

Note added in proof: O. L. Anderson has pointed out to us that the elastic constant measurements of McSkimin¹³ on diamond give an initial compressibility of 2.2×10^{-13} cm²/dyn which gives a value of $B_0 \cong 4400$ kbar. One then can write a quadratic equation of state as follows:

$$\frac{V}{V_0} = 1 - \frac{P}{B_0} + m \left(\frac{P}{B_0} \right)^2 \quad (7)$$

For a wide variety of substances, as Anderson¹⁴ has shown, $m = 2.5-3.0$. At 200 kbar one calculates $a/a_0 = 0.987$ for diamond compared with our measured value

¹³H. J. McSkimin, *Phys. Rev.* **105**, 116-121 (1957).

¹⁴O. L. Anderson (private communication).

0.989. This difference seems to be a little larger than the scatter of the data. A change of 10% in B_0 would bring the calculated result within the scatter. In any case there is no doubt that the compressibility of diamond is not independent of pressure. Within our scatter however a plot a/a_0 vs P is linear over the range 70-270 kbar where we have data.

It should be pointed out that the slight curvature discussed above will not account for the difference between the behavior of a/a_0 for diamond and graphite. It seems necessary to invoke some phenomenon such as puckering and subsequent stiffening of the rings to account for the large change in compressibility with pressure of the a axis in graphite.

Neutron Scattering in Stretch-Oriented Polyethylene*

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Measurements on stretch-oriented polyethylene held at 100°K have been undertaken in an attempt to clearly identify the frequency limit of the calculated stretch-bend acoustic mode. A simplified "constant-Q" scattering technique was used in order to isolate the longitudinal C-C-C motion. A frequency limit was observed at 525 ± 15 cm⁻¹. The persistence of the torsional mode response in the longitudinal experiment is unexpectedly large.

I. INTRODUCTION

ACCORDING to the model of an infinitely extended isolated molecule,^{1,2} the dispersion relation for polyethylene has only two acoustic branches below the lowest optical branch with lower limit at 720 cm⁻¹. These are the carbon skeletal torsion, with calculated frequency limit near 190 cm⁻¹, and the skeletal stretch-bend mode, with calculated limit near 510 cm⁻¹. Recent neutron-scattering measurements³⁻⁶ have been interpreted as demonstrating the existence of these two limits. A prominent scattering peak near 195 cm⁻¹ is clearly observed in all the low-temperature experiments and appears to verify the torsional-mode limit. The limit for the higher mode, however, has been obscure and heretofore not actually verified. The present experiment was particularly designed to reveal this mode limit with certainty.

Measurements of neutron-incoherent-scattering cross sections are usually made without regard to the orienta-

tion in the lattice of the neutron momentum-transfer vector κ . In particular all of the measurements on polyethylene have utilized targets in which the microcrystalline structure was randomly oriented with respect to κ .⁷ The present work extends these measurements to a polyethylene target which has been given a high degree of uniaxial orientation by stretching. Scattered neutrons are observed by a Brockhouse "constant-Q" technique,⁸ applied in this case to incoherent scattering. The method permits discrimination between modes of different phonon polarization so that the response of the longitudinal stretch-bend mode may be enhanced with respect to that from the transverse torsional mode.

II. THEORY

The total differential scattering cross section can be conventionally written as a Fourier time integral⁹:

$$\frac{d^2\sigma}{d\Omega d\epsilon} = \frac{N\sigma_0 k_f}{\pi k_i} \times \left\langle \exp[-Z(0)] \int_{-\infty}^{\infty} \frac{dt}{2\pi\hbar} \exp\left(-\frac{i\epsilon t}{\hbar}\right) \exp[Z(t)] \right\rangle, \quad (1)$$

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¹T. P. Lin and J. L. Koenig, *J. Mol. Spectry.* **9**, 228 (1962).

²M. Tasumi, T. Shimanouchi, and T. Miyazawa, *J. Mol. Spectry.* **9**, 261 (1962).

³H. R. Danner, G. H. Safford, H. Boutin, and M. Berger, *J. Chem. Phys.* **40**, 1417 (1964).

⁴J. S. King and J. L. Donovan, *Bull. Am. Phys. Soc.* **9**, 623 (1964).

⁵H. Boutin, H. Prask, S. F. Trevino, and H. R. Danner, *Inelastic Scattering Neutrons Solids Liquids*, Proc. Symp. 3rd Bombay, India 1964 (to be published).

⁶W. R. Myers, J. L. Donovan, and J. S. King, *J. Chem. Phys.* **42**, 4299 (1965).

⁷Reference 5 contains room-temperature data on stretched polyethylene, collected on a time-of-flight spectrometer. The authors made no reference to orientation.

⁸B. N. Brockhouse, "Methods for Neutron Spectroscopy," At. Energy Can. Ltd., Rept. No. CRNP-947 (1961).

⁹See, for example, A. C. Zemach and R. J. Glauber, *Phys. Rev.* **101**, 118 (1956).

where

$$Z(t) = \sum_{j\alpha\beta} \frac{\hbar^2 \kappa_\alpha \kappa_\beta \gamma_j^\alpha(\mathbf{q}) \gamma_j^\beta(\mathbf{q})}{2NM\hbar\omega_j(\mathbf{q})} \times \left[\frac{\exp[i\omega_j(\mathbf{q})t]}{1 - \exp[-\beta\hbar\omega_j(\mathbf{q})]} + \frac{\exp[-i\omega_j(\mathbf{q})t]}{\exp[\beta\hbar\omega_j(\mathbf{q})] - 1} \right], \quad (2)$$

where N is the number of unit cells in the sample, M is the mass of the scatterer, \mathbf{k}_f and \mathbf{k}_i are the final and initial neutron wave vectors, $\boldsymbol{\kappa} = \mathbf{k}_i - \mathbf{k}_f$, $\epsilon = \hbar^2(k_i^2 - k_f^2)/2m$, m is the neutron mass, $\beta = (k_B T)^{-1}$, $\hbar\omega_j(\mathbf{q})$ and $\boldsymbol{\gamma}_j(\mathbf{q})$ are the energy and hydrogen-atom polarization vector for the phonon of Branch j and Wave Vector \mathbf{q} . Since the scattering cross section of hydrogen is much greater than that of carbon and, in addition, almost completely incoherent, σ_0 is essentially the bound-atom incoherent-scattering cross section for hydrogen and M is the hydrogen (or neutron) mass. The brackets indicate an average over lattice orientation appropriate to a given target, and α, β indicate vector components in an orthonormal coordinate system.

The expression for $Z(t)$ is considerably simplified by transforming the summation on \mathbf{q} to an integration over energy, $\hbar\omega_j(\mathbf{q})$. If $F[\hbar\omega_j(\mathbf{q})]$ is an arbitrary function of the lattice, a function $G_j^{\alpha\beta}(\epsilon)$ is defined by¹⁰:

$$\sum_{j\alpha} \gamma_j^\alpha(\mathbf{q}) \gamma_j^\beta(\mathbf{q}) F[\hbar\omega_j(\mathbf{q})] = \sum_j \int_0^\infty G_j^{\alpha\beta}(\epsilon) F(\epsilon) d\epsilon. \quad (3)$$

In a lattice with cubic symmetry the function $G_j^{\alpha\beta}(\epsilon)$ has a simple interpretation; the only dependence of the cross section on lattice properties is through the phonon frequency spectrum, $g(\omega)$, which is defined to be the fractional number of normal mode frequencies per unit frequency interval at ω . For a cubic lattice with one atom per unit cell, (3) simplifies to:

$$\sum_{j\alpha} \gamma_j^\alpha(\mathbf{q}) \gamma_j^\beta(\mathbf{q}) F[\hbar\omega_j(\mathbf{q})] = \frac{1}{3} \delta_{\alpha\beta} \int_0^\infty g(\epsilon) F(\epsilon) d\epsilon, \quad (4)$$

where $g(\epsilon)$ is the usual phonon frequency distribution. $\sum_j G_j^{ii}$ is an amplitude-weighted directional frequency spectrum.

Equation (2) may now be written:

$$Z(t) = \sum_{j\alpha\beta} \int_0^\infty d\epsilon' \frac{\hbar^2 \kappa_\alpha \kappa_\beta G_j^{\alpha\beta}(\epsilon')}{2Nm\epsilon'} \times \left[\frac{\exp(i\epsilon't/\hbar)}{1 - \exp(-\beta\epsilon')} + \frac{\exp(-i\epsilon't/\hbar)}{\exp(\beta\epsilon') - 1} \right]. \quad (5)$$

The factor $\exp[-Z(0)]$ is the Debye-Waller factor and the argument $Z(0) = 2W$ becomes:

$$2W = \int_0^\infty \frac{\hbar c t g h(\frac{1}{2}\beta\epsilon')}{2Nm\epsilon'} d\epsilon' \sum_{j\alpha\beta} \kappa_\alpha \kappa_\beta G_j^{\alpha\beta}(\epsilon'). \quad (6)$$

The scattering cross section to zero and one-phonon

terms is obtained¹¹ by approximating $\exp[Z(t)] = 1 + Z(t)$, and performing the t and ϵ' integrations:

$$\frac{d^2\sigma}{d\Omega d\epsilon} = \left\langle \frac{N\sigma_0 k_f}{\pi k_i} \exp(-2W) \delta(\epsilon) + \frac{\sigma_0 \hbar^2 k_f}{\pi 2m k_i \epsilon [1 - \exp(-\beta\epsilon)]} \sum_{j\alpha\beta} \kappa_\alpha \kappa_\beta G_j^{\alpha\beta}(\epsilon) \right\rangle. \quad (7)$$

It is known that stretching polyethylene past the elastic limit orients the molecular chains along the direction of stretch, while leaving the other axes randomly oriented about the stretch direction (uniaxial orientation).¹² If the target orientation is controlled so that the stretch direction \mathbf{S} and the neutron momentum-transfer vector $\boldsymbol{\kappa}$ are kept parallel for all ϵ , then

$$\sum_{\alpha\beta} \kappa_\alpha G_j^{\alpha\beta}(\epsilon) \kappa_\beta = \kappa^2 G_j^{11}(\epsilon),$$

where the chain axis has been denoted by $\alpha = 1$. The only contribution to the cross section will be from those phonons that have some component of their polarization vectors along \mathbf{S} . In particular, if all phonons may be described as polarized longitudinally or transversally with respect to \mathbf{S} , one will observe only those that are longitudinal and no orientation average is required. The "longitudinal" cross section is

$$\frac{d^2\sigma_L}{d\Omega d\epsilon} = \frac{\sigma_0 N k_f}{\pi k_i} \exp(-2W_L) \delta(\epsilon) + \frac{\sigma_0 \hbar^2 \kappa^2 k_f}{\pi 2m k_i \epsilon (1 - e^{-\beta\epsilon})} \sum_j G_j^{11}(\epsilon), \quad (8)$$

with

$$2W_L = \int_0^\infty \frac{\hbar \kappa^2}{2Nm\epsilon} c t g h\left(\frac{\beta\epsilon}{2}\right) \sum_j G_j^{11}(\epsilon). \quad (9)$$

Since stretching leaves the other two axes randomly oriented about \mathbf{S} , it is necessary to calculate an orientation average to define the "transverse" cross section. This average has been approximated as follows: the Debye-Waller factor and the polynomial part of the cross section have been averaged separately. The result, then, for $\mathbf{K} \cdot \mathbf{S} = 0$, is

$$\frac{d^2\sigma_T}{d\Omega d\epsilon} = \frac{\sigma_0 N k_f}{\pi k_i} \exp(-2W_T) \delta(\epsilon) + \frac{\sigma_0 \hbar^2 \kappa^2 k_f}{2\pi 2m k_i \epsilon (1 - e^{-\beta\epsilon})} \sum_j [G_j^{22}(\epsilon) + G_j^{33}(\epsilon)], \quad (10)$$

with its appropriate Debye-Waller factor:

$$2W_T = \int_0^\infty \frac{\hbar \kappa^2}{4Nm\epsilon} c t g h\left(\frac{\beta\epsilon}{2}\right) \sum_j [G_j^{22}(\epsilon) + G_j^{33}(\epsilon)]. \quad (11)$$

These cross sections involve only the diagonal elements

¹⁰ G. C. Summerfield, J. Chem. Phys. **43**, 1079 (1965).

¹¹ A. Sjolander, Arkiv Fysik **14**, 315 (1958).

¹² P. H. Geil, Polymer Rev. **5**, 421 (1963).

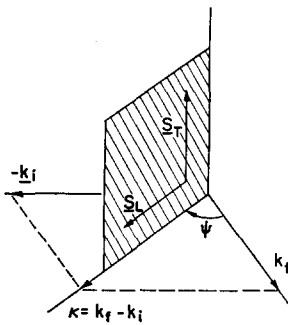


FIG. 1. "Constant- \hat{Q} " target orientation for the longitudinal ($\kappa \cdot \mathbf{S} = \kappa S$) and transverse ($\kappa \cdot \mathbf{S} = 0$) measurements; $\tan \psi = k_i/k_f$.

of $G^{\alpha\beta}$; off-diagonal terms occur only in the expression for an arbitrarily oriented single crystal, or a finite array of such crystals.

Examination of the symmetry coordinates for the two predicted acoustic modes indicates that the torsional and stretch-bend vibrations are almost entirely transverse and longitudinal, respectively. It is then reasonable to expect that the "longitudinal" cross section will be dominated by the stretch-bend mode, ν_s , and the "transverse" cross section by the torsional mode ν_t ; i.e.,

$$G_L(\epsilon) = \sum_j G_j^{11}(\epsilon) \simeq \gamma_s^2(\epsilon) g_s(\epsilon),$$

$$G_T(\epsilon) = \sum_j [G_j^{22}(\epsilon) + G_j^{33}(\epsilon)] \simeq \langle \gamma_t^2(\epsilon) \rangle g_t(\epsilon).$$

III. EXPERIMENTAL RESULTS

The scattering data were obtained on a triple-axis crystal spectrometer¹³ by downscattering neutrons from variable incident energies to a fixed final energy of 0.030 eV. The scattering angle was fixed at 90°. The target material was 86% crystalline Alathon 7511, which was stretched at room temperature to 9.5 times its original length. The target was composed of a 0.017-

in.-thick stack of stretched films having a transmission probability of 87% at 0.044 eV. The target was maintained at 100°K within a thin-walled aluminum cryostat.

The usual application of the Brockhouse "constant- \hat{Q} " technique is to single-crystal coherent scatterers, whose cross sections include delta functions on both the energy-transfer and the momentum-transfer vector. Both the magnitude and the direction of κ (i.e., \hat{Q}) are thereby held fixed so that an energy sweep directly measures a point on the dispersion curve for a particular phonon branch. The present experiment involves an incoherent cross section which is relatively insensitive to the magnitude of κ and sensitive to the direction of κ in the lattice. The method adopted here might be called a "constant- \hat{Q} " technique since only the direction of κ is held fixed. This is accomplished by varying the target orientation to fulfill $\tan \psi = k_i/k_f$ as illustrated in Fig. 1 for 90° scattering angle. The magnitude of k_i and the angle ψ are changed simultaneously during the scan, while k_f and the scattering angle are fixed. The vectors \mathbf{S}_L and \mathbf{S}_T indicate the orientation of the stretch direction for the longitudinal and transverse measurements, respectively.

Both the longitudinal and transverse data were collected using this "constant- \hat{Q} " program, although it is really necessary only for the longitudinal configuration. The method is particularly suitable to the triple-axis crystal spectrometer.

The two cross sections are shown in Fig. 2, normalized to unity at the elastic peaks. The data were corrected for incident-beam-monitor efficiency, for (substantial) calculated second-order response of the analyzing crystals, and for background measured by turning the analyzer crystals 4° out of the Bragg condition. (This procedure does not correct for the possible effect of incoherent scattering from the primary mono-

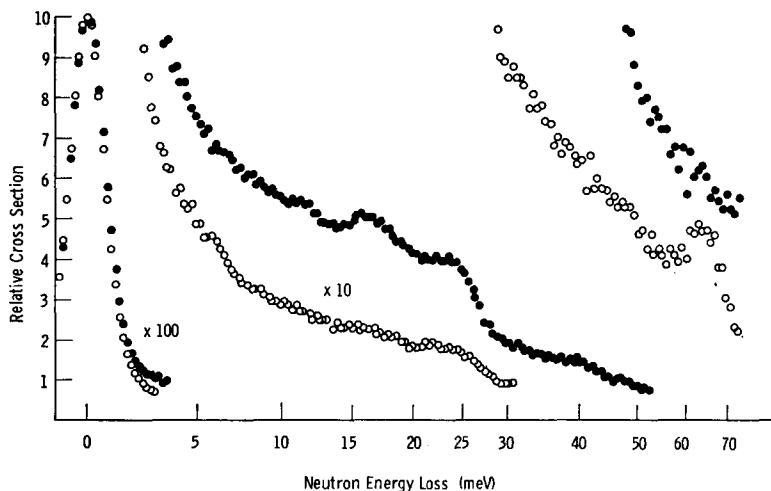


FIG. 2. The longitudinal (○) and transverse (●) polyethylene cross sections, normalized at the elastic peaks. $T=100^\circ\text{K}$, $\varphi=90^\circ$, $E_f=30$ meV.

¹³ The spectrometer has been described by J. L. Donovan, thesis, The University of Michigan, 1964.

chromators, but this is believed to be small.) The counting statistics are 6% in the 0.065-eV region, improving to better than 2% in the region below 0.030 eV. The unnormalized absolute cross sections in the elastic region are compared in Fig. 3, and show the longitudinal cross section to be 24% higher than that for the transverse. This is a reflection of the change in the Debye-Waller factor as a consequence of suppressing the lower-frequency transverse mode in the longitudinal configuration. No attempt has yet been made to calculate the two Debye-Waller factors from this data because it is difficult to accurately extract the inelastic component from beneath the elastic peak.

The cross-section data are converted, in Fig. 4, to the "frequency-distribution" functions, G_L and G_T , according to Eqs. (8) and (10). For clarity in comparison, the Debye-Waller factors for both have been set to unity and the two distributions normalized to unity at the peak near 0.025 eV. The actual longitudinal amplitude is 56% of that shown.

The longitudinal data in Figs. 2 and 4 clearly show a peak near 0.065 eV which is not present in the transverse data. This event occurs in the region calculated for the higher acoustic mode¹⁴ and has the correct

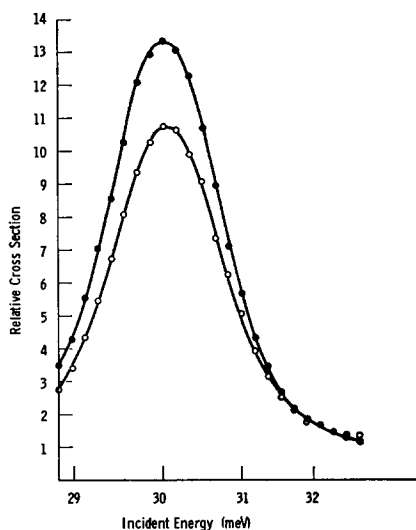


FIG. 3. The longitudinal and transverse elastic cross sections for stretched polyethylene (Alathon 7511). $T=100^\circ\text{K}$, $\varphi=90^\circ$, $E_f=30$ meV. ●, $\kappa \cdot \mathbf{S} = \kappa \cdot \mathbf{S}$; ○, $\kappa \cdot \mathbf{S} = 0$.

¹⁴ Calculated limits are 530 cm^{-1} (1), 505 cm^{-1} (2), and 540 cm^{-1} (private communication from C. Opaskar and S. Krimm, calculation based on the Schachtschneider and Snyder force constants).

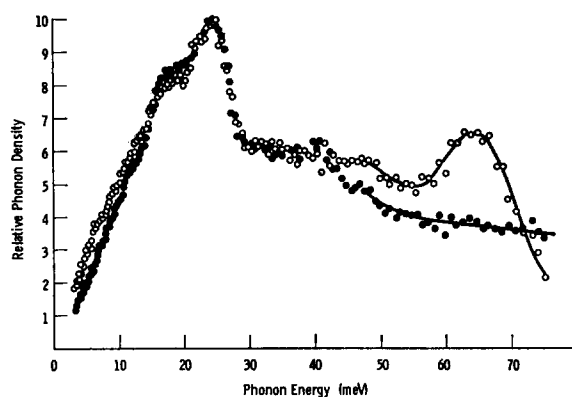


FIG. 4. The functions $G^{11}(\epsilon)$ and $[G^{22}(\epsilon) + G^{33}(\epsilon)]$ for stretched polyethylene, normalized at the 25-meV peaks. $T=100^\circ\text{K}$, $E_f=30$ meV. ○, longitudinal; ●, transverse.

polarization. It is therefore identified with the frequency limit for the stretch-bend acoustic mode; the best frequency assignment is 525 ± 15 cm^{-1} . The measurements were repeated with a fixed final energy of 0.034 eV and the results are not significantly different.

In addition to the peak at 525 cm^{-1} , the longitudinal data show that while the torsional (transverse) peak at 195 cm^{-1} has been substantially reduced it is still strongly present. This is not the result of poor vector resolution since the measurement was repeated with finer angular resolution in \mathbf{k}_f (and hence in κ) with no significant change. It must be concluded that either orientation by stretching is not sufficiently complete to eliminate all transverse effects, or the vibrational mode peaking at 195 cm^{-1} has a significant longitudinal component.¹⁵

There are other less prominent but consistent differences in the two configurations. The change in the amplitude of the subsidiary peaks⁶ near 150 cm^{-1} relative to the 195- cm^{-1} limit is particularly noted. A calculation based on a realistic three-dimensional lattice should provide an explanation for these differences.

ACKNOWLEDGMENTS

The authors wish to thank Professor John M. Carpenter for a number of valuable discussions, and to acknowledge the helpfulness of the FNR reactor operating staff.

¹⁵ A recent calculation for a polyethylene crystal indicates that ν_5 and ν_9 are mixtures of the skeletal deformation and torsional modes; M. Tasumi and T. Shimanouchi, *J. Chem. Phys.* **43**, 1245 (1965).