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R.C. Dye
University of Nebraska - Lincoln

J. Sartwell
University of Nebraska - Lincoln

Craig J. Eckhardt
University of Nebraska - Lincoln, ceckhardt1@unl.edu

Light scattering apparatus for angular dependent studies of anisotropic materials

R. C. Dye,[a] J. Sartwell,[a] and C. J. Eckhardt[b]

Department of Chemistry, University of Nebraska–Lincoln, Lincoln, Nebraska 68588-0304

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An improved method for light scattering from acoustic phonons in small, low-symmetry solids is described. This instrumentation greatly facilitates the determination of elastic constants in highly anisotropic materials. Elastic scattering can be greatly reduced so that weaker phonon modes can be observed. Errors associated with the determination of the polarization directions of an anisotropic material are minimized by considering crystal optics.

INTRODUCTION

Brillouin scattering has proven to be a powerful tool in the study of acoustic modes in gases, liquids, and solids.[1–3] It is most useful for determining the elastic constants of very small samples. Such measurements of elastic constants have, however, mainly been used for high-symmetry crystals. Extending the technique to crystals of lower symmetry increases the demands on the experimental procedure and instrumentation. For instance, in cubic crystals the elastic constant tensor consists of only three independent terms which require at most only two directional measurements to be made.[2] On the other hand, an orthorhombic crystal has 9 independent dyadic components, a monoclinic crystal has 13, and a triclinic crystal has 21.[4] The vast majority of molecular crystals are of low symmetry and obtaining their elastic constants by Brillouin scattering increases dramatically the number of scattering directions that must be measured.

In the typical scattering experiment, "pure" phonon modes are measured in the determination of a complete set of elastic constants. A "pure" phonon mode travels in a direction such that its motion can be described by a single elastic constant.[5] All other phonon modes depend on more than one elastic constant to describe their motion and will be referred to as "mixed" modes.

For low-symmetry crystals the samples must invariably be cut in order to obtain measurements of "pure" phonon modes.[6] Cutting molecular crystals to observe "pure" phonon modes degrades the quality of the sample, decreases the accuracy of the measurement, and induces unwanted strain that may adversely affect the results. It thus becomes important to establish alternative techniques that do not destroy the integrity of the sample. This requires the use of "mixed" rather than "pure" acoustic modes in the determination of elastic constants.

In the present study, we report a scattering system that allows the sample to rotate independently of the incident beam and vice versa. This arrangement, combined with a computational approach that minimizes the Christoffel equation in a least squares procedure, allows the determination of the complete set of elastic constants of a crystal of arbitrary symmetry by measuring "mixed" phonon modes. The elastic constants are calculated by an iterative optimization that fits all elastic constant tensor elements simultaneously to previously obtained sound velocities, frequencies, or mode stiffnesses.[7] This approach to the calculation of the elastic constants makes cutting the sample unnecessary and allows for increased accuracy.[8] However, to fully utilize the power of this calculative approach, a large number of phonons must be measured.

In low-symmetry crystals, the propagation of the polarization vector is markedly affected by the crystal optics.[9] Generally, this problem is ignored or simplifying assumptions are made.[6] For instance, a monoclinic system is often assumed to have the same optical behavior as an orthorhombic system. Such assumptions are made because the propagation of polarized light is simpler in the higher symmetry crystal and the instrumentation is not generally capable of handling the crystal optics of a low-symmetry system.

I. INSTRUMENT DESIGN

Two major considerations for the design of the scattering assembly were the measurement of several "mixed" phonon modes, and the handling of crystal optics that are encountered with low-symmetry crystals.

In measuring "mixed" modes, it is theoretically possible to sample all potential $\mathbf{q}$ vectors by simply rotating the crystal and keeping the incident beam fixed.[2] However, to obtain several $\mathbf{q}$ vectors in practice, it becomes necessary to rotate the crystal and incident beam to accommodate crystal morphology and crystal quality. By moving both sample and incident beam, the elastic scattering can be decreased. This prevents modes from being buried in a broadened Rayleigh line. For example, if a crystal possesses two faces at 70° to each other, it would be advantageous to have the incident beam perpendicular to a face as well as collecting the light scattered normally from the other face. Such an arrangement also establishes easily definable polarization directions. Rotating the sample and incident beam enables scattering and collection from naturally growing faces of the crystal at almost any angle.

A. Crystal optics

A determination of the principal dielectric axes and refractive indices of low symmetry crystals is necessary in order to consider the effects of the anisotropic dielectric medium on the polarization and propagation of light in the crystal. In uniaxial or biaxial crystal systems, the propaga-

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tion direction of light generally does not lie parallel or perpendicular to the scattering plane.[8] This is of importance in Brillouin scattering. The Brillouin equation for anisotropic materials is given by

$$\delta\nu = \pm \nu_0 v(n_i^2 + n_s^2 - 2n_i n_s \cos\theta)^{1/2}/c,$$

where $\delta\nu$ is the Brillouin shift and ν_0 is the frequency of the laser light, assuming the incident and elastically scattered light are of the same frequency. The velocity of the phonon is v and c is the velocity of light in vacuum. The indices of refraction of the incident and scattered light are n_i and n_s, respectively, and θ is the scattering angle. If the polarization direction of the laser beam does not match the principal propagation direction within the crystal, undefined phonon modes may arise for which the proper indices of refraction, n_i and n_s, cannot be assigned. When the incident and scattering polarization directions are not collinear with the principal directions of propagation, up to 12 such modes may arise. Thus, measurement of the scattered light intensity will be composed of light scattered by an undefined set of phonons. A polarization rotator has been employed in this study so that the incident polarization can be matched to the principal polarization directions of the crystal. A rotating analyzer is also used so that scattered light polarization can be selectively gathered along the principal directions.

B. Excitation beam path

The schematic diagram of the optical system is shown in Fig. 1. The first components are two irises ($I1$,$I2$). These are used to eliminate laser cavity reflections. A 10% beamsplitter (B) is used to pick off part of the beam. This beam permits rapid, accurate alignment of the scattered light path. The major part of the beam then passes under and up through the center of an Ealing (model 22-2166) large rotary stage (St). The stage has a range of 360° and a positioning accuracy of 5 minutes of arc. The stage itself is mounted on an X-Y translator enabling it to be properly positioned with respect to the rest of the system. Beam-steering mirrors mounted on the stage are used to send the light down a rotating arm, up and then back toward the center of the stage. A 250-mm lens ($L1$) then focuses the beam so the center of the beam waist is at the center of the stage. Because slight depolarization of the laser light can occur when the beam makes several reflections, a calcite Glan–Laser polarizer (Po) from Zeta International rejects any depolarized light. To allow for the proper orientation of the electric vector of the light, a polarization rotator (PR) from Continental Optical follows the polarizer. This half-wave rotator allows the polarization of the light to have a 360° range with a 0.5° positioning accuracy. To eliminate reflections and to fix the beam diameter, an iris is placed between the rotator (PR) and the sample (S). To reduce scattered laser light, the system employs a Klinger Scientific light trap placed at the end of the path to stop the beam.

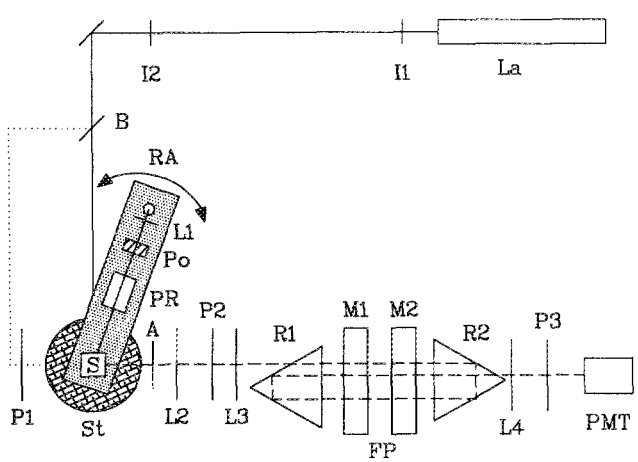

FIG. 1. Top view of Brillouin optical system. *La*: laser; *B*: 10% beamsplitter; *L*: lens; *Po*: polarizer; *PR*: polarizing rotator; *RA*: rotating arm (dotted); *S*: sample; *St*: stage; *A*: analyzer; *P*: pinhole; *R*: corner cube retroreflector; *FP*: Fabry-Perot interferometer; *PMT*: photomultiplier tube.

Because the scattered light in the Brillouin experiment has a directional dependence, it is necessary to accurately determine the incident beam direction relative to the scattered beam. Also, the incident polarization needs to be defined relative to the sample.[8]

The incident light path is established by sending the light through a series of four pinholes (BP) mounted in two removable alignment posts ($Al1$,$Al2$). The alignment geometry is shown in Fig. 2. The two alignment posts fit into 2.5-cm holes in the rotating arm (RA) and are accurately positioned to the stage with a straight rod. Each post holds a brass plug containing two pinholes (BP). The tilt plate (T) is adjusted until the laser beam passes through the center of all four pinholes.

The polarizer (Po) is set by maximizing the laser power throughput. The polarization rotator (PR) adjustment relies upon the alignment post. The edge of the post provides a reference point to align a polaroid sheet with a known polarization vector direction which is matched to the incident polarization direction by turning the rotator.

Calibration of the scale on the large rotating stage involves placing a 90° prism at the stage's center. Part of the incident light reflects off the front surface of the prism and travels back along the incident path. Another part of the beam travels a path 90° to the incident path giving a 90° reference angle. Therefore, when the stage is set at 90°, part of the alignment beam travels down the incident path and part of the incident beam travels down the alignment path.

C. Scattered beam path

The scattered light from the sample first passes through an iris. This defines the direction of the scattering vector and reduces the stray light. The next component encountered is a polarization analyzer (A) which can be rotated 360° (Fig. 1). The light is then gathered by a $f/1.9$ anastigmatic Dallmeyer lens ($L2$) mounted in an Oriel precision gimbal mount (model 14501). This mount is screwed onto an X-Y-Z micropositioner from Line Tool Co. This combination of components allows the collecting lens ($L2$) to be translated and rotated in order to orient it to the scattered light path. The light then travels through a Burleigh RC-41 collimator ($L3$) fitted with a 0.2-mm pinhole ($P2$) which is mounted

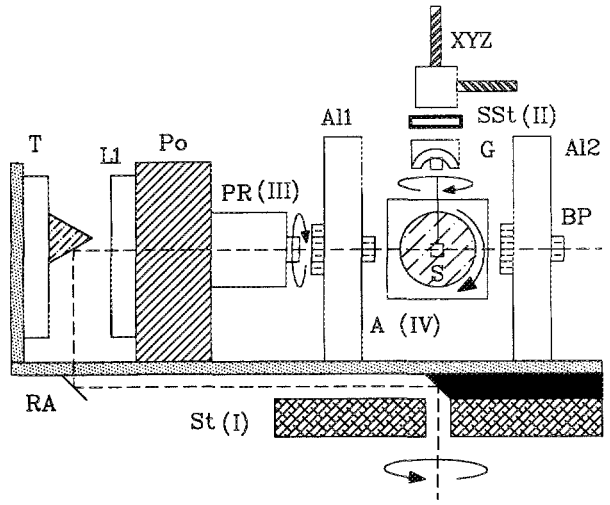

FIG. 2. Exploded side view of scattering assembly with rotating arm (dotted). *XYZ*: *x-y-z* micropositioner; *SSt*: rotating sample stage; *G*: goniometer; *S*: sample; *St*: large rotating stage; *RA*: rotating arm; *L* 1: focusing lens; *Po*: polarizer; *PR*: polarization rotator; *P* 1: 0.5 mm pinhole; *A*: analyzer. Roman numerals designate rotating elements on which other elements may be mounted.

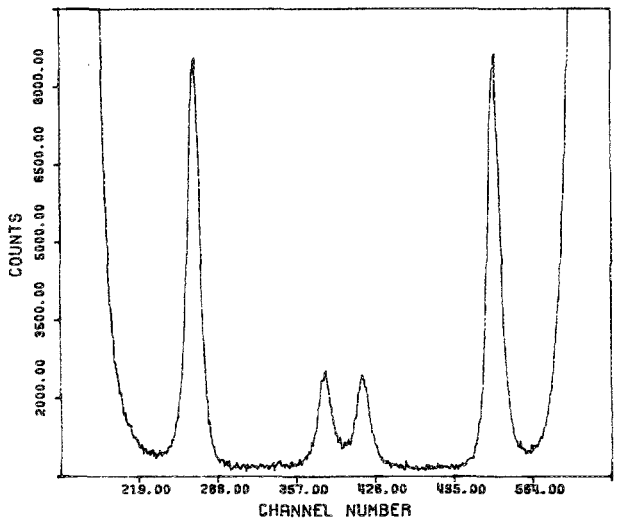

FIG. 3. A typical 162° Brillouin spectrum of crystalline anthracene with the incident beam normal to the (001) crystal face and the scattered beam 18° from the normal.

on an *X-Y-Z* translator connected to a tilt plate. The collimator brings the light to a multipass, piezoelectrically-driven, Burleigh Fabry–Perot interferometer (FP) (model RC-110). The mirrors in the interferometer have a flatness of $\lambda/200$ and a reflectivity of 96% at 514 nm and are mounted in a stabilization cavity made of super Invar that has a very low thermal expansion. Further stabilization of the interferometer consists of an NRC pneumatic isolation table type XL-A, a Burleigh RC-34 thermal box, and an active Burleigh DAS-10 stabilization system. The interferometer is used in the triple pass configuration. To achieve this, retroreflectors (*R* 1, *R* 2), Burleigh's RC-22 models, are placed at both ends of the interferometer. After passing through this series of reflections, the light proceeds through a lens (*L* 4) which focuses it onto a pinhole (*P* 3). Behind the pinhole, the light continues through a series of transfer optics which focuses the beam onto the gallium arsenide photocathode of a RCA C31034 photomultiplier tube (*PMT*) housed in a Products for Research thermoelectric refrigerated chamber that maintains a temperature of -30 °C.

The crystalline sample mount consists of an *X-Y-Z* micropositioner (*XYZ*) from Line Tool Co. and a NRC model RSX-1 rotation state (*SSt*) with a 360° range (Fig. 2). A goniometer head (*G*) which holds the sample is mounted onto the stage. This allows the crystal to be rotated independently of the rotation of the incident beam.

The crystal is placed at the point where the alignment beam (dotted line) and the incident beam (solid line) cross (Fig. 1), which is also the focus of the incident beam. Back reflection of the incident beam from the crystal surface also provides an alignment point for the sample orientation. Since this reflection is collinear with the vector normal to the face, the stage angle and crystal orientation can be set according to a predetermined scattering scheme. Using this alignment technique, an accuracy of better than 0.5° could be obtained in the scattering angle.

II. INSTRUMENTAL PERFORMANCE

The instrument generally maintained a finesse greater than 75 for approximately 48 h. This value for the finesse is close to the theoretical value of 88.[10]

A typical Brillouin scattering spectrum of crystalline anthracene is shown in Fig. 3, where θ in the Brillouin equation is equal to 162° and the incident beam is normal to the (001) crystal face. The spectrum is the result of 50 summed scans with no smoothing.

The achieved instrumental performance is equivalent to other reported Brillouin instruments and is easily adapted to low temperature studies. The system permits the sample to be rotated independently of the incident beam and vice versa. The incident and scattered beam polarizations may also be rotated independently. This "four-circle" system provides the versatility needed to obtain scattering directions which are inaccessible by conventional means without cutting the crystal. Other scattering techniques, such as Raman spectroscopy, can use a similar arrangement to the one described when measuring scattering from anisotropic materials.

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[a] Work completed in partial fulfillment of requirements for the Ph. D. at the University of Nebraska–Lincoln.

[b] Author to whom correspondence should be addressed.

[1]H. Z. Cummins and P. E. Schoen, in *Laser Handbook*, edited by F. T. Areechi and E. O. Schulz-duBois (North Holland, Amsterdam, 1972), pp. 1030–1075.
[2]R. Vacher and L. Boyer, Phys. Rev. B **6**, 639 (1972).
[3]R. Figgins, Contemp. Phys. **12**, 283 (1971).
[4]J. F. Nye, *Physical Properties of Crystals* (Oxford University Press, London, 1964).
[5]K. Brugger, J. Applied Phys. **36**, 759 (1965).
[6]C. Ecolivet and M. Sanquer, J. Chem. Phys. **72**, 4145 (1980).
[7]K.-H. Brose, Ph.D. Dissertation, University of Nebraska (1988).
[8]R. C. Dye and C. J. Eckhardt, J. Chem. Phys. **90**, 2090 (1989).
[9]F. D. Bloss, *An Introduction to the Methods of Optical Crystallography* (Holt, Rinehart, and Winston, New York, 1961).
[10]G. Hernandez, *Fabry-Perot Interferometers* (Cambridge University Press, Cambridge, 1986).