

The Elastic Properties of $C_{36}H_{74}$ Single Crystals from Brillouin-Spectroscopy

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SUMMARY

The elastic properties of $C_{36}H_{74}$ single crystals have been investigated at room temperature by Brillouinspectroscopy. A nearly complete set of data is presented for the crystallographic (a,b)-plane. Furthermore the longitudinal sound velocity normal to that plane could be determined.

1. EXPERIMENTAL

The Hexatriacontane $C_{36}H_{74}$ with a nominal purity of 97% was supplied by Humphrey, North Haven, Connecticut. The DSC-run of the as-received material shows three transitions at about 70°C, 72°C and 75°C corresponding to first order transitions (Broadhurst). The crystals investigated were grown from 0.15% solutions in petroleum ether by slowly evaporating the solvent at room temperature. A few platelet crystals were selected with respect to their perfect optical behaviour controlled by a polarization microscope.

Three different crystals, in the following designated as I, II and III where investigated by Brillouinspectroscopy. Crystal I and II had a rhombic habit of about 1 mm edge length and an acute angle of 73°. The thickness was estimated for both crystals to be about 20 μm. The extinction between crossed polarizers was checked as well as the relative magnitude of the refractive indices in the two directions being coincident with the diagonals of the crystals. By adding a λ -retardation plate the constancy of thickness was proved. From these crystals Weissenberg diagrams were obtained with $CoK\alpha$ -radiation in the zeroth and first zone for both diagonals as rotation axes.

The crystals turned out to be monoclinic with the same unit cell as given by SHEARER and VAND (1956) (space group $P2_1/a$). The short diagonal is the a-axis (5.5 Å), the long diagonal is the b-axis (7.42 Å). The b-axis is the diad axis. The chains are inclined to the a-axis by 63° but they are orthogonal to the b-axis. The data are consistent with the greater refractive index along the a-axis and with the habitus. (110)-growing faces should result in an acute angle of 73.4°. Polytypic overgrowth (BOISTELLE) was estimated from relative intensities to be less than 10% of the volume

for crystals I and II. The platelet surfaces correspond to the crystallographic (a,b)-plane.

Unfortunately crystal III could not be characterized by X-ray investigations because after termination of the Brillouin experiments the crystal was destroyed on removing it from the supporting glass slides. Crystal III had not the typical rhombic habit but showed also perfect optical properties. The crystal thickness was also about 20 μ m.

The spectrometer system as described elsewhere (Krüger, 1978) was modified by an automated data acquisition and stabilisation system DAS-1 from Burleigh Instruments and by a five pass Fabry-Pérot. Overloading of the photomultiplier tube by strong elastic scattering was eliminated by amplitude modulation of the laser light using a Pockels cell tandem. Both Pockels cells were driven by logical signals from the segmented timebase of the DAS-1 system resulting in a perfect synchronisation between the Pockels cells and the data acquisition system.

For the Brillouin investigations crystal I was mounted without further preparation on a goniometer. Crystals II and III were held with some immersion liquid between glass slides which were then also mounted on goniometers. The index matching with the glass slides and the immersion liquid avoids the backscattering from phonons with wave vectors \vec{q}_I and \vec{q}_{III} (fig. 1) but creates additional spectral components due to the glass slides and the immersion liquid.

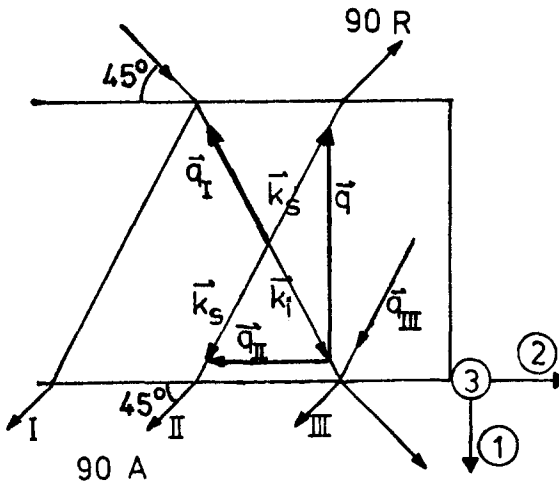


Fig.1: Scattering geometries used: ①, ②, ③ coordinates of the laboratory frame; \vec{k}_i , \vec{k}_s wave vector of incident and scattered light, \vec{q} , \vec{q}_I, II, III phonon wave vectors

All measurements were performed with an outer scattering angle of $\theta_a=90^\circ$. The crystal plates were aligned either in the 90A or in the 90R (fig.1) position (Krüger 1978, Unruh) within the outer scattering arrangement. The crystals could be rotated around the axis ① of the laboratory frame. The ②, ③)-plane corresponds to the crystallographic (a,b)-plane. The pure 90A scattering geometry is only realized (Krüger 1978, 1980) if the refractive indices for the incident laser light and the scattered light are the same. Because $C_{36}H_{74}$ is monoclinic, this condition is fulfilled only if the polarizations of the incident and the scattered light are parallel to the diad b-axis. However, as is seen from fig. 2 the phonon frequencies depend only slightly on the polarization when the 90A sample arrangement is used. The differences of the related refractive indices seem therefore to be insignificant. It is worth noting that in the pure 90A scattering geometry the phonon wave vector $\vec{q}_{||}$ (fig.1) lies in the crystallographic (a,b)-plane.

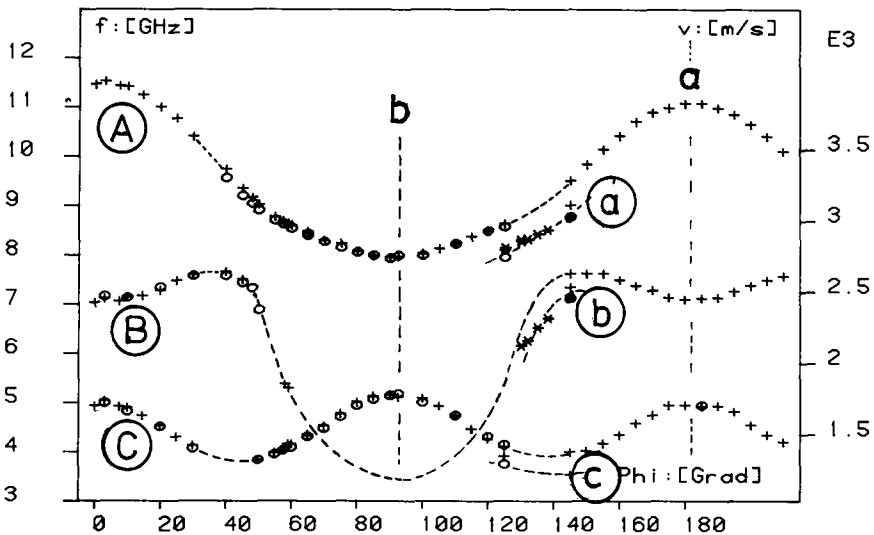


Fig.2: Sound frequency f and sound velocity v of crystal II versus the arbitrary rotation angle ϕ

- ① = rotation axis (s.fig.1), \vec{q} in (a,b)-plane.
- Ⓐ, ⓐ correspond to quasilongitudinal phonons
- Ⓑ, ⓑ, Ⓒ, Ⓒ correspond to quasitransverse phonons.
- Ⓐ, Ⓑ, Ⓒ = 488 nm, ⓐ, ⓑ, Ⓒ = 514.5 nm.
- a,b correspond to crystallographic axes.
- + VV, o VH, * HH scattering.

If the sample is surrounded by air, in the 90A geometry the sound frequency f_A and the sound velocity v are related by the equation

$$(1) \quad v = f_A \cdot \lambda_1 \cdot 2^{-0.5} ; \quad \lambda_1 \text{ laser wavelength in vacuum}$$

The 90R scattering geometry was used to determine the sound velocity orthogonal to the crystallographic (a,b)-plane. The polarization of the incident and the scattered light was chosen to be parallel to the b-axis. In this case the following relation between the measured sound frequency f_R and the sound velocity v holds:

$$(2) \quad v = f_R \lambda_1 \{ 2n_b \sin(\theta_i/2) \}^{-1}$$

n_b refractive index along the b-axis
 θ_i inner scattering angle

with

$$(3) \quad \theta_i/2 = \arccos \{ n_b^{-1} 2^{-0.5} \}$$

The refractive indices of paraffins are only known for the orthorhombic modification (Bunn, 1954): $n_a = 1.519$; $n_b = 1.514$; $n_c = 1.575 \pm 0.002$. To calculate θ_i we used an average value of $n_b = 1.5165$.

All Brillouin measurements were performed at $23 \pm 2^\circ\text{C}$. The accuracy of the measured phonon frequencies is about $\pm 1\%$. The sound velocities are estimated to be correct within 2% taking the uncertainty of the \vec{q} orientation into account because of the birefringence.

2. RESULTS AND DISCUSSION

The elastic properties of the monoclinic modification of paraffins have not yet been studied. For the orthorhombic modification only a few indirect measurements are available (e.g. Weir, Ito, Strobl). It seems that Brillouin spectroscopy is the only suitable method to study the complete elastic behaviour of single crystals with dimensions of about $1 \times 1 \times 2 \cdot 10^{-2} \text{mm}^3$.

In fig. 2 the sound frequency and sound velocity are shown for the crystal II versus the rotation angle around the $\textcircled{1}$ -axis. In this case the phonon wave vector is rotated in the crystallographic (a,b)-plane. The curves \textcircled{A} and \textcircled{a} in this figure correspond to a quasilongitudinal phonon and the curves \textcircled{B} , \textcircled{b} , \textcircled{C} and \textcircled{c} to quasitransverse phonons (capital letters refer to the laser wavelength of 488 nm and small letters refer to the laser wavelength of 514.5 nm). The sound frequencies at 514.5 nm are about 5% lower than those at 488 nm, which is expected. The sound velocity scale refers only to the VV polarization situation. The sound frequency

curve (B) could only be observed in a restricted angle region around the a-axis. This results from an extremely weak elastooptical coupling of the corresponding quasitransverse phonons to the light for \vec{q} near the b-axis.

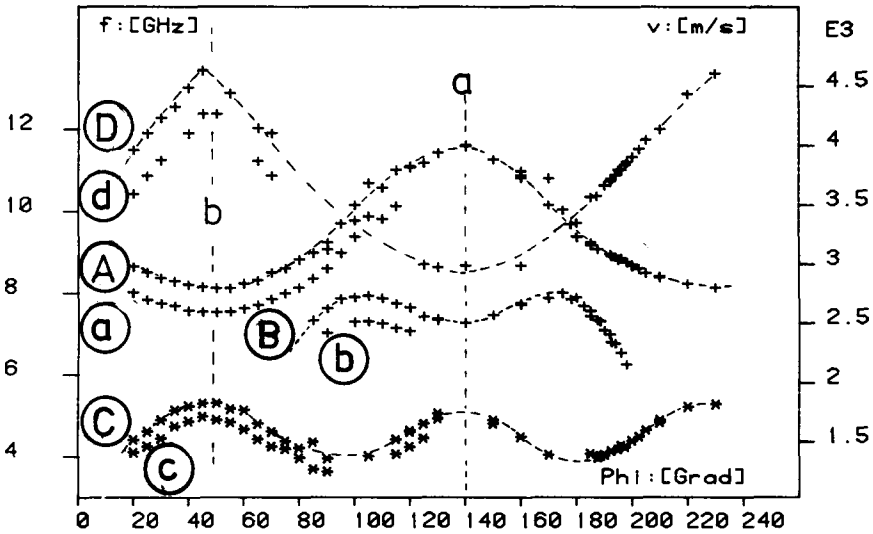


Fig.3: Sound frequency f and sound velocity v of crystal I versus the arbitrary rotation angle ϕ (s. also fig. 2). \vec{q} in (a,b)-plane. (A), (B), (C), (D) = 476.5 nm. (a), (b), (c), (d) = 514.5 nm. (D), (d) refer to wave vectors \vec{q}_I or \vec{q}_{III} (s. fig. 1).

As expected we found for crystal I (fig. 3) nearly the same elastic behaviour as for crystal II. For these measurements no polarization filter was used in the scattered light beam. The measurements were performed at 476.5 nm and 514.5 nm. In addition to a quasilongitudinal (A), (a) and two quasitransverse phonons (B), (b), (C), (c); referring to \vec{q}_{II} , s. fig. 1) a further phonon (D), (d) is observed in crystal I. Because no index matching was used for this crystal, a phonon of type \vec{q}_I or \vec{q}_{III} (s. fig. 1) might contribute to the spectra. Because \vec{q}_I and \vec{q}_{III} are in general not equivalent one should expect two different phonons from the backscattering. Since we observed only one additional phonon one may conclude that the deviation from an orthorhombic elastic behaviour is small.

Fig. 4 shows the hypersonic behaviour of crystal I in a polar plot. Fig. 5 shows a similar plot for the less perfect crystal III. Only the quasilongitudinal phonon could be observed here. We believe that this crystal was strongly polytypic resulting in a less pronounced elastic anisotropy in the (a,b)-plane.

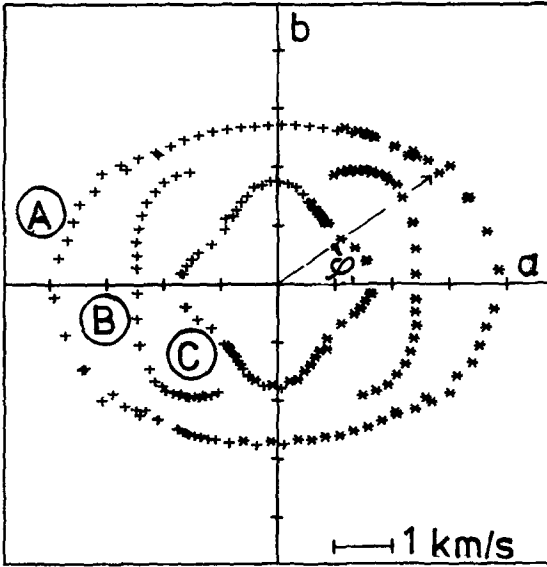


Fig. 4: Polar plot of the sound velocity of crystal I. + measured, * calculated.

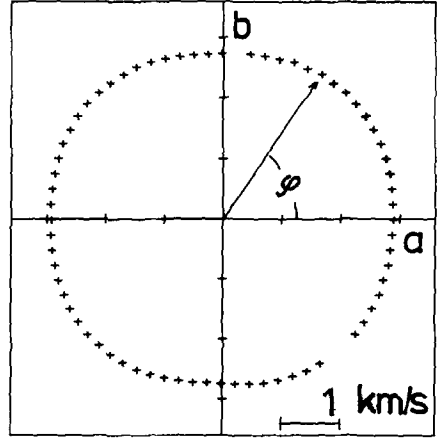


Fig. 5: Polar plot of the sound velocity of crystal III.

From the hypersonic data of crystal I and II we have tried to calculate most of the components of the elastic tensor. Using the Christoffel equation (Auld) one gets the following equation for the calculation of the eigenvalues E:

$$(4) \quad \det \begin{pmatrix} \underbrace{(c_{11} l_x^2 + c_{66} l_y^2)}_{\alpha} - E & \underbrace{(c_{12} + c_{66}) l_x l_y}_{\delta} & \underbrace{(c_{15} l_x^2 + c_{46} l_y^2)}_{\epsilon} \\ \delta & \underbrace{(c_{66} l_x^2 + c_{22} l_y^2)}_{\beta} - E & \underbrace{(c_{25} + c_{46}) l_x l_y}_{\zeta} \\ \epsilon & \zeta & \underbrace{(c_{55} l_x^2 + c_{44} l_y^2)}_{\gamma} - E \end{pmatrix} = 0$$

with $l_x = q_x/q$ and $l_y = q_y/q$ (l_x, l_y direction cosines).

This leads to a third order equation for the eigenvalues E:

$$(5) \quad (\alpha - E)(\beta - E)(\gamma - E) - \delta^2(\gamma - E) - \zeta^2(\alpha - E) - \epsilon^2(\beta - E) + 2\epsilon\delta\zeta = 0$$

Third order equations can be solved analytically, but the solution is difficult to handle. Some of the elastic constants could be determined directly, all other elastic constants contained in eq. 4 have been determined numerically after solving eq. 5 for seven experimentally given eigenvalues. These eigenvalues were chosen from fig. 2 and 3 for \vec{q} vectors rotated by angles of $0^\circ, 45^\circ, 55^\circ$ and 90° from the a-axis.

From eq.(4) one gets for $\vec{q} \parallel a$ and $\vec{q} \parallel b$:

(6a)	$\vec{q} \parallel b$	(A)	L	$E_1 = c_{22}$
(6b)		(B)	T	$E_2 = 1/2(c_{44} + c_{66}) + (1/4(c_{44} - c_{66})^2 + c_{46}^2)^{0.5}$
(6c)		(C)	T	$E_3 = 1/2(c_{44} + c_{66}) - (1/4(c_{44} - c_{66})^2 + c_{46}^2)^{0.5}$
(7a)	$\vec{q} \parallel a$	(C)	T	$E_1 = c_{66}$
(7b)		(A)	QL	$E_2 = 1/2(c_{11} + c_{55}) + (1/4(c_{11} - c_{55})^2 + c_{15}^2)^{0.5}$
(7c)		(B)	QT	$E_3 = 1/2(c_{11} + c_{55}) - (1/4(c_{11} - c_{55})^2 + c_{15}^2)^{0.5}$

L and T designate longitudinal and transverse polarized phonons, QL and QT stand for quasilongitudinal and quasitransverse respectively. c_{22} can be directly deduced from curve (A) of figures 2,3 or 4 at the b-axis because it is reasonable to get larger elastic constants for the QL-phonons than for the QT-phonons. This seems to be in agreement with the larger scattering cross section for "phonon lines" of type (A). Using this fact we get $c_{22} = (7.5 \pm 0.6)$ GPa. At this point it is not clear whether c_{66} should be calculated from curve (C) ($\vec{q} \parallel a$ -axis) as indicated by eq. 7a or from curve (B) ($\vec{q} \parallel a$ -axis) which leads to $c_{66} = 3$ GPa or $c_{66} = 6$ GPa, respectively. From eq.(6b) one gets the condition

$$(8) \quad \frac{E^2 - E c_{66} - c_{46}^2}{E - c_{66}} = c_{44} > 0$$

$c_{66} = 6$ GPa would result in an eigenvalue $E [\vec{q} \parallel b, (B)] \gg 6$ GPa which would not agree with the tendency of curve (B) around the b-axis.

Using $c_{66} = 3$ GPa (curve (C), $\vec{q} \parallel a$) one gets the following conditions: $c_{46} < 0.8$ GPa, $0 < c_{44} \leq 3.2$ GPa and $E_3 [(C), \vec{q} \parallel b] \leq 3$ GPa. $E_3 \leq 3$ GPa gives the correct tendency of curve (B) near the b-axis and therefore $c_{66} = (3 \pm 0.3)$ GPa is the correct value. The elastic constants $c_{11} = (15.6 \pm 1.5)$, $c_{44} = (1.6 \pm 0.8)$, $c_{55} = (6.4 \pm 1.2)$, $c_{15} = (4 \pm 1.4)$, $c_{25} = (0.9 \pm 0.9)$, $c_{12} = (-2 \pm 0.9)$, and $c_{46} = (0.6 \pm 0.5)$ GPa were calculated numerically by solving eq.5 for seven different eigenvalues. c_{44} and c_{46} satisfy the above mentioned conditions. Along the a-axis the eigenvalues are $E_2 = 15.5$ GPa and $E_3 = 6$ GPa. From eq. 7b,c the conditions $(E_2 + E_3) = (c_{11} + c_{55})$ and $(E_2 - E_3)^2 = (c_{11} - c_{55})^2 + 4c_{46}^2$ are obtained. Within the margin of error both conditions are fulfilled. We have also recalculated eigenvalues for different \vec{q} vectors, starting with the above given tensor components. Within the margin of errors the calculated eigenvalues agreed with the measured ones.

A further condition for the correctness of the above elastic constants requires that all principal minors of the elastic tensor must be positive. This is true too.

The elastic constant of the quasilongitudinal phonon for \vec{q}_{\parallel} (a,b)-plane was also measured (90R scattering geometry): $E = 15.4$ GPa. This value deviates only slightly from that of the orthorhombic phase (\vec{q}_{\parallel} chain direction) extrapolated to 23°C: $c_{33} \sim 15$ GPa (Krüger, 1980b). One may therefore conclude that the elastic stiffness orthogonal to the (a,b)-plane is largely determined by the interlayer forces of the $C_{36}H_{74}$ single crystals. From the Christoffel equation with $l_x = l_y = 0$ together with c_{55} and c_{33} the value for c_{35} can also be estimated: $c_{35} = (1.9 \pm 1)$ GPa. The elastic constants c_{13} and c_{23} are still lacking. Further investigations are underway.

The obtained elastic stiffness tensor has then the following form:

$$\begin{bmatrix} 15.6 & -2 & x & 0 & 4 & 0 \\ -2 & 7.5 & x & 0 & 0.9 & 0 \\ & & 15 & 0 & 1.9 & 0 \\ & & & 1.6 & 0 & 0.6 \\ & & & & 6.4 & 0 \\ & & & & & 3 \end{bmatrix}$$

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