PHYSICAL REVIEW B VOLUME 44, NUMBER 9 1 SEPTEMBER 1991-I

Elastic constants of As_2S_3

L. E. McNeil* and M. Grimsditch
Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439

(Received 8 November 1990; revised manuscript received 7 March 1991)

We have used Brillouin scattering to measure ten of the thirteen independent elastic constants of crystalline As_2S_3. We find that the phonon propagation within the layer plane is largely controlled by the orthorhombic symmetry of the layer rather than the monoclinic symmetry of the crystal. The stiffness within the plane displays a large anisotropy, and the smaller of the stiffnesses within the plane is less than that along the axis perpendicular to the plane, an unexpected result for a layered crystal. For phonons propagating near the [001] direction the two branches of the velocity show a "mode repulsion" and exchange their polarizations. In this direction the velocity of the shear wave is larger than that of the compressional wave.

INTRODUCTION

Because of their quasi-two-dimensional nature, layered materials have attracted considerable attention. As expected, the weak van der Waals bonding between layers has profound effects on many physical properties.[1]

In particular, the elastic constants of many such materials [graphite,[2] mica,[3] GaSe (Ref. 4)] exhibit a clear anisotropy associated with the weak interlayer bonding. However, all elastic measurements to date have been on materials of hexagonal or higher symmetry so that, within the layers, the material is elastically isotropic. Here we explore the effects of lower in-plane symmetry on the elastic constants. We have chosen to investigate these effects in As_2S_3 since it has already been shown that the properties of the dielectric tensor are governed more by the orthorhombic symmetry of the individual layers than by the overall monoclinic symmetry of the entire crystal. Our results show that the elastic constants also possess a symmetry very close to that expected for an orthorhombic material. However, they exhibit an anisotropy which is completely unexpected given the layered nature of the compound: one direction in the plane is actually "softer" than the direction normal to the layers.

The compound As_2S_3, which occurs in nature as the mineral orpiment, is unusual in the sense that it is far better studied in its amorphous form than in its crystalline form. This is because the amorphous form is of technological importance in infrared optics and is isomorphic with As_2Se_3, which is used in xerography, and also because it displays interesting photoinduced phenomena such as photodarkening[5] and photoenhanced diffusion.[6] Crystalline As_2S_3 has a layered structure and is of interest both as a guide to understanding the amorphous form and in its own right as a prime example of a highly anisotropic molecular solid, in which the diperiodic symmetry of the individual layer (i.e., the symmetry of the layer considered as a three-dimensional object with translational symmetry in two dimensions and finite extent in the third) is dominant over the triperiodic crystal symmetry in determining the properties of the solid.[7] Previous optical and vibrational measurements[7,8] of crystalline As_2S_3 have included optical absorption and reflection from infrared[7] to ultraviolet[9] frequencies, index of refraction in the visible regime for different polarization directions,[8,10] Raman scattering and its temperature[7] and pressure[11] dependence, and neutron scattering.[12] In addition, photoconductivity and internal photoemission measurements have been made.[8] The absence to date of detailed information about the elastic constants of the crystal may be attributable to the difficulties of obtaining high-quality samples suitable for ultrasonic measurements. By using Brillouin scattering we have been able to measure ten of the thirteen independent elastic constants, and to give further evidence of the importance of the layer symmetry in this compound.

The crystal structure of orpiment is made up of covalently bonded layers which are coupled only weakly to one another, giving the crystal a very pronounced cleavage plane parallel to the layers, i.e., in the [010] plane. Within the layers the bonding is exclusively heteropolar, with each S atom bonded to two As atoms and each As threefold-coordinated by S. The repeating unit within the plane contains ten atoms (two formula units) and has orthorhombic ($Pnm2_1$) symmetry. These planes are stacked to form a three-dimensional monoclinic crystal ($P2_1/n$) with two layers (and thus 20 atoms) in the unit cell. It has been shown that the selection rules for the vibrational spectra are determined not by the three-dimensional symmetry of the crystal, but by the higher symmetry of the individual layers.[7] The dominance of the diperiodic symmetry is also apparent in the dielectric tensor, whose principal axes coincide with the crystal axes although that is not required in a monoclinic crystal.[9] As will be described below, the elastic stiffness tensor displays similar behavior.

EXPERIMENTAL CONDITIONS

The sample upon which these measurements were made was a natural crystal from Macedonia, and as is usual it was in the form of a thin plate roughly 5 mm square and 1 mm thick with only two good-quality surfaces (both perpendicular to the [010] axis). By using several different Brillouin scattering geometries we were able to measure or set limits on ten of the thirteen independent elastic stiffness constants. The measurements were made at room temperature using a 5+4 pass tandem Fabry-Pérot interferometer and 50 mW of 5145-Å radiation from a single-mode Ar^+ laser. The refractive indices $n_1=3.40$ and $n_3=3.01$ necessary to convert the phonon frequencies to sound velocities v were taken from Ref. 9. Further conversion to the appropriate combination of elastic constants made use of the value $\rho=3.43$ g/cm^3 for the density.

RESULTS

In the "platelet" geometry with the phonon wave vector q lying in the [010] plane (the layer or b plane) we observed two Brillouin peaks for each direction of q, one corresponding to a phonon of quasilongitudinal polarization and the other corresponding to a quasitransverse phonon. In this geometry the index of refraction does not enter. In a monoclinic crystal the Christoffel equations for phonons in the plane perpendicular to the dyad axis ([010] axis) produce solutions which as functions of direction in the plane do not have extrema along the crystal axes, i.e., the [100] and [001] directions are not special directions in the crystal. These solutions are functions of the elastic constants C_{11}, C_{33}, C_{55}, C_{13}, C_{15}, and C_{35}. The values for ρv^2 as a function of the angle θ between the phonon wave vector and the c axis are given by the following expression:

$$\begin{aligned}\rho v^2=\tfrac{1}{2}(&\sin^2\theta(C_{11}+C_{55})+2\sin\theta\cos\theta(C_{15}+C_{35})+\cos^2\theta(C_{33}+C_{55})\\&\pm\{[\sin^2\theta(C_{11}+C_{55})+2\sin\theta\cos\theta(C_{15}+C_{35})+\cos^2\theta(C_{33}+C_{55})]^2\\&\quad-4[\sin^4\theta(C_{11}C_{55}-C_{15}^2)+2\sin^3\theta\cos\theta(C_{11}C_{35}-C_{13}C_{15})\\&\qquad+\sin^2\theta\cos^2\theta(C_{11}C_{33}+2C_{15}C_{35}-C_{13}^2-2C_{13}C_{55})\\&\qquad+2\sin\theta\cos^3\theta(C_{33}C_{15}-C_{13}C_{15})+\cos^4\theta(C_{33}C_{55}-C_{35}^2)]\}^{1/2})\ .\end{aligned}\tag{1}$$

By making a linear least-squares fit of Eq. (1) to the data obtained in the platelet geometry we were able to extract the values of C_{11}, C_{33}, C_{55}, C_{13}, C_{15}, and C_{35} shown in Table I. The uncertainties given in the table correspond to the ranges of values of the constants, varied individually, which gave acceptable fits to the data. The data and the resulting fit are shown in Fig. 1.

In the backscattering geometry with $q//[010]$ we observed three modes and were thus able to obtain the value of $C_{22}=27.1\pm0.3$ GPa directly from the longitudinal phonon (the uncertainty here arising from uncertainty in the index of refraction) and to obtain information about C_{44}, C_{66}, and C_{46} from the two quasitransverse modes. For these modes ρv^2 is given by Eq. (2):

$$\rho v^2=\tfrac{1}{2}\{C_{44}+C_{66}\pm[(C_{44}-C_{66})^2+4C_{46}^2]^{1/2}\}\ . \tag{2}$$

If we designate the two measured values of ρv^2 as $X_+=1.3$ GPa and $X_-=0.5$ GPa (corresponding to the positive and negative roots), we have

$$X_+-X_-=[(C_{44}-C_{66})^2+4C_{46}^2]^{1/2}\ , \tag{3}$$

$$X_++X_-=C_{44}+C_{66}\ . \tag{4}$$

Given that C_{44} and C_{66} are positive, then $0\le(C_{44}-C_{66})^2\le(C_{44}+C_{66})^2$ and thus $2|C_{46}|\le X_+-X_-\le+[(C_{44}+C_{66})^2+4C_{46}^2]^{1/2}$, giving $|C_{46}|\le(X_+-X_-)/2=0.4$ GPa. If $|C_{46}|=0.4$ GPa, then $C_{44}-C_{66}=0$ and $C_{44}=C_{66}=0.9$ GPa. If $|C_{46}|=0$, then X_+ and X_- give C_{44} and C_{66} directly. The two can be distinguished by examining the change in ρv^2 as the direction of q is changed from [010] toward [100] or [001]. For $q//[100]$, ρv^2 for the two transverse phonons gives C_{66} and $\frac{1}{2}\{C_{11}+C_{55}-[(C_{11}-C_{55})^2+4C_{15}^2]^{1/2}\}$, while for $q//[001]$, $\rho v^2=C_{66}$ or $\frac{1}{2}\{C_{33}+C_{55}-[(C_{33}-C_{55})^2+4C_{35}^2]^{1/2}\}$. The second expression in

TABLE I. Elastic constants of As_2S_3 (GPa).

C_{11}	99.6 ± 1.0
C_{22}	27.1 ± 0.3
C_{33}	21.9 ± 1.4
C_{44}	1.1 ± 0.2
C_{55}	24.0 ± 0.8
C_{66}	0.7 ± 0.2
C_{13}	20.6 ± 1.9
C_{15}	-0.3 ± 0.8
C_{35}	-1.2 ± 0.9
$\lvert C_{46}\rvert$	0.2 ± 0.2

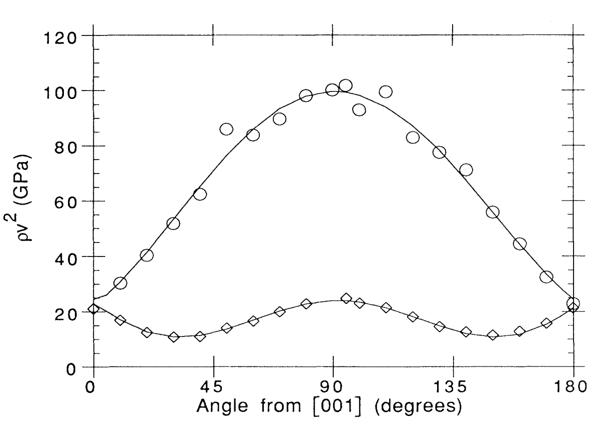

FIG. 1. ρv_2 as a function of angle between the [001] axis and the phonon wave vector q. The symbols represent the measured values and the lines result from a least-squares fit of Eq. (1) to the data.

each case is $\approx C_{55}$ because C_{15} and C_{35} are small compared to the diagonal components. Since $C_{55} \gg X_+$ and X_-, we can assign C_{44} to the phonon that increases strongly in frequency as **q** shifts from [010] toward [100], and C_{66} to the one which does the same as **q** shifts from [010] toward [001]. Our backscattering measurements for **q** inclined to [010] allow us to associate X_+ with C_{44} and X_- with C_{66} and lead to the ranges of values given for the two constants in Table I.

DISCUSSION

The remarkable aspect of the data shown in Fig. 1 and the elastic constants given in Table I is how closely they resemble what would be expected from an orthorhombic crystal. For that symmetry, since $C_{15}=C_{35}=0$, ρv^2 in the layer plane is symmetric about the [100] and [001] axes (i.e., about 0° and 90°). The small values of C_{15} and C_{35} imply that the weak coupling between the layers allows the vibrations of the individual layers to be largely determined by the orthorhombic symmetry of the layer (for which $C_{15}=C_{35}=0$) rather than the monoclinic symmetry of the crystal.

In layered materials the weak interlayer bonding results in small values of C_{22}, C_{44}, and C_{66}, which should vanish in the absence of interlayer interactions.[13] This expectation is consistent with our finding $C_{22} \ll C_{11}$ and $C_{44}, C_{66} \ll C_{55}$.

The values of the elastic constants given in Table I reveal an additional aspect of the unusual structure of crystalline As_2S_3, namely the large anisotropy *within* the layer plane. This is apparent from the large disparity between the values of C_{11} and C_{33}. Not only is the value of C_{33} only about 20% that of C_{11}, it is actually smaller than that of C_{22}, the compressive constant along the axis perpendicular to the layer plane. Large disparities between C_{11} and C_{33}, while unusual, are not unknown in monoclinic and orthorhombic crystals. For example, in deuterated pyridine[14][$(CD)_4N_2$] the ratio $C_{33}/C_{11}=0.225$. However, in a layered material it is quite surprising to find C_{33}, which is dominated by *intralayer* interactions, to be smaller than C_{22}, which arises from *interlayer* interactions. We are aware of no other layered material whose elastic constants display this peculiar property. The in-plane anisotropy is consistent with the large birefringence:[8,10] the refractive index for the electric vector **E**//[100] is 13% greater than that for **E**//[001], a difference comparable to that of calcite or rutile.

This elastic anisotropy in the plane manifests itself in the values of the linear compressibility. The compressibility along [001] is a complicated function of various elastic constants, including the values C_{12} and C_{23} which are not known. However, measurements of the sample dimensions in a diamond anvil cell[11] have shown that $\chi_{001}<0$, i.e., that under hydrostatic pressure the [001] axis actually *expands* rather than contracting. This has been attributed to the fact that strain occurs by an accordianlike bond bending as is seen in trigonal Se and Te. The small force constants associated with this bond bending lead to the small values of the associated elastic constants. These small constants in turn result in compressibilities which are actually negative for certain directions.

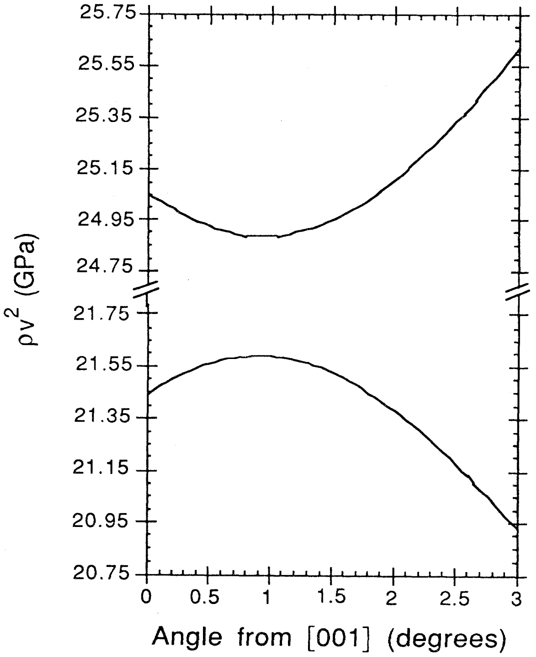

FIG. 2. ρv^2 as a function of angle between the [001] axis and the phonon wave vector q, for angles near 0°. Note the break in the vertical scale. Calculated from Eq. (1) with the values for the elastic constants given in Table I.

The calculation of ρv^2 at angles very close to 0° (i.e., for phonons propagating very near the [001] direction) leads to an interesting "mode repulsion" shown in Fig. 2. As can be seen from Eq. (1) at $\theta=0°$,

$$\rho v^2=\tfrac{1}{2}\{C_{33}+C_{55}\pm[(C_{33}-C_{55})^2+4C_{35}^2]^{1/2}\}\ , \qquad (5)$$

and since $C_{35}\approx 0$ and $C_{33}\approx C_{55}$, the upper and lower branches become nearly degenerate.

For an orthorhombic crystal Eq. (5) would give the ex-

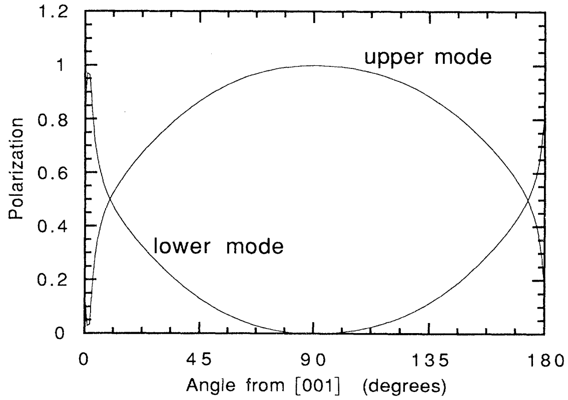

FIG. 3. Polarization of the phonons propagating in the [010] plane as a function of angle between the [001] axis and the phonon wave vector q. Polarization $=1$ represents longitudinal and polarization $=0$ transverse polarization.

trema of the two branches, but for C_{15}, $C_{35}\neq 0$ the closest approach of the two branches occurs at some other angle. In our case since C_{15} and C_{35} are very small this angle is $\theta \approx 1°$. Unfortunately, the angular resolution of our apparatus did not permit us to observe this behavior directly.

An additional remarkable feature of the phonons in the [010] plane of this material is revealed in the polarizations of the two branches of the spectrum. We define the polarization as the square of the scalar product of the displacement vector and the propagation direction so that it is unity for longitudinal and zero for transverse modes. Calculation of the polarizations using the measured values of the elastic constants shows that the two branches exchange their polarizations for phonon propagation near the [001] direction. As can be seen in Fig. 3, near $\theta = 90°$ (the [100] direction) the upper branch is a pure longitudinal mode and the lower branch is purely transverse in character, as expected. In this direction the ratio of the shear wave velocity to that of the compressional wave is 0.49. As θ departs from 90° the polarizations of both branches become mixed, until for θ approximately 10° from the [001] direction the polarizations of the two are at 45° to the propagation direction. At the extrema of the two branches near $\theta = 1°$, the polarizations are almost completely exchanged so that the upper branch is transversely polarized and the lower branch is longitudinally polarized. The ratio of the shear wave velocity to the compressional wave velocity in that direction is 1.07. This is comparable to values in the range 1.02–1.10 measured along the [100] direction in paratellurite[15] (TeO_2), one of the few other cases in which this ratio is larger than unity. In As_2S_3 the slower speed of the compressional wave near [001] compared to that of the shear wave results from the very low value of C_{33} (smaller than C_{55}) arising from the easy bending of the As—Se—As bond angle.

SUMMARY

We have used Brillouin scattering to measure ten of the thirteen independent elastic constants of the layered crystal As_2S_3, and find that the phonon propagation within the layer plane is largely controlled by the orthorhombic symmetry of the layer rather than the monoclinic symmetry of the crystal. The layer itself is highly anisotropic, with the stiffnesses along the two in-plane axes differing by a factor of nearly 5. The smaller of these stiffnesses is less than that along the axis perpendicular to the plane, an unexpected result for a layered crystal. For phonons propagating near the [001] direction the two branches of the velocity show a "mode repulsion" and exchange their polarizations. In this direction the velocity of the shear wave is larger than that of the compressional wave.

ACKNOWLEDGMENTS

We would like to thank B. A. Weinstein and R. Zallen for helpful discussions and for providing the crystal used in this study. One of us (L.E.M.) received support from the Division of Educational Programs of Argonne National Laboratory during the course of this work, which was supported by the U.S. Department of Energy, BES–Materials Sciences under Contract No. W-31-109-ENG-38.

---

[*] Permanent address: Department of Physics and Astronomy, University of North Carolina, Chapel Hill, NC 27599-3255.

[1] See, for example, *Electrons and Phonons in Layered Crystal Structures,* edited by T. J. Wieting and M. Schlüter (Reidel, Dordrecht, 1979).

[2] O. L. Blakslee, D. G. Proctor, E. J. Seldin, G. B. Spence, and T. Weng, J. Appl. Phys. **41**, 3373 (1970); E. J. Seldin and C. W. Neszbada, *ibid.* **41**, 3389 (1970).

[3] K. S. Alexandrov and T. V. Ryzhova, Bull. Acad. Sci. USSR, Geophys. Ser. **12**, 1165 (1961).

[4] T. C. Chiang, J. Dumas, and Y. R. Shen, Solid State Commun. **28**, 173 (1978).

[5] K. Tanaka, in *Fundamental Physics of Amorphous Semiconductors,* edited by F. Yonezawa (Springer-Verlag, New York, 1981), p. 104, and references therein.

[6] P. J. S. Ewen, A. Zakery, A. P. Firth, and A. E. Owen, Philos. Mag. B **57**, 1 (1988).

[7] R. Zallen, M. L. Slade, and A. T. Ward, Phys. Rev. B **3**, 4257 (1971).

[8] For reviews of the measurements performed on As_2S_3, see R. Zallen and D. F. Blossey, in *Optical and Electrical Properties of Compounds with Layered Structures,* edited by P. A. Lee (Reidel, Dordrecht, 1976), p. 231, and D. F. Blossey, Phys. Rev. B **9**, 5183 (1974).

[9] R. Zallen, R. E. Drews, R. L. Emerald, and M. L. Slade, Phys. Rev. Lett. **26**, 1564 (1971).

[10] B. L. Evans and P. A. Young, Proc. R. Soc. London, Ser. A **297**, 230 (1967).

[11] J. M. Besson, J. Cernogora, and R. Zallen, Phys. Rev. B **22**, 3866 (1980); R. Zallen, *ibid.* **9**, 4485 (1974).

[12] O. L. Kukhto, V. I. Mikhailov, R. P. Ozerov, and S. P. Solov'ev, Fiz. Tverd. Tela (Leningrad) **18**, 1707 (1976) [Sov. Phys.—Solid State **18**, 991 (1976)].

[13] N. Wakabayashi and R. M. Nicklow, in *Electrons and Phonons in Layered Crystal Structures* (Ref. 1), p. 409.

[14] *Landolt-Börnstein Numerical Data and Functional Relationships in Science and Technology,* edited by K.-H. Hellwege and A. M. Hellvege, New Series Group III Vol. 11 (Springer-Verlag, Berlin, 1979).

[15] N. Uchida and Y. Ohmachi, J. Appl. Phys. **40**, 4692 (1969); G. Arlt and H. Schweppe, Solid State Commun. **6**, 783 (1968); M. Grimsditch (unpublished).