}^m and α_{33}^m (in the reduced notation) appear individually or as a difference inside the absolute value sign in a relation like (1) for a transverse A_1 mode. Therefore, the individual scattering efficiencies as well as the sign of α_{33}/α_{13} can be determined and are noted in Table I. The number of combinations available for longitudinal A_1 modes is more restricted and an ambiguity arises in the determination of individual efficiencies. In the case of E modes, we are only able to find the sign of $\alpha_{42}^m/\alpha_{22}^m$ relative to $\alpha_{42}^{m'}/\alpha_{22}^{m'}$, where $m \neq m'$.

Using scattering efficiencies with appropriate relative sign constraints from Table I(a), and $\Delta\kappa_k^m$ from infrared measurements,⁸ and the absolute value of ξ_{ijk} from SHG measurements,^{15,16} we calculate from (3) for LiNbO_3 ,

$$\begin{aligned} r_{33} &= 33.2\{\pm 1 \pm 0.12 \pm 0.02 \mp 0.24\} \pm 3.5 \doteq (30.6 \pm 3.5), \\ r_{13} &= 9.4\{\pm 1 \pm 0.25 \pm 0.07 \mp 0.49\} \pm 0.5 \doteq (7.8 \pm 0.5); \\ r_{42} &= \pm 17.2\{\pm 0 \pm 1 \pm 0.15 \pm 0.17 \pm 0.14 \pm 0.14 \\ &\quad \pm 0.02 \pm 0.02 \pm 0\} \pm 0.5 \doteq \pm (28.2 \pm 0.5), \\ r_{22} &= 5.0\{\pm 0 \pm 1 \pm 0.09 \pm 0.23 \mp 0.18 \pm 0.05 \mp 0.05 \\ &\quad \mp 0.25 \mp 0\} \pm 0.2 \doteq (3.95 \pm 0.2), \end{aligned} \quad (4)$$

in units of 10^{-12} m/V, where the first terms give the lattice contributions in order of increasing mode frequencies and the last term gives the SHG-determined electronic contribution of undetermined sign. If an upper (lower) sign inside the brackets is taken for the contribution of a given lattice mode to r_{33} or r_{42} , then an upper (lower) sign must be taken for the contribution of that mode to r_{13} or r_{22} . The ratios r_{33}/r_{13} and r_{42}/r_{22} are relatively insensitive to any consistent choice of signs and, according to (4), the calculated r_{33}/r_{13} will always be positive. It is possible to find a consistent set of signs to give good agreement with the measured clamped electro-optic coefficients. Thus, all upper signs inside the brackets give the numbers following the

(\doteq) sign in (4) with the electronic part displayed separately. For comparison the measured electro-optic values are¹⁷

$$\begin{aligned} r_{33} &= 30.8, & r_{13} &= 8.6, & r_{33}/r_{13} &= +3.6; \\ r_{42} &= 28, & r_{22} &= 3.4, & r_{42}/r_{22} &= \pm 8.2. \end{aligned} \quad (5)$$

The physical model and experimental method used here allow a quantitative determination of the various contributions to the electro-optic effect. The lowest A_1 mode and the next lowest E mode which make the strongest contributions to κ_k and are "softest"¹⁸ also dominate the electro-optic behavior. The pure electronic contribution is less than 10% of the lattice contributions.

For LiTaO_3 , ξ_{ijk} is known¹⁵ but $\Delta\kappa_k^m$ is not. Assuming only one effective A_1 or E mode with $\Delta\kappa_k = (\kappa_k - \kappa_k^\infty)$, the calculated values are

$$\begin{aligned} r_{33} &\approx 44 \pm 1.8, \\ r_{13} &\approx 9.5 \pm 0.1; \\ r_{42} &\approx \pm 14 \pm 0.1, \\ r_{22} &\approx 2.2 \pm 0.2, \end{aligned} \quad (6)$$

which agree with the measured electro-optic values¹⁷

$$\begin{aligned} r_{33} &= 35.8, & r_{13} &= 7.9, & r_{33}/r_{13} &= +4.5; \\ r_{42} &= 20, & r_{22} &\approx 1, & r_{42}/r_{22} &\approx \pm 20 \end{aligned} \quad (7)$$

to the same degree that this one dominant mode approximation holds for LiNbO_3 . As with LiNbO_3 , the agreement for r_{33}/r_{13} is especially good.

It has been noted^{1,16,18} previously that, in certain cases $r_{ij,k}/\Delta\kappa_k$ is insensitive to temperature or wavelength variations for a given substance and, for a wide variety of substances, falls within a restricted range of values. From (2) and the alternative expression for β_k^m , the above expression may be approximated by $(\alpha_{ij,k}^m v/n_i^2 n_j^2 Z_k^m)$ when a lattice mode is dominant, by $(\xi_{ijk}/\epsilon_0 n_i^2 n_j^2)$ when the electronic contribution is dominant, and in general by a combination of terms. At present, we do not understand quantitatively what determines the magnitudes of $\alpha_{ij,k}$ and ξ_{ijk} , although it is clear by symmetry that these polar-mode parameters must vanish as the substance approaches centric symmetry.¹⁹

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¹⁷ E. H. Turner, Appl. Phys. Letters 8, 303 (1966).

¹⁸ F. Jona and G. Shirane, *Ferroelectric Crystals* (MacMillan and Company, Ltd., London, 1962).

¹⁹ F. N. H. Robinson, Bell Syst. Tech. J. 46, 913 (1967).

¹⁵ R. C. Miller and A. Savage, Appl. Phys. Letters 9, 169 (1966).

¹⁶ R. C. Miller, Appl. Phys. Letters 1, 17 (1964).