

Elastic properties of trigonal laminar systems: Brillouin scattering study of $\text{Hf}_{1-x}\text{Zr}_x\text{S}_2$

J. M. Karanikas and R. Sooryakumar

Department of Physics, The Ohio State University, Columbus, Ohio 43210

C. Carlone and M. Aubin

Département de Physique, Université de Sherbrooke, Quebec, Canada J1K 2R1

(Received 3 August 1989)

Brillouin scattering measurements on the layered transition-metal dichalcogenides have been performed on samples of the general composition $\text{Hf}_{1-x}\text{Zr}_x\text{S}_2$. By selecting the exciting frequency to be in resonance with the absorption edge, both surface and bulk acoustic phonons were simultaneously observed. They are utilized in a self-consistent manner to calculate the six independent elastic constants of trigonal ($\bar{3}m$) HfS_2 , one of the lowest-symmetry structures studied to date by Brillouin spectroscopy. The method also eliminates the need for the refractive indices, a consequence that is particularly valuable in such highly anisotropic or birefringent samples.

There exist several experimental obstacles in the determination of elastic properties of thin films and layered compounds. Ultrasonic attenuation requires samples to be of sufficient size and of a minimum thickness comparable to the acoustic wavelength employed and thus is not suited for laminar systems. Furthermore, for crystals of low symmetry, such as trigonal, the increased number of independent elastic parameters necessitates ultrasonic wave propagation along crystallographic directions that are not accessible due to the difficulty of growing and cleaving the specimen parallel to the appropriate plane of symmetry. Brillouin scattering has generally been viewed as an alternate technique that could overcome most such problems associated with ultrasonic attenuation. Nevertheless, the latter is burdened by other difficulties. In transparent samples, bulk phonon velocities along specific crystallographic directions can be measured from the Brillouin frequency shift by selection of a suitable scattering geometry, but this requires knowledge of the material refractive indices. Surface phonons are generally absent or weak in this situation. For opaque samples, however, the Brillouin spectra are dominated by the surface Rayleigh wave¹ while the weak and/or broad bulk modes are normally unreliable for velocity measurements. Although the Rayleigh mode is independent of macroscopic dielectric material properties, it depends on combinations of the elastic constants. In general, and certainly in low-symmetry materials, it is not feasible to extract individual elastic parameters solely from these surface modes. Thus in addition to weak intensities of bulk excitations in opaque systems and the inadequacy of studying only surface waves the techniques of Brillouin scattering requires reliable indices of refraction, including in materials exhibiting optical anisotropies or birefringence as is often the case in layered systems.

One means to overcome these drawbacks associated with Brillouin scattering is to select, when possible, the energy of the incident exciting frequency to lie below but close to an absorption edge of the sample. The intensities of both surface and bulk excitations under these cir-

cumstances are strong and of comparable magnitude. Consequently, by demanding self-consistency between surface and bulk measurements, it is possible to evaluate an accurate and complete set of elastic constants, even for systems of low symmetry, that are devoid of the uncertainties identified above.

In this work we report Brillouin scattering measurements on a series of highly anisotropic samples having the general formula $\text{Hf}_{1-x}\text{Zr}_x\text{S}_2$ and extract the six independent elastic constants for HfS_2 in the self-consistent manner outlined above. These compounds crystallize in the trigonal system (space group $\bar{3}m$), forming layered structures consisting of sandwiches of three hexagonally arranged sheets of atoms.² The elastic properties are described by constants C_{11} , C_{33} , C_{44} , C_{12} , C_{13} , and C_{14} , their values reflecting the weak van der Waals forces that hold the stacks of quasi-two-dimensional layers together. The compounds are indirect-gap semiconductors³ with a direct band gap ranging from 2.58 eV for HfS_2 to 2.17 eV for ZrS_2 . We hence chose the 5145-Å line (2.41 eV) of the Ar^+ laser as our exciting source since strong Brillouin peaks from both surface and bulk excitations were expected from HfS_2 due to the near-resonant absorption. With increasing Zr the elastic parameters are observed to stiffen while the compound progressively becomes opaque to this exciting frequency. Enhancement in the relative intensities of the surface versus bulk modes as x increases reflects the difficulties of evaluating elastic constants associated with the strongly absorbing trigonal system.

BACKGROUND

The velocity of bulk acoustic phonons propagating along any crystallographic direction depends on the density of the material and a combination of elastic constants. In isotropic systems and along a few special directions of symmetry in anisotropic materials these acoustic waves separate into purely transverse (shear) and purely longitudinal (compressional), their velocity often being a function of a single elastic constant. The surface mode

velocity, on the other hand, always depends on some combination of elastic constants even for directions that correspond to axes of symmetry on the surface.⁴ Along these symmetry directions the polarization of the surface Rayleigh phonon is confined in the sagittal plane containing the direction of propagation and the normal to the surface. For other directions on the surface the elastic wave is described by a combination of all three polarizations but its velocity retains its dependence on an appropriate combination of elastic constants.

Inelastic light scattering from bulk acoustic phonons is well known and arises from coupling of photons to the vibrations via the elasto-optic (EO) mechanism.⁵ This corresponds to a modulation of the dielectric constant that results in inelastic scattering of the light. The resulting photon frequency shift δf is related to the bulk phonon velocity v through

$$v = \frac{\lambda \delta f}{2\eta},$$

where λ is the wavelength of the incident light and η the refractive index of the specimen. The direction of the phonon wave vector, coincident with that of the light inside the sample, also depends on η through Snell's law. Scattering from thermally generated surface phonons, on the other hand, is a relatively new phenomenon.¹ The velocity v_s of the surface acoustic mode is given by

$$v_s = \frac{\lambda \delta f}{2 \sin \theta_i},$$

θ_i being the angle of incidence relative to the surface normal. The EO mechanism is also active in light scattering from surface phonons in conjunction with the ripple mechanism.^{6,7} The latter relates to a corrugation of the surface by the phonon resulting in a propagating diffraction grating from which the incident radiation is scattered. This mechanism dominates scattering from highly reflecting materials.^{6,7} Qualitative analysis of the scattering cross sections from HfS_2 indicates that in the semitransparent region below the direct gap surface scattering is also predominantly due to the ripple mechanism.

EXPERIMENT AND RESULTS

The crystals were grown by the iodine transport method.⁸ X-ray diffraction patterns confirmed the space group of the structure to be trigonal ($\bar{3}m$). The density ρ of HfS_2 was calculated to be 6.03 g/cm^3 , based on a hexagonal unit cell⁹ of dimensions $a = 3.622 \text{ \AA}$ and $c = 5.88 \text{ \AA}$. The weak van der Waals forces that hold the layers together enabled cleavage along the a - b , plane exposing an atomically flat plane. These smooth surfaces with the c axis lying normal to them are thus well suited for light scattering studies.

Most of the Brillouin measurements were performed in the backscattering geometry with different angles of incidence and polarization appropriate for the phonons under consideration. The experiments were conducted at room temperature and the scattered light collected by an $f/1.4$ camera lens. Approximately 30 mW of 5145-Å in-

cident radiation was used on HfS_2 and the polarization of the scattered light was not analyzed. The incident power was gradually raised with increasing x up to 55 mW incident on ZrS_2 without signs of any surface damage. The spectrum of the scattered radiation was analyzed by means of a tandem Fabry-Perot interferometer¹ operating in a sequential six-pass arrangement.

In order to probe the longitudinal and two degenerate transverse phonons propagating parallel to the c axis, light was incident normal to the surface of a HfS_2 platelet. The velocity¹⁰ of the former depends only on C_{33} while that of the latter on C_{44} , with η being retained as an unknown parameter. These two elastic parameters, especially C_{44} , are intimately related to the strength of the van der Waals forces bonding different layers.

Due to the trigonal symmetry a series of Brillouin spectra were obtained using s -polarized light incident at 45° with the sample being rotated through discrete steps about the c axis. s polarization ensures that the incident electric field \mathbf{E} is maintained perpendicular to the c axis. Measurements on other HfS_2 samples have shown that the reflectance¹¹ at 2.41 eV, and thus η , is the same for light with \mathbf{E} normal to \hat{c} incident at $\theta_i = 0^\circ$ and $\theta_i = 90^\circ$ to the c axis. It is therefore reasonable to assume that η is the same for all intermediate θ_i in the s -polarization geometry. The choice of $\theta_i = 45^\circ$ in our measurements is a compromise between the need to probe phonons propagating at a large angle relative to the c axis, which requires large θ_i , while staying well below $\theta_i \approx 70^\circ$, the Brewster angle of the specimen. At this angle the penetrating intensity of the incident s -polarized light and thus the Brillouin cross section of the bulk modes is markedly diminished.

Measurements were taken in this particular geometry at intervals of 10° steps about the c axis, spanning an arc of 130° . This, as discussed below, was sufficient to verify the trigonal symmetry of the crystals which was manifested by the variation of the relative frequencies of the two quasitransverse modes. the quasilongitudinal mode frequency did not change appreciably. This series of measurements served a dual purpose. First, it identified the direction of the Y and X (dyad axis of $\bar{3}m$) axes of the crystal. Subsequently the spectra provided velocities of bulk modes in crystallographically independent directions, allowing the evaluation of different combinations of elastic constants. The inset¹⁰ in Fig. 1 depicts inverse velocity curves, on the XY plane, of a typical trigonal structure (quartz). It can be seen that the velocities—and thus the Brillouin frequency shifts—of the two quasitransverse modes are closest for propagation along the Y axis and lie farther apart along the X axis. The quasilongitudinal mode, on the other hand, shows much smaller variations in the XY plane. Qualitatively similar results are expected, and observed in our experiments, for bulk phonons propagating in the YZ and XZ planes, respectively. Brillouin spectra for wave propagation in these planes are depicted in Fig. 1 and clearly reveal the merging of T_2 and T_1 , the quasitransverse modes along the YZ plane. Thus it was possible to identify these special crystallographic planes by monitoring the frequencies of Brillouin peaks

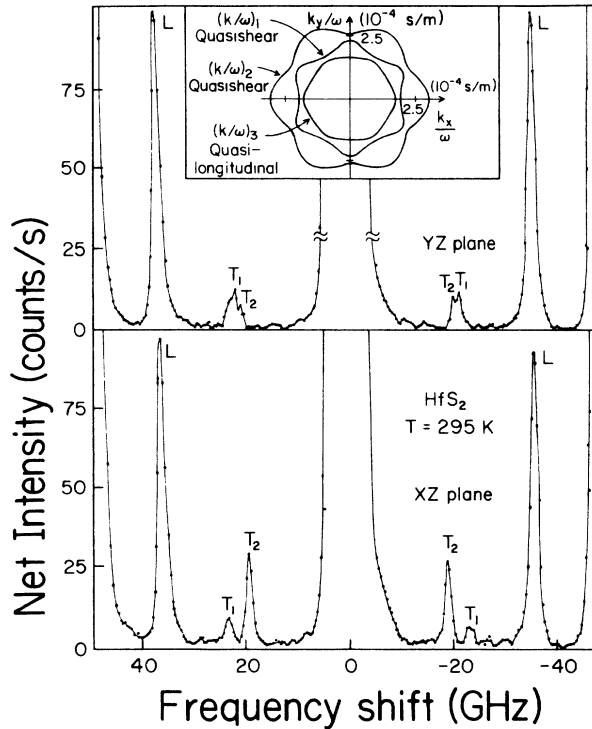


FIG. 1. Measured Brillouin spectra of HfS_2 for phonons propagating in the YZ (top) and XZ (bottom) planes of the structure. The angle of incidence was 45° and the 2.41-eV incident radiation was s polarized. The inset shows typical inverse velocity curves for phonons lying in the XY plane of a trigonal crystal (Ref. 10). At this free spectral range (50 GHz) the Rayleigh phonons are buried in the central elastic peak.

T_1 and T_2 from the discrete set of sample orientations noted above.¹²

Analytic expressions for the velocity of the three acoustic modes can be obtained for the YZ plane. However, numerical computation is required for phonons lying in the XZ plane. The velocities of the acoustic phonons in the YZ plane are given by¹⁰

$$v_1 = \{ [A + (B^2 + D)^{1/2}] / 2\rho \}^{1/2} \quad (\text{quasilongitudinal}),$$

$$v_2 = \{ [A - (B^2 + D)^{1/2}] / 2\rho \}^{1/2} \quad (\text{quasitransverse}),$$

$$v_3 = \{ [(C_{66} \sin^2 \theta + C_{44} \cos^2 \theta + C_{14} \sin 2\theta) / \rho]^{1/2} \} \quad (\text{quasitransverse}),$$

where

$$A = C_{44} + C_{11} \sin^2 \theta + C_{33} \cos^2 \theta - C_{14} \sin 2\theta,$$

$$B = (C_{44} - C_{11}) \sin^2 \theta + (C_{33} - C_{44}) \cos^2 \theta + C_{14} \sin 2\theta,$$

$$D = [(C_{13} + C_{44}) \sin 2\theta - 2C_{14} \sin^2 \theta]^2,$$

$C_{66} = (C_{11} - C_{12})/2$, and θ identifies the angle between the phonon wave vector and the Z ($\equiv c$) axis. These re-

sults from the bulk modes provided a sufficient number of independent equations and allowed a consistent calculation of the remaining constants C_{11} , C_{12} , C_{13} , and C_{14} in terms of η which, as always, remains as an unknown parameter.

Despite the fact that all the C_{ij} 's had been evaluated in terms of η it was felt that the numerical errors associated with C_{11} , C_{12} was unacceptably high, over 30%. This can be traced to the relatively high η of the sample that results in the phonon—and thus the phonon—wave vector being almost parallel to the c axis. It can be seen in the equations above that only C_{11} is always multiplied by $\sin^2 \theta$, a very small number. Thus the magnitude of C_{11} can vary substantially and still have a negligible impact on the overall numerical fit to the measured bulk velocities. Hence, in order to improve the measurement of C_{11} we exploited the relative transparency of the material to 5145-Å radiation and its layered nature in another scattering geometry. s -polarized light was incident on one side of the platelet and the scattered photons collected from the other parallel face. The angle between incident and scattered optical paths was maintained at 45° with the sample, in the form of a flake, lying on the bisector. The phonons probed are thus characterized by wave vectors that are constrained to lie on the XY plane of the crystal and are independent of the refractive index. The sample was rotated every 10° about its c axis in this geometry, spanning an arc of 60° . The latter was adequate since the XY plane exhibits a sixfold symmetry. The (quasi)longitudinal mode observed in this geometry was strong, hence allowing C_{11} , which is closely tied to the intralayer forces, to be evaluated solely from this measurement with a 5% error.

We now turn to the surface phonon. The Rayleigh velocity along the Y axis depends on a combination of five C_{ij} 's (except C_{12}), though generally dominated by C_{44} and independent of η .¹⁰ A typical Brillouin spectrum from HfS_2 showing the surface Rayleigh mode propagating in the XY plane and of comparable strength to the bulk modes is shown at the top of Fig. 2. The measured surface and bulk velocities were correlated by requiring that a single set of elastic constants be sufficient to satisfy the boundary condition of zero stress at the free surface and simultaneously fit the measured frequency shifts δf of bulk phonons propagating on the XZ and YZ planes of the crystal. There was only one adjustable parameter—the refractive index. The η required to achieve this consistency is 3.6. The results for the six elastic constants of this trigonal system that were thus evaluated are summarized in Table I.

The layered nature of the compound manifests itself in the relative values of C_{ij} . For example, the large C_{11} reflects strong intralayer forces while C_{44} , which is over an order of magnitude weaker, arises from the weak van der Waals forces. The uncertainty in the value of C_{14} appears to be quite large. This is not entirely due to the absolute error itself (only ± 2 GPa) but in large part to the very small value of the elastic constant itself. The magnitude of C_{14} reflects the trigonal character of a structure, as opposed to hexagonal symmetry where it vanishes.

Therefore the small value of C_{14} in HfS_2 indicates that the compound, although trigonal in structure, has acoustic properties lying close to that of a hexagonal solid. This is hardly surprising since a large number of other transition-metal dichalcogenides do indeed crystallize in

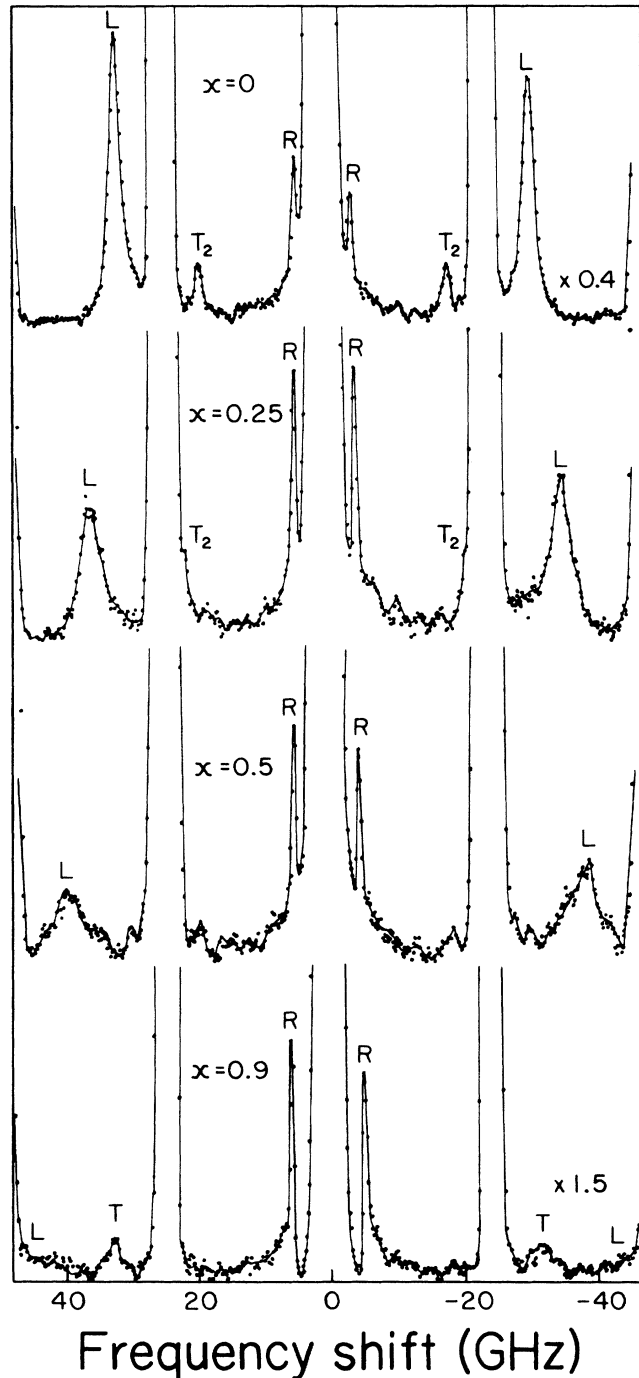


FIG. 2. Measured Brillouin spectra showing Rayleigh wave R and bulk phonons (L, T) of $\text{Hf}_{1-x}\text{Zr}_x\text{S}_2$ with increasing Zr concentration. The angle of incidence was 70° and the 5145-\AA radiation was p polarized. The Rayleigh phonon R is along the Y axis for $x=0$; its direction is random on the XY plane for all other x . The free spectral range is 25 GHz. The spectra have been normalized to account for the different incident power.

the hexagonal system.²

In order to investigate the mechanism that dominates scattering from the surface phonon, several scans on HfS_2 were conducted at $\theta_i=45^\circ$ in backscattering with s - and p -polarized light. The free spectral range of the interferometer was reduced to allow the emergence of the Rayleigh mode away from the elastic peak. The Brillouin cross section of the Rayleigh phonon in the p geometry was measured to be approximately 3.5 times that of the s geometry. At $\theta_i=45^\circ$ and $\eta \approx 3.6$, theory¹³ predicts equal contributions by the EO mechanism for both s - and p -polarized incident light while the ripple scattering amplitude is about 2.5 times larger in the p than in the s geometry. The experimentally observed differences between the two polarizations indicate that Brillouin surface scattering in HfS_2 , at 2.41 eV, occurs predominantly via the ripple mechanism. Its contribution is expected to increase, of course, with metallic character as we have observed in TiS_2 .

Finally, we comment on a series of experiments in the backscattering geometry that monitored the change in the Brillouin spectra with increasing Zr concentration. The spectra obtained with the same exciting radiation, 5145 \AA , and p polarized are shown in Fig. 2. The $x=0$ spectrum has already been discussed. The direction of propagation of the surface mode for the other samples was random on the XY plane. A rise in the intensity of the surface mode relative to the bulk phonons is clearly observed while the gradual increase of all Brillouin frequencies indicates a stiffening of the bonds as x increases. It is seen that above $x \approx 0.5$, the spectra are dominated by the Rayleigh mode. Subsequently the bulk modes become ineffective in evaluating the elastic parameters. Indeed it is this feature that highlights the importance of selecting an appropriate exciting frequency. This step renders both surface and bulk Brillouin peaks to be of comparable intensity and hence of value to derive the elastic properties of these low-symmetry systems.

In summary, we find that for semiconducting materials by choosing the energy of the incident radiation to lie in the vicinity of, but below, a strong absorption band both the surface and the bulk modes in the Brillouin spectrum are sufficiently strong to allow a self-consistent calculation of all elastic parameters without accurate knowledge of the refractive indices, even for crystals with very low symmetry. The trigonal structure, though only weakly departing from hexagonal symmetry in the present case, is revealed by the frequencies of the quasitransverse modes. The materials become stiffer as the Zr concentration increases. Finally, we have identified the ripple amplitude as the dominant contribution to the intensity of the Rayleigh mode in HfS_2 at 2.4 eV.

TABLE I. Elastic constants of HfS_2 as derived from the self-consistent fit to Rayleigh and bulk acoustic modes. All values are in GPa.

C_{11}	C_{33}	C_{44}	C_{13}	C_{12}	C_{14}
143(± 7)	39.4(± 1.4)	10.1(± 0.4)	10(± 1)	50(± 15)	1(± 2)

ACKNOWLEDGMENTS

Work at The Ohio State University was supported by the National Science Foundation through Contract No.

DMR-87-03980 while C.C. and M.A. acknowledge support from the Natural Sciences and Engineering Research Council of Canada (NSERC). J.M.K. and R.S. thank M. Grimsditch for a valuable discussion on this work.

-
- ¹J. R. Sandercock, in *Light Scattering in Solids III*, Vol. 51 of *Topics in Applied Physics*, edited by M. Cardona and J. Guntherodt (Springer-Verlag, Berlin, 1982).
- ²J. A. Wilson and A. D. Yoffe, *Adv. Phys.* **18**, 193 (1968); C. Y. Fong, J. Camassel, S. Kohn, and Y. R. Shen, *Phys. Rev. B* **13**, 5442 (1976).
- ³L. Roubi and C. Carlone, *Can. J. Phys.* **66**, 633 (1988).
- ⁴G. W. Farnell, in *Physical Acoustics*, edited by W. P. Mason and R. N. Thurston (Academic, New York, 1972), Vol. VI.
- ⁵A. M. Marvin, V. Bortolani, and F. Nizzoli, *J. Phys. C* **13**, 299 (1980).
- ⁶S. Mishra and R. Bray, *Phys. Rev. Lett.* **39**, 222 (1977).
- ⁷R. Loudon, *Phys. Rev. Lett.* **40**, 581 (1978); N. L. Rowell and G. I. Stegeman, *Phys. Rev. B* **18**, 2598 (1978); K. R. Subbaswamy and A. A. Maradudin, *ibid.* **18**, 4181 (1978).
- ⁸H. P. B. Remington, A. A. Balchin, and B. K. Turner, *J. Cryst. Growth* **15**, 51 (1972).
- ⁹D. L. Greenaway and R. Nitsche, *J. Phys. Chem. Solids* **26**, 1445 (1965).
- ¹⁰B. A. Auld, in *Acoustic Fields and Waves in Solids* (Wiley, New York, 1973), Vols. 1 and 2.
- ¹¹S. C. Bayliss and W. Y. Liang, *J. Phys. C* **15**, 1283 (1982).
- ¹²Sukmock Lee, B. Hillebrands, G. I. Stegeman, B. Dunn, L. A. Momoda, and F. Nizzoli, *Solid State Commun.* **70**, 15 (1989).
- ¹³A. M. Marvin, V. Bortolani, F. Nizzoli, and G. Santoro, *J. Phys. C* **13**, 1607 (1980).