# Temperature dependence of the elastic moduli of diamond: A Brillouin-scattering study

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Elastic moduli and refractive index of diamond, in the temperature range 300–1600 K, are determined using Brillouin scattering. The elastic moduli decrease by only  $\approx 8\%$  up to 1600 K, indicating that diamond retains its reputed hardness even at high temperatures. We review the most commonly employed scattering geometries in Brillouin scattering (viz. backscattering, 90° scattering, and platelet geometries), and discuss in detail the experimental errors which must be considered in each case. [S0163-1829(98)02205-X]

# I. INTRODUCTION

The strong, tetrahedrally coordinated, covalent bonds between nearest neighbors and the light mass of the constituent atoms lead to many striking and unique properties of diamond, e.g., the largest elastic moduli  $(c_{ij})$  known for any material and correspondingly, the largest sound velocities;<sup>1,2</sup> a very large Debye temperature, making it a "quantum" crystal even at room temperature.<sup>1,3,4</sup> Its hardness and abrasive qualities, highly valued in technology and gem industry, are controlled by the large elastic moduli.<sup>5</sup> The diamond anvil cell, which has literally revolutionized high pressure research, exploits the extreme hardness of diamond.<sup>6</sup> These illustrative examples clearly underscore the importance of establishing precise values of elastic moduli and their variation with temperature.

It is in this context that we have measured the elastic moduli of diamond in the temperature range 300 to 1600 K. We note here that Zouboulis and Grimsditch<sup>7</sup> (see also Herchen and Capelli<sup>8</sup>) have reported the behavior of the Raman active zone center optical phonon as a function of temperature up to 1900 K. Since the frequency ( $\omega_0$ ) of the  $F_{2g}$  zone center optical mode is determined by the bond stretching ( $k_1$ ) and bond bending ( $k_2$ ) force constants which also determine the elastic constants, a combination of the Raman and Brillouin results will allow the temperature dependence of the microscopic force constants to be extracted.

The elastic moduli of a material can be measured with great precision from the frequency shifts of monochromatic radiation inelastically scattered by the long wavelength acoustic phonons, viz., from the Brillouin shifts.<sup>1</sup> Determination of ultrasonic velocities from the round trip transit time<sup>9</sup> is the alternative technique which is equally precise. However, Brillouin scattering offers special advantages: it is a "contactless" technique; oriented specimens as small as a few millimeters in dimension are entirely satisfactory and can be conveniently placed in a high-temperature environment, the incident light being brought to the samples and the scattered light collected with appropriate optical windows. In contrast, the ultrasonic technique requires, for precision, large specimens and a suitable bond to the transducer. We note here that Grimsditch and Ramdas employed diamond

specimens as small as  $\frac{1}{3}$  carat, in contrast to the 22 carat sample used by McSkimin *et al.*<sup>9</sup> Finally, the Brillouin scattering geometries can be suitably devised which obviate the need for the knowledge of the refractive index in deducing the elastic moduli from the Brillouin shifts.<sup>10</sup>

Various aspects of Brillouin scattering are considered here. After a brief review of the fundamental and wellknown aspects, we review the scattering geometries which were used in these experiments and present a detailed discussion of the errors which affect Brillouin scattering experiments in each scattering geometry. The equations pertaining to the uncertainties are presented in the Appendix.

### **II. BACKGROUND**

There are many excellent accounts of the theory of Brillouin scattering.<sup>11,12</sup> In the context of the present article it is sufficient to recall that the phonons, satisfying wave vector conservation in a given Brillouin scattering geometry in a cubic and hence optically isotropic material, have wave vectors given by

$$\mathbf{q} = \pm (\mathbf{k}_i - \mathbf{k}_s); \quad |\mathbf{q}| = \pm 2 |\mathbf{k}_i| \sin(\theta/2), \tag{1}$$

where  $\mathbf{q}, \mathbf{k}_i$ , and  $\mathbf{k}_s$  are the wave vectors of the phonon, and incident and scattered light, respectively, and  $\theta$  is the angle subtended by  $\mathbf{k}_i$  and  $\mathbf{k}_s$ . Note that the *k*'s and  $\theta$  are defined inside the material so that refraction effects at the surfaces are not yet included in Eq. (1). Each phonon in a given material is characterized by a combination of  $c_{ij}$ 's which we call  $X = \rho v^2$  ( $\rho$  density and v sound velocity).

The frequency shifts of Brillouin components (typically  $0.1-5 \text{ cm}^{-1}$ ) make the multipassed<sup>13</sup> tandem<sup>14</sup> Fabry-Perot interferometer<sup>15</sup> the instrument of choice. In the context of the present experiments both multipassing and tandem operation are crucial: multipassing provides the necessary contrast so that the Brillouin lines can be observed in the presence of the, sometimes strong, background due to the unshifted radiation; tandem operation is necessary to reduce the blackbody radiation by eliminating the folding of successive interference orders present in nontandem operation.

The furnace we used is described in detail in Refs. 16 and 17; it allows for both backscattering and  $90^{\circ}$  scattering ge-

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FIG. 1. Most common scattering geometries used in Brillouin scattering. (a)  $90^{\circ}$  scattering, (b) backscattering, and (c) platelet. Diagram (d) defines the incident and scattering angles for more general scattering geometries. The magnitude of the wave vector is indicated for each geometry.

ometries to be implemented. The three diamond samples used in our experiments were  $\approx 2 \times 0.5 \times 0.5$  mm<sup>3</sup> in size and had (100), (010), (001); (110), (110), (001); and (111), (110), (112) orientations. To avoid rapid graphitization of the samples, they were enclosed under vacuum in quartz cuvettes. The highest temperature reached in these experiments was 1800 K. At these temperatures partial devitrification of the fused quartz rendered the cuvettes less transparent. Furthermore, shrinking of the cuvette at temperatures higher than 1600 K—because of the pressure difference inside and outside the cuvette—made optical focusing on the surface of the sample extremely difficult so that data above 1600 K were not reliable. Some evidence of graphitization was barely noticeable after a few temperature cycles, particularly on the (110) faces.

The three scattering geometries we employed are shown in Fig. 1; we shall refer to them as backscattering,  $90^{\circ}$  scattering, and platelet geometries. The last diagram in Fig. 1 defines the angles of incidence for more general scattering geometries. In Fig. 1 we also show the magnitude and direction of the phonon wave vector derived from Eq. (1) assuming no uncertainties in the geometrical setup.

In evaluating elastic moduli from the measured frequency shifts, a number of sources of error must be considered. Errors in the measured frequency shift, error in the calculated magnitude of the wave vector, and errors in the direction of q (which determines the combination of  $c_{ij}$ 's to which the velocity is assigned). The only source of random error stems from the frequency measurements; all other sources of error, being systematic, are not evident in the data themselves. Since we are not aware of any previous detailed discussion of these errors, they are presented in detail below and in the Appendix.

Sound velocities are obtained from  $v = \Delta \omega/|q|$  so that errors in both  $\Delta \omega$  and |q| must be considered. Random errors in  $\Delta \omega$  arise due to statistical noise in the spectra and the resulting uncertainty in locating the position of the Brillouin peaks; it gives rise to scatter in the experimental data and can be reduced by longer accumulation times and curve fitting procedures. These errors can also be greatly reduced by observing the Brillouin lines in higher-order interference;<sup>1,2</sup> to do so, however, requires the use of the interferometer without its tandem feature, not possible in the present experiments since tandem operation is needed to reduce the blackbody radiation. Systematic errors in  $\Delta \omega$  are possible if the free spectral range has not been accurately calibrated; however, very accurate calibration is possible using standard spectral lamps<sup>1,2</sup> so that this source of error can be made negligible and will not be considered here. Errors in |q| depend on the accuracy with which the various angles in the experiment are known and therefore depend on the particular geometry being used. The errors specific to each scattering geometry are discussed in the Appendix. Uncertainties in the refractive index also lead to errors in |q|.

The final source of error is related to uncertainties in the direction of q relative to the crystalline axes. This depends not only on uncertainties in the incident and scattered directions, but also on the precision with which the crystal faces are cut and polished relative to the crystal axes. The resulting error in the  $c_{ii}$  due to these "misalignments" also depends on the particular phonon directions being probed. Close to propagation along high symmetry directions, the angular dependencies of the phonon velocities possess extrema and hence do not depend strongly on small angular variations, whereas along nonsymmetry directions the effects of misalignment can be considerably more serious. All but one of the velocities to be reported in this work correspond to high symmetry directions where the effects of misorientation are minimal. Even along these directions effects of misorientation can be clearly experimentally observed in the high resolution experiments described in Refs. 1 and 2. However, in the present case, where we have investigated only high symmetry directions, and the Brillouin lines were observed in the same interference order as the laser line, the errors due to misalignment are negligible and will not concern us. The single exception to this statement is the transverse mode for q along [111]. Although it is doubly degenerate along [111], away from [111] it splits into two modes, the splitting depending linearly on angle away from [111]. As discussed in the Appendix we expect systematic errors of up to 1.5% for the combination of  $c_{ii}$ 's of this phonon.

Summarizing, the significant sources of error in this investigation are (i) random errors in the determination of Brillouin peak positions, (ii) systematic errors introduced by uncertainties in scattering angles, and (iii) a possible misalignment error for the shear mode along [111].

### **III. RESULTS**

In a crystal of cubic symmetry there exist only three independent elastic moduli, namely,  $c_{11}$ ,  $c_{12}$ , and  $c_{44}$ . In our experiments we have probed phonons along [100], [110], [111] directions. The particular combinations of elastic moduli observed in a given experiment depends, through the scattering tensors, on the scattering geometry; they are summarized in Table I. Figure 2 shows representative Brillouin spectra of diamond recorded in various scattering geometries and temperatures. The peaks are identified as longitudinal (*L*) or transverse (*T*). As can be seen in the spectra, the background due to blackbody radiation is still not a serious

TABLE I. Phonon wave vector, phonons observed, and combination of  $c_{ij}$  measured in various scattering geometries. Samples A, B, and C refer to the (100), (010), (001); (110), (110), (001), and (111), (110), (112) orientations, respectively.

Geometry and sample	Phonon wave vector	Observed phonons	Measured $c_{ij}$
Backscattering A	[100]	L	c <sub>11</sub>
Backscattering B	[110]	L	$(c_{11}+c_{12}+2c_{44})/2$
Backscattering C	[111]	L	$(c_{11}+2c_{12}+4c_{44})/3$
Backscattering C	[111]	Т	$(c_{11} - c_{12} + c_{44})/3$
90° scattering B	[100]	L	<i>c</i> <sub>11</sub>
90° scattering B	[100]	Т	C 44
90° scattering A	[110]	L	$(c_{11}+c_{12}+2c_{44})/2$
90° scattering A	[110]	Т	c 44
Platelet B	[100]	L	<i>c</i> <sub>11</sub>
Platelet B	[100]	Т	c 44
Platelet B	[110]	L	$(c_{11}+c_{12}+2c_{44})/2$
Platelet B	[110]	Т	c 44

problem at 1600 K. As mentioned in the previous section we were able to record spectra as high as 1800 K but sample movement due to deformation of the quartz cuvettes introduced such large errors that the results were not suitable for quantitative analysis.

The first step in the data analysis of the 90°- and backscattering geometries is to determine the refractive index n. This was done by taking the appropriate ratios of the frequency shifts measured in the 90°- or back-scattering geometries to those measured in the platelet geometry. As can be seen in Fig. 1, because q depends on n in the former but not in the latter, the ratio of frequency shifts is proportional to n. Two difficulties are immediately evident in such a scheme; the spectra in different geometries are seldom recorded at exactly the same temperature and the errors in  $\theta$  result in unacceptably large errors in n. The first problem is circumvented by fitting a quadratic to the measured frequencies in each geometry and then using the fit values to determine the ratios. The second is obviated by normalizing the value of nat room temperature to the value of 2.4293 known from the literature. The temperature dependence of n thus determined is shown in Fig. 3; the dotted lines were obtained from different combinations of scattering geometries and are intended to provide the reader with a feel for the errors and uncertainties associated with this approach. The full line is the average of all our determinations, the triangles are experimental data,<sup>18</sup> and the dashed line is an extrapolation of these data. Our determination of n is in good agreement with Ramachandran's data.<sup>18</sup> In fitting our Brillouin results we have chosen to use the polynomial fit obtained in Ref. 18 and its extrapolation to 1600 K, viz.,



FIG. 2. Brillouin spectra recorded at various temperatures and different scattering geometries. L and T denote longitudinal and transverse, respectively. No significance should be attached to relative intensities between spectra. Backgrounds observed at room temperature are due to luminescence.



FIG. 3. Refractive index of diamond vs. temperature. The dotted lines are from individual ratios of scattering geometries and are intended to provide an estimate of the experimental errors. The full line is the average of all our determinations. The triangles are data from Ref. 18 and the dashed line is the extrapolation of that data.

$$n(T) = 2.429 + 2.2 \times 10^{-5} (T - 300) + 1.7 \times 10^{-8} (T - 300)^2.$$
(2)

The increase of the index of refraction of diamond with temperature has its origin in two distinct physical phenomena: the thermal expansion and the temperature dependence of the electron band structure.<sup>19–21</sup> The former usually produces a decrease in the refractive index but in diamond because  $p_{11} + 2p_{12}$  is negative,<sup>1</sup> it produces an increase (See footnote in Ref. 2): using the  $p_{ij}$  from Ref. 1 this increase is only about one fifth of the measured change in *n*. The rest of the measured change must originate in thermally induced changes in the band structure. In general the change in *n* is expected to be linear above half its Debye temperature. Since for diamond  $\Theta_D$  2246 K, over the range of our measurements (300–1600 K), a quadratic temperature dependence is appropriate.

With the above considerations for the refractive index and taking the density as  $\rho = 3.513 + 7.4 \times 10^{-6} T - 3.8 \times 10^{-8} T^2 + 7.1 \times 10^{-12}T^3$  as deduced from the thermal expansion data of Slack and Bartram,<sup>22</sup> the measured frequency shifts lead to the elastic moduli shown in Figs. 4–6. The dots are our measured values; the full and dashed lines are fits to be described below.

Figures 4–6 contain all our experimental data obtained at different temperatures, different scattering geometries and for different samples. To fit the data we proceeded as follows: each one of the three elastic moduli was assumed to be described by a quadratic of the form

$$c_{ii} = C_0 + C_1(T - 300) + C_2(T^2 - 300^2) \tag{3}$$

thereby introducing nine fitting parameters. Furthermore, because only the longitudinal backscattering data are free from possible systematic errors, the data from other scattering geometries were allowed an additional multiplicative factor. Since this factor must be the same for all phonons observed in a given experiment, it introduces five extra fitting parameters. All the data in Figs. 4–6 were "least squares fit" to such a scheme and produced  $C_0$  values in agreement with literature values. Based on this agreement the room temperature values in Eq. (3) were replaced with the more accurate literature<sup>2</sup> ones, viz.,  $c_{11}$ =1080.4,  $c_{12}$ =127.0, and  $c_{44}$ 



FIG. 4. Elastic moduli obtained in the backscattering geometry along different crystallographic directions. The lines are fits described in the text.

= 576.6 GPa. The fitting procedure was then repeated. At this stage we found that some of the linear terms in Eq. (3) were positive—since this appeared to be rather unphysical we attempted fits setting the linear terms to zero—the surprising result was that the overall chi squared value of the fit changed by less than 0.3% indicating essentially no deterio-



FIG. 5. Elastic moduli obtained in the 90°-scattering geometry along different crystallographic directions. The lines are fits described in the text.

ration of the fit quality. The  $T^2$  coefficients for the three constants are given in Table II. The full lines in the figures are calculated using only the values given in Table II, the dashed lines include the additional fitting parameters which account for systematic errors. Note that the multiplicative factors give us an estimate of the systematic error involved in each particular geometry. From the values of these multi-



FIG. 6. Elastic moduli obtained in the platelet scattering geometry along different crystallographic directions. The lines are fits described in the text.

plicative factors the percentage systematic error for the 90° scattering geometry is between 0.6 and 0.9 %, while in the case of the platelet geometry it is between 1.5 and 4 %. These values are consistent, albeit slightly larger in one case, with the estimates made in the appendix. The systematic error of  $\approx 1\%$  in the shear mode along [111] is also consistent with our estimates.

TABLE II. Temperature dependence of the three independent elastic stiffness constants of diamond (300–1600 K);  $c_{ij}=C_0 + C_2(T^2-300^2)$ . The  $C_0$  values are taken from Ref. 2, the linear temperature coefficient is zero within experimental accuracy (see text), and the  $C_2$  terms are obtained from our fits.

	$C_0$ (GPa)	$C_2(10^{-6} \text{ GPa/K}^2)$
c <sub>11</sub>	1080.4	$-29\pm 8$
c <sub>12</sub>	127.0	$-3\pm 18$
c <sub>44</sub>	576.6	$-22\pm$ 7

The volume compressibility of diamond, or equivalently its inverse the bulk modulus *B*, is an important parameter for experimenters using diamond-anvil cells (DAC), or other applications involving high hydrostatic pressures at elevated temperatures. For a cubic crystal the bulk modulus is equal to  $(c_{11}+2c_{12})/3$ . Using the values in Table II we obtain, in the temperature range from 300 to 1600 K,

$$B(T) = 444.8 - 0.000012(T^2 - 300^2).$$
 (4)

We conclude that the bulk modulus and the elastic stiffness constants of diamond soften only by 7-9 %, when diamond is heated from ambient temperature to 1600 K.

# **IV. MICROSCOPIC FORCE CONSTANTS**

The temperature dependence of the elastic constants reported here together with that of the zone center optical phonon previously reported<sup>7,8</sup> enables an estimate to be made of the temperature changes in the force constants at the atomic level. There are two well-known models that relate the Raman active  $F_{2g}$  frequency ( $\omega_0$ ) and elastic moduli to microscopic interatomic force constants: formulated by Keating<sup>23</sup> and by Musgrave and Pople.<sup>24</sup> The assumptions in the two models are similar but lead to slightly different expressions for the various physical properties. Keating's model has only two parameters  $\alpha$  and  $\beta$  related to bond stretching and bending, respectively, the other model includes four force constants which describe stretching and bending ( $k_1$  and  $k_2$ ). We list below expressions and values for our measured physical properties in terms of these atomic force constants:

$$c_{11} = 1080.4$$
 GPa= $(k_1 + 6k_2)/3a = (\alpha + 3\beta)/a$ ,  
 $c_{12} = 127.0$  GPa= $(k_1 - 3k_2)/3a = (\alpha - \beta)/a$ ,

 $c_{44} = 576.0 \text{ GPa} = 3k_1k_2/[a(k_1+4k_2)] = 4\alpha\beta/[a(\alpha+\beta)],$ 

$$M\omega_0^2/8a = 440 \text{ GPa} = (k_1 + 4k_2)/3a = (\alpha + \beta)/a,$$
 (5)

where *a* is the lattice constant (3.567 Å) and *M* the mass of a carbon atom. Performing a least squares fit to the expressions and values in Eq. (5) we obtain  $k_1/a = 1090$  GPa,  $k_2/a = 280$  GPa,  $\alpha/a = 315$  GPa, and  $\beta/a = 240$  GPa. In Table III we recalculated the various constants using these values. Considering that the models contain only two adjustable parameters and attempt to describe the complete dispersion curves, the overall agreement is reasonable.

To extract the temperature dependence of the force constants we assume that their temperature dependence is of the

TABLE III. Comparison of experimental and calculated properties based on the Keating (Ref. 23) and Musgrave-Pople (Ref. 24) models. The force constants used are  $k_1/a = 1090$  GPa,  $k_2/a$ = 280 GPa,  $\alpha/a = 315$  GPa, and  $\beta/a = 240$  GPa.

Model	<i>c</i> <sub>11</sub>	<i>c</i> <sub>12</sub>	c <sub>44</sub>	$M\omega_0^2/8a$
Experimental	1080.4	127.0	576.6	440
Keating	1035	75	544	555
Musgrave-Pople	923	83	414	736

form  $k(1-k'T^2)$ . The k's were least squares fitted to the experimental values (we ignored the temperature dependence of  $c_{12}$  because of its large error, see Table II) to yield  $k'_1$ =4.8,  $k_2'=0.8$ ,  $\alpha'=2.3$ , and  $\beta'=3.0$  in units of  $10^{-8}$  K<sup>-2</sup>. The uncertainty in these temperature coefficients is large because there is a very strong correlation between each pair of values: equivalent fits can be obtained by decreasing one of the values and increasing the other. Nonetheless, using the above values we have recalculated the experimental ones; the results are summarized in Table IV. We note that, for the experimental value of  $(\Delta \omega_0^2/T^2 \omega_0^2)$  given in Table IV, it can be shown that the temperature dependence of a can be ignored. Given the substantial discrepancies between experiment and fit values in Table IV and the uncertainties in the parameters themselves, it does not seem reasonable to attribute any quantitative physical significance to the temperature dependence of the force constants other than the obvious decrease as temperature increases.

#### V. CONCLUSIONS

In the literature, the interesting subject of the "obvious" relation between the elastic moduli and the hardness (H) of a material has received the most detailed discussion in Ref. 5. The author makes a universal plot of  $\log H$  (Moh's hardness) of different materials vs the corresponding value of  $\log c_{11}$ , and discovers that a straight line through the data yields  $c_{11} \alpha H^{7/4}$ . The author cautions the reader "not to attach any great significance to this relation" but he also points out that "it may be useful in indicating the order of magnitude to be expected for an elastic constant in a new substance." If we consider diamond at 1600 K as "new substance," we can estimate the decrease in its hardness compared with the hardness at ambient temperature. The result is  $H(1600 \text{ K}) \sim 0.96 H(300 \text{ K})$ . Although this is only a rough estimate, it nevertheless tends to indicate that diamond "conserves" a large portion of its reputed hardness even at temperatures as high as 1600 K.

TABLE IV. Temperature dependence of elastic properties calculated at T = 1600 K. We have used  $k'_1 = 4.8$ ,  $k'_2 = 0.8$ ,  $\alpha' = 2.3$ , and  $\beta' = 3.0$  in units of  $10^{-8}$  K<sup>2</sup>. Values in the table are given in the same units.

Model	$\Delta c_{11}/T^2 c_{11}$	$\Delta c_{44}/T^2 c_{44}$	$\Delta \omega_0^2/T^2 \omega_0^2$
Experimental	$2.5 \pm 0.6$	$3.5 \pm 1.2$	$2.1 \pm 0.1$
Keating	2.8	2.7	2.6
Musgrave-Pople	2.4	2.8	2.8

Finally, we cite two more references (Refs. 25 and 26) in which the phenomenological hardness of a crystal is related to an "elastic coefficient." In Ref. 25 the author relates the "shear modulus" of a crystal with its phenomenological hardness, while the authors of Ref. 26 correlate "Young's modulus" of a crystal with its phenomenological hardness. Both of these elastic moduli can be expressed as combinations of the  $c_{ij}$  of the material. The relation is linear on a log-log scale in Ref. 25, and almost linear—with a positive second derivative in the region of large Young's modulus—in Ref. 26. Irrespective of which approach is adopted our elastic moduli indicate only a small loss of hardness at high temperatures.

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#### APPENDIX

In discussing the directions of the wavevectors of the incident and scattered light it is necessary to distinguish between directions inside and outside the sample. In the following, superscripts e and i will be used to designate parameters external and internal to the sample. Outside the sample it is trivial to determine the direction of the incident beam relative to a sample surface since one usually deals with a well collimated laser beam. The direction of the scattered beam is less easy to establish: it is not always exactly along the line joining the center of the collection lens to the entrance pinhole. Although methods can be devised to accurately establish the "center" of the scattered beam direction (usually involving auxiliary laser beams and/or retroreflection from the interferometer mirrors), this procedure becomes unwieldy when a furnace or a cryostat is utilized. For example, a 1 mm adjustment made to a 35 mm collection lens translates into an error of  $1.5^{\circ}$  in the direction of  $k_s$ . In many cases, especially with samples placed in cryostats or furnaces, errors of this magnitude may be unavoidable. Since the effect of this uncertainty is different for the different scattering geometries we discuss them individually below.

(i) *Backscattering*. The diagram for backscattering shown in Fig. 1(b) is the strict definition when  $k_i$  and  $k_s$  are antiparallel and normal to the surface. In general the term backscattering is used whenever the incident and scattered light enter and leave the sample through the same surface. If the incident and scattered beams subtend angles  $\theta_i^e$  and  $\theta_s^e$  with the surface normal [see Fig. 1(d)] it is trivial to calculate  $\theta_i^i$ and  $\theta_s^i$  using Snell's law. As mentioned above the error in  $\theta_i^e$ can usually be made quite small by appropriate use of retroreflection of the incident laser beam. Let the error in  $\theta_s^e$  be  $\delta$  (typically  $\approx 1.5^\circ$  as mentioned above). From Eq. (1) it follows that (where  $\delta$  is expressed in radians). In our experiments, in order to avoid the direct reflection of the laser beam into the spectrometer, we used  $\theta_i^e = \theta_s^e = 10^\circ$ . This translates into an error of around 0.3% in *q* which can be neglected compared to the random errors in  $\Delta\omega$ .

It is also easy to show that, in this geometry, q makes an angle of  $(\theta_i^i + \theta_s^i)/2 \pm \delta/2n$  with the surface normal, in our case  $\approx 4^\circ$ . As discussed in the main text, this misalignment has a negligible effect ( $\approx 0.4\%$ ) on the combination of  $c_{ij}$  near an extremum. For the transverse mode along [111], however, it leads, using the known  $c_{ij}$  to calculate the angular dependencies of the velocities, to a 1.5% uncertainty. When evaluating the combination of  $c_{ij}$ 's which enters the expression for the velocity it must also be recalled that, unless the surface is prepared by cleavage, the normal to the surface may not coincide exactly with the desired crystallographic direction. Samples oriented with Laue x-ray photographs can often be off by a few degrees.

(ii) 90° scattering. The ideal 90°-scattering geometry is shown in Fig. 1(a). It assumes that the incident and scattered light are exactly at 90° and that the entrance and exit faces on the sample are also exactly at 90°. Let the error in these two angles be  $\delta$  and  $\varepsilon$ , respectively. It is easy to show that the (internal) scattering angle  $\theta$ , defined in Eq. (1) is

$$\theta = 90 - \varepsilon + \varepsilon/n + \delta/n, \qquad (A2)$$

so that the error in q is

$$\Delta q/q = (-\varepsilon + \varepsilon/n + \delta/n)/2. \tag{A3}$$

Uncertainties of 1° in  $\varepsilon$  and  $\delta$  lead to systematic errors of around 1% in q and in the velocities; the resulting error in the  $c_{ij}$  is  $\approx 2\%$ . If the sample is accurately cut so that  $\varepsilon$ = 0 the errors in velocity and  $c_{ij}$ 's are 0.5 and 1%, respectively. The uncertainty in the direction of q will again depend trivially on  $\varepsilon$  and  $\delta$  and also on the accuracy with which the sample faces are known relative to the crystallographic axes. These two latter effects lead to negligible errors in our case.

(iii) *Platelet*. The ideal platelet geometry is shown in Fig. 1(c). Since it is relatively easy to fabricate samples with accurately parallel faces, it is usually safe to ignore the error resulting from nonparallelicity. The usually relevant uncertainties are in the (external) scattering angle  $\delta$  and the requirement that the sample bisect the incident and scattered directions. Let us assume that the incident beam makes an angle of  $45+\zeta$  with the surface normal. It is convenient in this geometry to consider the components of q parallel and perpendicular to the sample faces. Simple geometrical considerations yield

$$q_{\parallel} = k_L [\sin(45 + \zeta) + \sin(45 - \zeta + \delta)].$$
 (A4)

If  $\zeta$  and  $\delta$  are small,

and

$$q_{\parallel} = \sqrt{2}k_L(1 + \delta/2) \tag{A5}$$

$$\Delta q/q \approx (\delta/n)^2 + (\delta/n)\sin(\theta_i^i - \theta_s^i)$$
(A1)

$$\Delta q_{\parallel}/q_{\parallel} = \delta/2. \tag{A6}$$

Notice that the error in |q| does not depend on  $\zeta$  and that  $\delta = 1^{\circ}$  leads to a  $\approx 1\%$  error in q, 2% in  $c_{ij}$ .

The component of q perpendicular to the film is, to first order in the angles,

$$q_{\text{perp}} = k_L (\delta/2 - \zeta)/n.$$
 (A7)

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