symmetry than does infrared absorption. Complementary to the EPR and infrared methods, laser Raman spectroscopy will prove to be a very useful tool in the study of impurities in semiconductors.

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# Measurement of the Rotational Contribution to Brillouin Scattering

D. F. Nelson and P. D. Lazay

*Bell Telephone Laboratories, Murray Hill, New Jersey 07974 and Holmdel, New Jersey 07733*

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The first measurement of light scattering from rotations, as contrasted to strains, is reported in solids. Brillouin-scattering cross sections in rutile, previously expected to be equal in intensity, were found to differ by $\sim 10^3$. The difference between the deduced photoelastic coefficients confirms quantitatively the recent prediction of this effect.

We report the first measurement of light scattering from rotations, as contrasted to strains, in solids. Scattering from rotations can occur when shear distortions are present in a birefringent medium. This effect, recently predicted,[1] lowers the symmetry expected of the Pockels photoelastic tensor $p_{ijkl}$. Our measurements, which used Brillouin scattering in rutile, confirm the effect quantitatively.

The physical basis of the effect can be described as follows: In the inhomogeneous strain field of thermally induced lattice vibrations (or of acoustic shear waves), rotations of the medium varying within an acoustic wavelength occur. Also, in a pure shear distortion the rotation is numerically equal to the strain. If the medium is optically anisotropic, a rotation of it obviously affects the propagation of light through it. Hence, an appreciable contribution to light scattering—Brillouin or acousto-optic—should arise from the rotation effect.

The intensity of light scattered from rotations will depend upon the mean rotation tensor,

$$\tilde{R}_{[kl]} \equiv \tfrac{1}{2}\{u_{k,l} - u_{l,k}\}, \tag{1}$$

which is the antisymmetric combination of displacement gradients $u_{k,l} \equiv \partial u_k / \partial x_l$ (brackets indicate antisymmetry upon interchange). Light scattering also, of course, arises from strains in the medium which are characterized by the infinitesimal strain tensor,

$$S_{(kl)} \equiv \tfrac{1}{2}\{u_{k,l} + u_{l,k}\}, \tag{2}$$

which is the symmetric combination of displacement gradients (parentheses indicate symmetry upon interchange). An effect depending on both $\tilde{R}_{[kl]}$ and $S_{(kl)}$ must depend simply on $u_{k,l}$. Thus the basic measure of elastic deformation relevant to acousto-optic or Brillouin scattering (and higher order interactions between elastic deformations and light[1]) is the displacement gradient, not the strain.[2] Since $u_{k,l}$ is not symmetric upon interchange of its two indices, the photoelastic tensor need not be symmetric upon interchange of its two elastic indices. Thus, for instance, $p_{2323} \neq p_{2332}$ for any noncubic crystal.[1] This lack of symmetry had gone unnoticed from the time of Pockels' phenomenological formulation of the photoelastic interaction in 1889 until its recent theoretical prediction.[1] The long-accepted Pockels form of the photoelastic interaction,

$$(\delta\kappa^{-1})_{(ij)} = p_{(ij)(kl)}S_{(kl)} \tag{3}$$

can be corrected by adding to it an elastically antisymmetric term to give

$$(\delta\kappa^{-1})_{(ij)} = p_{(ij)(kl)}S_{(kl)} + p_{(ij)[kl]}\tilde{R}_{[kl]}, \tag{4}$$

where

$$p_{(ij)[kl]} = \tfrac{1}{2}\{(\kappa^{-1})_{il}\delta_{kj} + (\kappa^{-1})_{lj}\delta_{ik} - (\kappa^{-1})_{ik}\delta_{lj} - (\kappa^{-1})_{kj}\delta_{il}\}. \tag{5}$$

Here $\kappa_{ij}$ is the optical dielectric tensor and $\delta_{ij}$ is the Kronecker delta. Equation (4) can be rewritten more simply as

$$(\delta\kappa^{-1})_{(ij)} = p_{(ij)kl}u_{k,l}, \tag{6}$$

where $p_{(ij)kl} = p_{(ij)(kl)} + p_{(ij)[kl]}$ has no symmetry upon interchange of $k$ and $l$.

The object of the experiments reported here is to verify the prediction of Eq. (5). To do this we have chosen rutile (crystalline $TiO_2$) because (1) it is strongly birefringent ($n_0 = 2.690$ and $n_e = 3.007$ at $\lambda = 5145$ Å, (2) it is not piezoelectric, (3) it is not optically active, and (4) it possesses rather high symmetry (optically uniaxial, tetragonal point group $4/mmm$).

Most of the experiments were performed with the 5145-Å emission from an argon-ion laser. A linearly polarized output beam of 0.2 W was available in this line. A Littrow prism in the laser cavity allowed exclusive oscillation on the 5145-Å line while an etalon in the cavity maintained stable operation on a single mode. A 25-cm focal length lens focused the beam into the rutile which was at room temperature (23°C). The rutile crystal had polished faces perpendicular to the three crystallographic axes. It was fabricated from an annealed, "stabilized" (0.02% by weight $Al_2O_3$ dopant) boule grown by the flame fusion technique by the National Lead Company. A pressure-scanned Fabry-Perot interferometer which had collection optics with an $f/6.3$ aperture, an operating finesse of 40, and a spacer chosen to give a 69-GHz free spectral range was used to analyze the Brillouin scattered light. Following the exit pinhole of the interferometer were a narrow-band filter (20 Å between wavelengths of half transmission), used to discriminate against the Raman-scattered light, and a Polaroid polarizer. The light was detected by a low-dark-current EMI 6256S photomultiplier tube whose anode current was amplified and recorded on a strip chart.

The phonons responsible for the scattering were identified by their frequencies (Brillouin splittings) in conjunction with the polarization and propagation directions of the incident and scattered light beams and the orientation of the crystal. The observed Brillouin splittings were compared with those calculated from the refractive-index data of DeVore[3] and the elastic constants of Wachtman, Tefft, and Lam.[4] Since the Brillouin splittings are proportional to the laser frequency, changing the oscillating laser wavelength to 4765 Å confirmed the identification of the Brillouin components. One Brillouin component in rutile has been observed previously.[5] The intensity of a Brillouin component is proportional to a function of the refractive indices and to the square of a photoelastic tensor element (or combination of elements) determined by crystal symmetry and the phonon responsible for the scattering, and inversely to the appropriate elastic stiffness tensor element (or combination of elements).[6]

Equation (5) predicts that there will be antisymmetric parts only for $p_{44}$ and $p_{55}$ (abbreviated notation) in rutile. Specifically it predicts that $p_{(23)[23]} = p_{(13)[13]} = +0.0138$ for $\lambda = 5145$ Å based on DeVore's refractive-index data.[3] Thus we wish to measure the difference $\{p_{(23)23} - p_{(23)32}\}$, which requires the accurate absolute measurement of each. To obtain absolute values for the photoelastic tensor elements we have measured the scattered light intensities relative to that in toluene, whose photoelastic coefficient[7] is well known, in the same experimental arrangement.

A number of tests were performed to establish that the numerical values deduced were correct. First, it was established that there was no significant resonant reflection of the laser beam within the rutile crystal, i.e., the crystal did not form a Fabry-Perot cavity. Second, it was found that, when the exit direction of the scattered light was along the optic axis, certain strong Brillouin spectral components appeared in a symmetry-forbidden polarization. The intensity of such components was found to increase with the distance between the scattering volume and the crystal face through which the scattered light emerged. This effect was attributed to a combination of strain birefringence and the effect of finite aperture[8] altering the polarization state of the scattered light along its emergence path. This effect was minimized by directing the laser beam very close (0.3 mm) to the surface through which the scattered light emerged. The residual effect was measured in this situation and a small correction (4%) was made to account for it. Lastly, several photoelastic coefficients which have been previously measured[9,10] were remeasured by the above technique. We found $|p_{66}| = 0.0716$, $|p_{31}| = 0.0959$, and $|0.828p_{21} + 0.564p_{23}| = 0.227$. These are to be compared with the measurements of Reintjes and Schulz[10] which yield $|p_{66}| = 0.071$, $|p_{31}| = 0.095$, and $|0.828p_{21} + 0.564p_{23}| = 0.230$, and with Dixon's measurements[9] which yield $|p_{31}| = 0.0965$ and $|0.828p_{21} + 0.564p_{23}| = 0.237$. The agreement is seen to be excellent even though the previously published results[9,10] were normalized to the known absolute value for fused silica while ours were normalized to that for toluene. Also, the earlier measurements[9,10] were made in the 200- to 400-MHz range while ours were in the 36- to 86-GHz range.

The experiments carried out to measure $p_{(23)23}$ and $p_{(23)32}$ detected Brillouin-scattered light perpendicular to the incident beam. We will designate a typical experimental geometry by $X(ZX)Y$ by which we mean that, in order, the incident beam propagated in the $x$ crystallographic direction, its electric field vector pointed in the $z$ direction, the electric field of the scattered beam pointed in the $x$ direction, and it propagated in the $y$ direction. Figure 1 shows spectra from an $X(ZX)Y$ experiment which detects $|p_{1331}|(=|p_{2332}|)$ directly and an $X(ZY)Z$ experiment which should detect $|p_{2323}|$ directly. If the photoelastic tensor possessed symmetry under interchange of its last two (elastic) indices, Brillouin scattered lines in the two traces should be of equal intensity; it is seen that they are drastically different.

A summary of the several experiments performed is given in Table I. An average of the results from experiments $A$ and $B$ yields the result

$$|p_{(23)32}| = |p_{(13)31}| = 0.0255 \tag{7}$$

while comparison with $C$ yields

$$|p_{(23)23}| = |p_{(13)13}| = 0.0009. \tag{8}$$

Experiment $D$ is seen to be consistent with the latter result. There have been no measurements of the coefficients in Eqs. (7) and (8) previously in rutile for comparison. Since the scattered light intensities depend on the square of the coefficients in Eqs. (7) and (8), it is seen that the Brillouin lines in Fig. 1, which were previously expected to be equal, differ by almost $10^3$.

The results (7) and (8) can be divided into a symmetric coefficient

$$p_{(23)(23)} = p_{(13)(13)} = \pm 0.0123, \tag{9}$$

and an antisymmetric coefficient

$$p_{(23)[23]} = p_{(13)[13]} = \mp 0.0132, \tag{10}$$

where the upper (and lower) signs in both equations are associated. The magnitude of the latter is in fine agreement with the prediction of +0.0138 from Eq. (5) for rutile at 5145 Å. On the basis of this agreement one is justified in choosing the lower signs in Eqs. (9) and (10) as the cor-

Table I. Summary of Brillouin-scattering results. Each value of a photoelastic coefficient was derived from many spectra. The best estimate of error in these results is furnished by a comparison of the results from $A$ and $B$ which should be identical by symmetry.

| | Orientation | Acoustic mode | Splitting (GHz) Obs. | Splitting (GHz) Calc. | Measured coefficient |
|---|---|---|---|---|---|
| $A$ | $X(YZ)Y$ | Pure transv. | 42.2 | 42.3 | $\|p_{3232}\| = 0.0257$ |
| $B$ | $X(ZX)Y$ | Pure transv. | 42.2 | 42.3 | $\|p_{1331}\| = 0.0253$ |
| $C$ | $X(ZX)Z$ | Quasilong. | 38.8 | 39.1 | $\|p_{1331} - 1.19\, p_{1313}\| = 0.0265$ |
| $D$ | $X(ZY)Z$ | Pure transv. | ⋯ | 48.1 | $\|p_{2323}\| < 0.005$ |

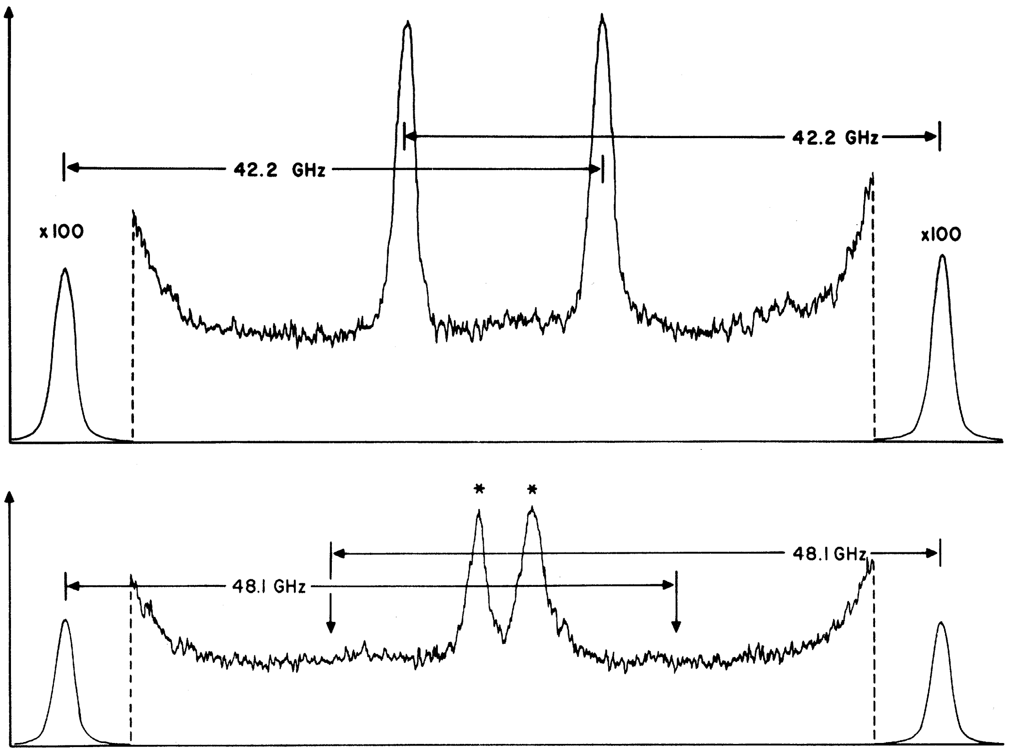

FIG. 1. Brillouin spectra for $X(ZX)Y$, upper trace, and for $X(ZY)Z$, lower trace. The two spectra are shown at identical gain settings. Scattering from a pure transverse mode which measures $|p_{1331}|=|p_{2332}|$ is observed in the upper trace while that which should measure $|p_{2323}|$ is not observed in the lower trace. The expected position of the unobserved mode (splitting of 48.1 GHz) is indicated. In each spectrum the Stokes peak and the anti-Stokes peak which is associated with the adjacent order of the interferometer appear. The strong peaks at the ends of the traces are caused by scattering from static imperfections. The weak modes indicated by an asterisk are due to scattering from the quasilongitudinal mode in $X(ZX)Z$, 4% of whose intensity has "leaked" into the wrong output polarization because of a combination of strain birefringence and the finite-aperture effect (Ref. 8) in its emergence path (see text).

rect ones. This, in turn, means $p_{(23)32}=p_{(13)31} = -0.0255$ and $p_{(23)23}=p_{(13)13}=+0.0009$ showing that these coefficients are of opposite sign as well as greatly different in magnitude. The large ratio of intensities seen in Fig. 1 is thus seen to be due to a near exact and fortuitous cancelation of the symmetric and antisymmetric parts of the photoelastic tensor in rutile.

The dramatic effect that rotational scattering was found to have in rutile suggests a variety of other experiments where the rotational scattering will be important. For instance, when the absolute intensity of Brillouin scattering is used as a probe to determine the absolute strain or stress level in a crystal, it will be important to consider the contribution of rotational scattering when shear waves are generated in birefringent crystals. Another instance could occur in the measurement of photoelastic anomalies near a phase transition in a ferroelectric crystal. If the crystal were cubic on one side of the transition temperature and strongly birefringent on the other and if the symmetric and antisymmetric parts of $p_{(ij)kl}$ were nearly canceling (as happened in rutile) in the birefringent phase, then a large change in Brillouin scattering intensities would occur as the transition was approached in the birefringent phase caused by the rotational scattering alone.

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# Raman Spectra of Polycrystalline Solids; Application to the $PbTi_{1-x}Zr_xO_3$ System*

Gerald Burns and Bruce A. Scott
*IBM Watson Research Center, Yorktown Heights, New York 10598*

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It is shown that Raman scattering from polycrystalline piezoelectric solids contains all of the essential features of Raman single-crystal spectra even when the crystal spectrum is quite anisotropic. As an illustration of the Raman powder technique, the ceramic ferroelectric-antiferroelectric system $PbTiO_3$-$PbZrO_3$ has been investigated and the "soft" $E$(TO) optical phonon modes measured in the tetragonal ferroelectric region.

The Raman spectra of solids are normally obtained using single crystals. By carefully selecting the directions ($\vec{q}_i$ and $\vec{q}_s$) and polarizations ($\vec{\epsilon}_i$ and $\vec{\epsilon}_s$) of the incident and scattered laser light it is possible to measure the frequencies of the various symmetry longitudinal optic (LO) and transverse optic (TO) phonons which propagate along the principal axes of the piezoelectric single crystal.[1] In this paper we point out and demonstrate that the same information can be obtained from powdered or ceramic samples even when the spectra are quite anisotropic. As an example, we have measured the modes in ceramics of the interesting system[2] $PbTi_{1-x}Zr_xO_3$, single crystals of which are very difficult to grow.[2,3] At room temperature this system contains a tetragonal ferroelectric region ($x < 0.52$), two rhombohedral ferroelectric phases ($0.52 < x < 0.64$ and $0.64 < x < 0.94$), and an antiferroelectric region ($0.94 < x$).[2] As will be subsequently shown, these various phase fields are defined in the ceramic Raman results.

Powder line-shape function.—It is relatively straightforward to show how peaks in the Raman spectra of ceramics occur at just those frequencies corresponding to the actual modes propagating along the principal crystal axes. The treatment is similar although not totally analogous to that used to obtain, for example, the nuclear quadrupole coupling constant $eqQ$ in a nuclear magnetic resonance experiment,[4a,4b] or the zero-field splitting parameter $D$ in electron paramagnetic resonance experiment.[4c,4d] The peaks in the powder spectra in these cases are simply related to $eqQ$ and $D$, even though the single-crystal spectra may be quite anisotropic.[4]

Raman spectra are measured by sweeping a monochromator in energy and detecting the signal at $\omega$, the energy shift from the exciting laser line. Since the monochromator has bandwidth $d\omega$, and a direct relationship exists between $\omega$ and $\theta$ (the angle between the $z$ axis and phonon momentum $\vec{k}$), at a given frequency the amount of signal obtained due to crystallites properly oriented for the scattered Raman light to pass through the monochromator is proportional to $d\theta/d\omega$. The number of crystallites at a given $\theta$ is also proportional to $\sin\theta$. Thus, we may write the line shape for any mode in crystallites with axial symmetry as

$$g(\omega) = |\sin\theta d\theta/d\omega(\theta)|S(\omega), \tag{1}$$

where the scattering efficiency $S(\omega)$ is a smoothly varying intensity function for the particular mode.[5] It is important to realize that Eq. (1) and its generalization to the lower symmetry case,[4b] $g(\omega(\theta, \varphi))$, will result in "infinite" peaks or "step" discontinuities in the powder spectrum whenever $\omega(\theta, \varphi)$ exhibits extrema unless $S$ goes to zero. The manner in which $\omega(\theta, \varphi)$ approaches the extrema will not influence the peak positions in the Raman powder pattern. Of course, the finite width of the absorption lines will broaden to some extent the peaks and step discontinuities.