SHIFT OF [111] PHONON ENERGIES AT THE BRILLOUIN ZONE BOUNDARY UNDER UNIAXIAL STRESS IN GERMANIUM*

R. T. Payne†
Department of Physics and Institute for the Study of Metals, University of Chicago, Chicago, Illinois
(Received 4 June 1964)

An anomalous negative volume coefficient of thermal expansion α has been measured by several experimenters[1-3] in diamondlike materials at low temperatures. Within the limits of the quasiharmonic oscillator model,[4] the anomaly can be described in terms of the temperature dependence of the Grüneisen constant

$$\gamma=\frac{\alpha KV}{C_v}=\sum_{q,b}^{6N}C_b(q)\gamma_b(q)\Big/\sum_{q,b}^{6N}C_b(q) \quad (1)$$

where

$$\gamma_b(q)=-\frac{d\ln E_b(q)}{d\ln V}=K^{-1}\frac{d\ln E_b(q)}{dP} \quad (2)$$

is the volume dependence of phonon energy $E_b(q)$ of the point q in the Brillouin zone (BZ) and the bth branch of the reduced zone. K is the isothermal bulk modulus, C_v the specific heat at constant volume, and V the volume per mole. Since $C_b(q)$ (the heat capacity of the normal mode q, b of the crystal) is a monotonically increasing function of temperature T, the observed minimum in the curve of γ vs T requires some $\gamma_b(q)$ to be negative.[3,5,6] The only values of $\gamma_b(q)$ which have been measured of far are those of the long-wavelength transverse acoustic (TA) and longitudinal acoustic (LA) modes and they cannot explain the minimum in γ. In the case of germanium, γ as obtained from Eq. (1) reaches a minimum value[3] of $\gamma=-0.1$ near $T=20\,^\circ$K whereas all long-wavelength $\gamma_b(q)$ were found to be positive. The long-wavelength $\gamma_b(q)$ in the [111] direction denoted by $\gamma_b(\Gamma\rightarrow L)$ are listed in the seventh column of Table I.[5]

It has been pointed out[5] that some $\gamma_b(q)$ near the BZ boundary can be determined by measuring the hydrostatic-pressure-induced shifts of the threshold of phonon-assisted tunneling in Esaki-type tunnel junctions at low temperatures. Because of the difficulties associated with producing large hydrostatic pressures below 4.2°K, experiments using uniaxial compressional stress were undertaken. By varying the crystallographic orientations of the stress and tunneling directions the effects due to the shear and the volume change can be separated.[7]

This Letter reports the values of the $\gamma_b(L)$ and of the deformation potentials of the TA, LA, longitudinal optic (LO), and transverse optic (TO) phonons in germanium at the point L in the BZ. Table I lists the energies, the stress-induced shifts of the energies, and the $\gamma_b(L)$ of these phonons for stress along [110] and [100]. Table II lists the corresponding deformation potentials.

The samples used were made of germanium bars doped with 5×10^{18} atoms/cm^3 antimony, with the long axis along either the [110] or the [001] direction. Tunnel junctions were fabricated by alloying indium + 0.68% gallium pellets to opposite sides of the bar which were cut parallel to either the $(1\bar{1}0)$, (001), or the (110) plane. Measurements were made on both junctions, to correct for effects introduced by a possible buckling of the bar.

The indirect tunneling threshold voltage is

Table I. The branch assignment b, phonon energy, energy shift per unit stress along the [110] and [001] directions, and the Grüneisen constant $\gamma_b(L)$ at the point L for germanium. Also given are the theoretical $\gamma_b(L)$ of Bienenstock and the acoustic long-wavelength $\gamma_b(\Gamma\rightarrow L)$ along the [111] direction.

Branch b	Phonon energy (mV)	Energy shift per unit stress [110] (10^{-15} V-cm^2-dyne^{-1})	Energy shift per unit stress [001] (10^{-15} V-cm^2-dyne^{-1})	$\gamma_b(L)$ This experiment	$\gamma_b(L)$ Theory	$\gamma_b(\Gamma\rightarrow L)$
TA	7.805 ± 0.006	-6 ± 2	-0.5 ± 0.4	-0.4 ± 0.3	-0.19	0.36
LA	27.49 ± 0.01	-4.5 ± 1.5	6 ± 1	0.5 ± 0.1	1.14	1.27
LO	30.55 ± 0.02	47 ± 4	16 ± 3	1.2 ± 0.2	1.29[a]	
TO	36.04 ± 0.01	20 ± 1	14 ± 2	0.9 ± 0.1	1.29[a]	

[a]This value is considered constant over the whole zone.

Table II. The dilatation and shear-deformation potentials E_1 and E_2, respectively, for the phonons at the point L in the Brillouin zone of germanium.

Branch b	E_1 (meV)	E_2 (meV)
TA	1 ± 0.9	22 ± 8
LA	-14 ± 2	40 ± 10
LO	-37 ± 7	-130 ± 30
TO	-32 ± 5	-25 ± 12

rather difficult to determine from current vs voltage curves. Chynoweth, Logan, and Thomas[8] have shown that by electronically measuring the second derivative in current with respect to voltage, the tunneling threshold appears as a sharp peak when plotted against a dc bias voltage.

In the present experiment the second derivative in current was obtained by measuring the first harmonic in current produced by a small ac voltage (≤300 μV rms) under conditions approaching a constant-voltage source. The fundamental can, through nonlinear electronic circuitry, introduce a first-derivative distortion which is superimposed on the second-derivative signal. The fundamental was bandpass filtered at the signal generator and the first harmonic was bandpass filtered before the first amplifier to reduce the total first-derivative distortion to less than 0.5 % of the maximum second-derivative signal. The second-derivative signal was detected by a phase-sensitive detector and applied to the Y axis of an X-Y recorder. The dc sweeping voltage was detected across each junction, amplified by a high-impedance microvoltmeter, and applied to the X axis. The output of the microvoltmeter was calibrated by placing a standardized voltage from a potentiometer on the input and recording it on the X axis of each recorder graph. A typical recording is shown in Fig. 1.

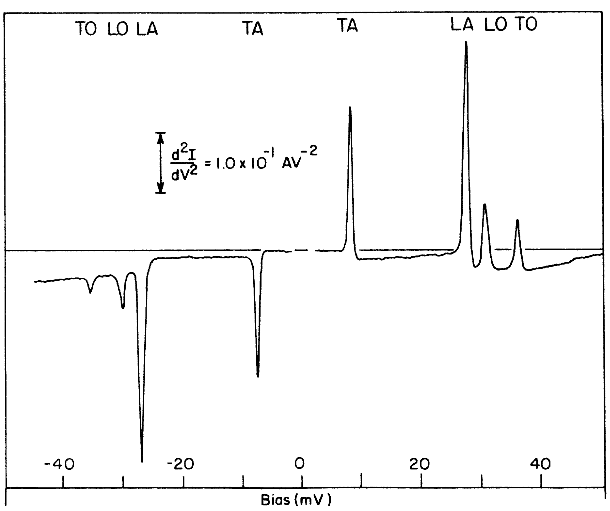

FIG. 1. The second derivative of tunneling current with respect to bias voltage of an Sb-doped germanium p-n junction at 1.22°K with current along the [1$\bar{1}$0] direction. The peaks give the threshold voltages for indirect tunneling current assisted by the phonons indicated in the figure.

Forward and reverse bias peaks (see Fig. 1) were recorded for both opposite face junctions. The process was then repeated under uniaxial compression. From these eight measurements of the peak voltages, the phonon energies and their stress-induced shifts were obtained. The presence of thermoelectric voltages was independently monitored. They did not vary by more that 10 μV during the time of the measurements.

Complete measurements on samples with tunneling current along the [1$\bar{1}$0] and [001] direction and stress along the [110] and [001] direction have been made. Energy shifts were found to be linear in stress. While line shapes are in the process of being analyzed, they show no significant change up to the maximum stress of 8×10^9 dyne-cm^{-2}.

Considerable shear-induced energy shift was observed when stress was applied along the [110] direction (see Fig. 2). However, the shifts in phonon energies were the same for the tunneling directions [1$\bar{1}$0] and [001]. This indicates that the shift in peak voltage is a true phonon-energy shift and not dependent upon effects on the tunneling current caused by the shear-induced shifts of the [111] conduction-band valleys.

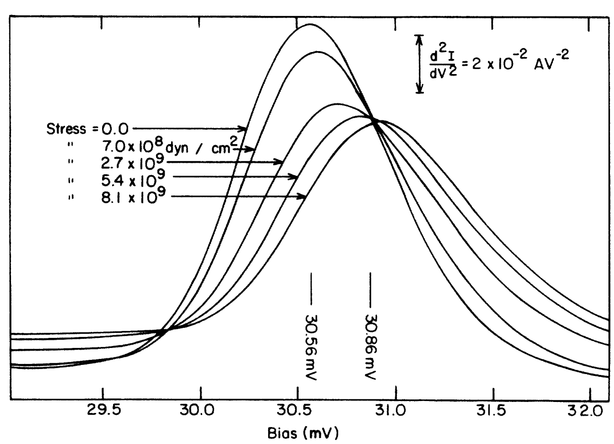

FIG. 2. Detail of Fig. 1 for the LO phonon branch for several [110] compressional stress values.

Since the effect of shear on the phonon energies at the point L in the BZ is zero for stress along [001], the energy shifts measured with stress along this direction are caused by an equivalent hydrostatic pressure $P = X/3$. Hence, using Eq. (2) and a value[9] $K = 1.31 \times 10^{-12}$ cm^2/dyne, the individual phonon Grüneisen constants $\gamma_b(L)$ can be calculated. These are listed in column 4 of Table I.

Bienenstock[6] has carried out a semiempirical calculation of the $\gamma_b(q)$ for germanium using the acoustic $\gamma_b(q)$, a nonrigid shell model with an adjustable parameter, and treating the optic modes in an Einstein approximation where $\gamma_{\rm TO} = \gamma_{\rm LO} = 1.29$ for all the points in the BZ. His results for the $\gamma_b(L)$ are given in column 6 of Table I. With the exception of the $\gamma_{\rm LA}(L)$ the agreement with experiment is as good as can be expected.

By subtracting the pressure-induced shifts as obtained from stress measurements along [001] from the energy shifts measured with stress along [110] one obtains the energy shifts caused by the shear part of the stress tensor alone. Following the notation of deformation potential theory[10] the energy shifts ΔE of the phonons at L for an arbitrary stress can be expressed in terms of the deformation potentials E_1 and E_2 for pure dilatation and pure shear, respectively, as

$$\Delta E^{(i)} = \vec{n}^{(i)} \cdot \{E_1 \mathrm{Tr}(u) I + E_2[u - \tfrac{1}{3}\mathrm{Tr}(u) I]\} \cdot \vec{n}^{(i)}. \quad (3)$$

Here u is the strain tensor and $\vec{n}^{(i)}$ is the unit vector pointing to the ith point L in the BZ. The values of E_1 and E_2 for the four phonons at L are listed in Table II.

While it is still to be shown that the line shapes are adequately understood to relate completely the peak voltage with the phonon energy, it is believed that these effects will only slightly change the magnitude of the stress-induced energy shifts and the phonon energies. If this is the case the presence of a negative $\gamma_{\rm TA}(L)$ is sufficient to explain qualitatively the anomalous temperature dependence of α.

The author is indebted to Dr. J. J. Tiemann for valuable assistance in preparing samples and to Dr. H. Fritzsche who suggested this experiment and has constantly advised and encouraged the author.

---

*This work was supported in part by Air Force Office of Scientific Research Grant No. 148-63, and relied on the facilities of the Low Temperature Laboratory of the Institute for the Study of Metals, supported by the National Science Foundation and the U. S. Atomic Energy Commission.

†An Advanced Research Projects Agency Research Assistant.

[1]D. F. Gibbons, Phys. Rev. 112, 136 (1958).

[2]S. I. Novikova, Fiz. Tverd. Tela 1, 1841 (1959); 2, 43, 1617, 2341 (1960); 3, 178 (1961) [translations: Soviet Phys.—Solid State 1, 1687 (1959); 2, 37, 1464, 2087 (1960); 3, 129 (1961)].

[3]R. D. McCammon and G. K. White, Phys. Rev. Letters 10, 234 (1963).

[4]J. C. Slater, Introduction to Chemical Physics (McGraw-Hill Book Company, Inc., New York, 1939), Chap. XIII, Sec. 4.

[5]W. B. Daniels, Proceedings of the International Conference on Semiconductor Physics (Institute of Physics, London, 1962), p. 482.

[6]A. Bienenstock, to be published.

[7]H. Fritzsche and J. J. Tiemann, Phys. Rev. 130, 617 (1963).

[8]A. G. Chynoweth, R. A. Logan, and D. E. Thomas, Phys. Rev. 125, 877 (1962).

[9]M. E. Fine, J. Appl. Phys. 26, 862 (1955).

[10]H. Brooks, Advances in Electronics and Electron Physics, edited by L. Marton (Academic Press, Inc., New York, 1955).

β DECAY AND THE STRUCTURE OF H^3 AND He^3

R. J. Blin-Stoyle
Physics Laboratory, University of Sussex, Brighton, Sussex, England
(Received 3 June 1964)

Recent measurements[1,2] of the electromagnetic form factors of H^3 and He^3 have directed attention to the detailed forms of the H^3 and He^3 wave functions. In particular, arguments have been presented[3,4] for and against the inclusion of a $^2S_{1/2}$ state (S') of mixed spatial symmetry, in addition to the dominant space-symmetric $^2S_{1/2}$ state (S) and the usual $^4D_{1/2}$ states (D). It is the purpose of this Letter to point out that the β decay of H^3 to He^3 serves as a sensitive test of the presence or otherwise of the state S' and, incidentally, of other states which might be proposed.

A comparison of the ft values for the β decay of H^3 and the neutron gives

$$\frac{(ft)_n}{(ft)_{H^3}} = \frac{G_V^{\,2} + |M_A|^2 G_A^{\,2}}{G_V^{\,2} + 3G_A^{\,2}} \quad (1)$$