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The thermal conductivity of polymer and monomer diacetylene single crystals

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Abstract. The thermal conductivity of a diacetylene monomer has been measured over the temperature range 2.8–25 K. The data are found to have a temperature dependence and magnitude very close to those previously obtained for the polymer form of the diacetylene. It is shown that the data support the model of acoustic phonon scattering by low energy optical modes associated with the side groups. The optical mode energies have been determined by far-infrared spectroscopy and it is shown that by using these values to model the data a good fit is obtained with each mode having an acoustic-optical phonon coupling of 6.3 meV.

1. Introduction

The symmetrically substituted diacetylenes 1,6-di(N-carbazolyl)-2,4 hexadiyne (DCH) and 2,4 hexadiyne-1,6-diol-bis(p-toulene sulphonate) (pts) are among the very few polymerisable organics to form macroscopic single crystals. Studies of the structure of these crystals, by x-ray topography and electron beam microscopy, have shown them to be of high perfection (Young 1985). On polymerisation, covalently bonded chains are formed that extend through the crystal in a parallel array. These chains have a conjugated structure $\text{--[RC}\equiv\text{C-C}\equiv\text{CR]--}_n$ where R is the side group. The interchain bonding is of van der Waals character and so the elastic properties of these crystals are highly anisotropic (Rehwald *et al* 1983). As a result of this anisotropy the low temperature thermal transport of these materials is of considerable interest.

We have previously reported measurements of the thermal conductivity of pts parallel and perpendicular to the polymer chains and of DCH parallel to the chains (Wybourne *et al* 1985a, b). The most significant feature of the data was a very weak temperature dependence of the conductivity over the temperature range 1–30 K. This was surprising since, at least for pts, the measured specific heat (Engeln and Meissner 1980) has a cubic temperature dependence up to 10 K and so for such perfect crystals the temperature dependence of the thermal conductivity would also be expected to be cubic up to ≈ 10 K. It was also found that for heat currents parallel and perpendicular to the pts backbone, the anisotropy of the thermal conductivity itself showed a temperature dependence: above ≈ 1 K the ratio was 1.5 which increased by a factor of 2 below 1 K. The behaviour below 1 K appears to have its origin in phonon scattering from macroscopic planar defects which are preferentially oriented parallel to the chains

(Rehwald *et al* 1983). Above 1 K, the very weak temperature dependence of the thermal conductivity and the reduced anisotropy have been modelled using a linear Raman phonon scattering process in which the heat carrying acoustic phonons have a frequency dependent mean free path (MFP) determined by the scattering from low energy optical modes. Using far-infrared spectroscopy and neutron scattering techniques, these optical modes have been identified as the modes of vibration associated with the massive side groups of these materials. The optical mode energies thus determined have been used in the resonance term of the Raman process to obtain a quantitative fit to the pts polymer data (Wybourne *et al* 1985a).

Far-infrared spectroscopy of pts has shown that the low energy optical modes do not differ significantly between the monomer and polymer form of the diacetylene (Bloor and Kennedy 1980). Thus, we expect that above 1 K the MFP of the acoustic phonons will not suffer any substantial change as a result of the polymerisation process; hence, the thermal conductivity of the monomer form of these materials should be similar, both qualitatively, and quantitatively, to that of the polymer form. This prediction therefore provides a stringent test of the acoustic-optical phonon scattering model.

Recently, Morelli *et al* (1986) reported thermal conductivity measurements of pts monomer and polymer. Their polymer data were qualitatively similar to the previously reported work by Wybourne *et al* (1985a) and we have suggested possible reasons for the quantitative discrepancies (Wybourne *et al* 1987). Unlike the polymer data, their reported data for the monomer had a broad peak at ≈ 10 K. In comparing the polymer and monomer data, Morelli *et al* modelled their results in terms of a reduced Umklapp scattering rate in the polymer due to the increased anisotropy of the Brillouin zone upon polymerisation. We do not feel that these data provide a conclusive determination of the phonon scattering in diacetylene crystals having a low defect density. Mass spectroscopy has demonstrated that upon cleaving, pts monomer and polymer crystals give off acetone and oxygen (Poole and Batchelder 1984). The ease with which pts cleaves suggests that the acetone and oxygen are incorporated into planar defects. This would explain both the magnitude of the thermal conductivity of pts crystals in the boundary scattering limit and the difficulty experienced by Rehwald *et al* (1983) in propagating sound perpendicular to the chains. In contrast to pts, DCH crystals are much more difficult to cleave and there is no evidence of solvent inclusion.

In this communication we present the first thermal conductivity measurements for the monomer DCH crystal parallel to the diacetylene stacking direction and compare them with previous data for the polymer. We show that the thermal conductivities of the two forms have a similar temperature dependence and magnitude, consistent with the acoustic-optical phonon scattering process. In addition, far-infrared data for the polymer DCH are presented and from the optical frequencies observed we have been able to obtain a quantitative fit to the thermal conductivity data.

2. Experimental details

The monomer DCH samples used for these studies were prepared by the method of Kennedy *et al* (1980) based on the original preparation of Yee and Chance (1978). The crystals were needle-like in shape, about 15 mm long and 0.5 mm^2 in cross section, with the largest dimension being the stacking direction of the diacetylene units. The crystals were of translucent blue appearance indicating a low polymer content ($\approx 1\%$).

Thermal conductivity measurements on these samples were performed over the temperature range 2.8–25 K using a steady state potentiometric apparatus with Allen–

Bradley carbon resistance thermometers, configured to measure the conductivity in the stacking direction.

The samples were thermally attached to a variable temperature heat sink using silver paint. Small, stress-free thermometer contacts, fabricated from 25 μm copper foil, were attached to the sample also with silver paint. The delicate nature of the samples together with the fact that the DCH monomer undergoes a first-order phase transition at 142 K, in which the crystal volume changes by $\approx 5\%$, necessitated the use of strain-free linkage between the copper thermometer contacts and the Allen–Bradley resistors. For this purpose we used 20 μm thick aluminium foil in the form of a concertina. This, combined with a cooling rate from room temperature of less than 0.3 K min^{-1} , ensured a high probability of sample survival. Three samples remained intact during the cooling cycle, but on warming two of these fractured. The data we present below are taken from the sample that survived a complete temperature cycle. The results for the other samples were the same to within experimental uncertainty.

A heater was attached to the end of the sample in a similar manner to the thermometers. To avoid non-linear effects the temperature gradient established between the heater and heat sink was kept below $10^{-3} T \text{ mm}^{-1}$. The absolute temperature was measured with a 27 Ω Rh–Fe thermometer and the absolute accuracy of the above arrangement is $\approx 10\%$.

Far-infrared absorption measurements were carried out on a DCH single crystal which was in the form of a crude rectangular slab with dimensions $10 \times 2 \times 0.3 \text{ mm}^3$. The spectral transmission was measured using a Martin–Puplett polarising Fourier transform spectrometer with a composite bolometric detector operated at 1.5 K. The suitably masked crystal was placed in front of the detector and maintained at the same temperature; the responsivity of the detector was determined using an appropriate reference aperture. The spectra were measured at sufficiently low resolution to remove the ambiguity caused by interference fringes. Since the crystal was illuminated by polarised radiation, measurements were made for both orthogonal planes by rotating the polarising analyser in the spectrometer. No polarisation effects were seen at low frequencies. As a check on the repeatability and noise levels, single spectra were compared with averaged spectra and found to be virtually identical.

3. Results and discussion

The thermal conductivity for the DCH monomer parallel to the diacetylene unit stacking direction is shown in figure 1. For comparison, we also show in this figure the polymer data. It is seen that the monomer conductivity has only a weak temperature dependence over the temperature range investigated and is almost independent of temperature above 10 K. Moreover, the polymer and monomer data are the same to within the accuracies of the experiment above 8 K. Thus, even on first inspection, the monomer data appear to support the acoustic–optical phonon scattering model of Wybourne *et al* (1984).

A more complete analysis of the DCH data involves quantitative fitting using the usual expression for the thermal conductivity,

$$K = \frac{k_B}{2\pi^2 v} \left(\frac{k_B}{\hbar} \right)^3 T^3 \int_0^{\theta_D/T} \frac{\tau(x) x^4 e^x}{(e^x - 1)^2} dx \quad (1)$$

where $x = \hbar\omega/k_B T$ and $\tau(x)$ is the scattering time appropriate to the given model. A

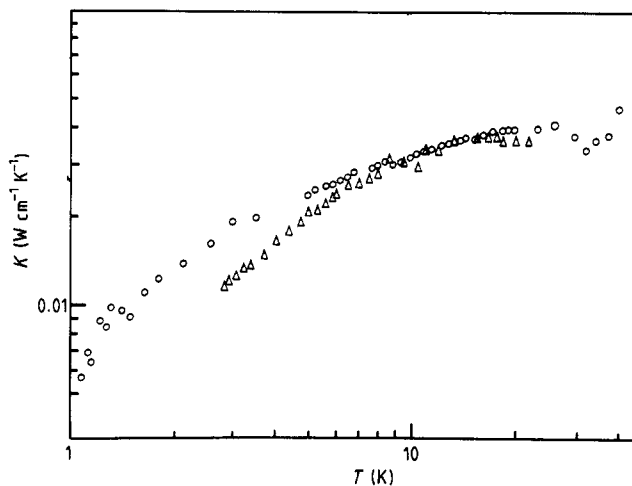


Figure 1. The thermal conductivity of the DCH monomer (Δ) in the diacetylene unit stacking direction compared with DCH polymer data (\circ).

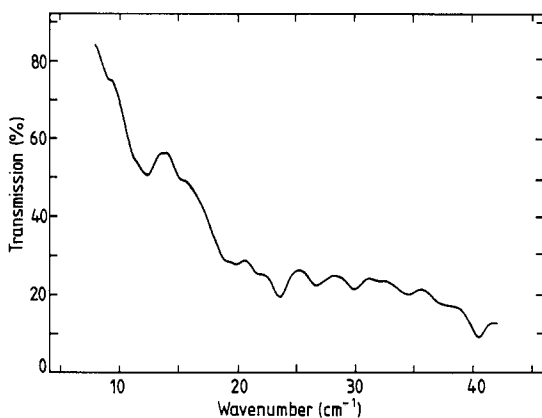


Figure 2. Far-infrared spectra of DCH polymer from which we have identified 14 resonances at 9, 11, 12, 15, 19, 20, 22, 23, 27, 30, 32, 34.5, 37, and 40.5 cm^{-1} .

detailed fit requires knowledge of many parameters, several of which have not been measured for DCH, in particular the average sound velocity, \bar{v} , and the optical mode energies. We have determined the optical mode energies from the far-infrared absorption spectrum of DCH polymer, shown in figure 2. The reproducibility of the data lay within the thickness of the line in the figure. Most of the transmission loss was due to the high refractive index of the crystal in this spectral region but numerous absorption peaks can be clearly seen. The increase in transmission below 20 cm^{-1} is attributed to the wavelength of the radiation becoming comparable to the thickness of the crystal. Similar measurements were made for monomer crystals but these were found to be almost completely transparent. As the number and frequencies of the low frequency vibrations were found to be very similar for monomer and polymer pts (Bloor and Kennedy 1980),

this was a surprising result. We assume that the increased conjugation resulting from the formation of the polymer backbone has greatly increased the infrared activity of the low frequency vibrations. The DCH monomer itself, unlike pTS, has no permanent dipole moments in any of its constituent chemical groups.

From the infrared spectrum we have identified 14 optical modes (figure 2) which lie within the acoustic phonon energy range of these experiments. Therefore, we assume these optical modes are able to couple to, and so scatter, the acoustic modes.

In order to obtain a quantitative fit to the data it is necessary to estimate the average sound velocity in the DCH polymer. From Brillouin scattering measurements (Enkelmann *et al* 1980) the longitudinal velocities both parallel and perpendicular to the stacking direction are known in DCH. However, the transverse velocities have not been measured and we must estimate the values. To do this we have made a comparison between the velocities of sound for pTS, measured by Rehwald *et al* (1983) and the known values for DCH. The longitudinal velocity in the direction of the diacetylene chain of the polymer is determined by the elastic constants characteristic of the covalent bonding of the carbon chain; thus the values are very similar for pTS and DCH. The transverse velocities in this direction, however, are determined by a combination of elastic constants which are governed by the van der Waals forces between the side groups as well as by the C–C covalent bond strength (Rehwald *et al.* 1983) and so we expect these velocities to be different for pTS and DCH. The difference in the strength of the van der Waals forces is also reflected in the longitudinal velocity perpendicular to the polymer backbone which is known for both pTS and DCH. Therefore, to estimate the transverse velocity for DCH in the direction of the backbone, we have adjusted the transverse velocity for pTS in this direction ($0.86 \times 10^3 \text{ m s}^{-1}$) by the ratio of the average perpendicular longitudinal velocities for pTS ($2.5 \times 10^3 \text{ m s}^{-1}$) and DCH ($3.8 \times 10^3 \text{ m s}^{-1}$). We obtain $v_T = 1.3 \times 10^3 \text{ m s}^{-1}$ and so an average sound velocity for the DCH polymer in the direction of the diacetylene chains,

$$\bar{v} = 3^{1/3} (1/v_L^3 + 2/v_T^3)^{-1/3} = 1.5 \times 10^3 \text{ m s}^{-1}. \quad (2)$$

As the packing of the two materials before polymerisation is very different, we do not feel justified in using similar arguments to estimate the velocity of sound in the DCH monomer. Consequently, we will only present a fit to the polymer data. Another parameter that is required to analyse the data is the Debye temperature. For pTS, we used the Debye model to fit the measured specific heat (Engeln and Meissner 1980) and found $\theta_D = 50 \text{ K}$. Simple scaling by the ratio of the average sound velocities for pTS and DCH and by the cube root of the ratio of the number of molecules per unit cell gives a Debye temperature of $\theta_D \approx 59 \text{ K}$ for the DCH polymer.

The total phonon scattering rate used to calculate the thermal conductivity may be expressed as

$$\tau^{-1}(\omega) = \tau_b^{-1} + \tau_s^{-1}(\omega) \quad (3)$$

where τ_b^{-1} is the frequency independent boundary scattering rate that dominates at the lowest temperatures and $\tau_s^{-1}(\omega)$ is a summation of frequency dependent scattering rates. For pTS it was found that the conductivity could be modelled with $\tau_s^{-1}(\omega)$ comprising two terms, a Raman scattering term to describe the acoustic–optical phonon scattering, $\tau_{\text{TLS}}^{-1}(\omega)$, and a term describing the scattering from stacking faults, $\tau_{\text{SF}}^{-1}(\omega)$. The scattering of the acoustic phonons by the optical modes of side groups we have described by (Wybourne *et al* 1985a)

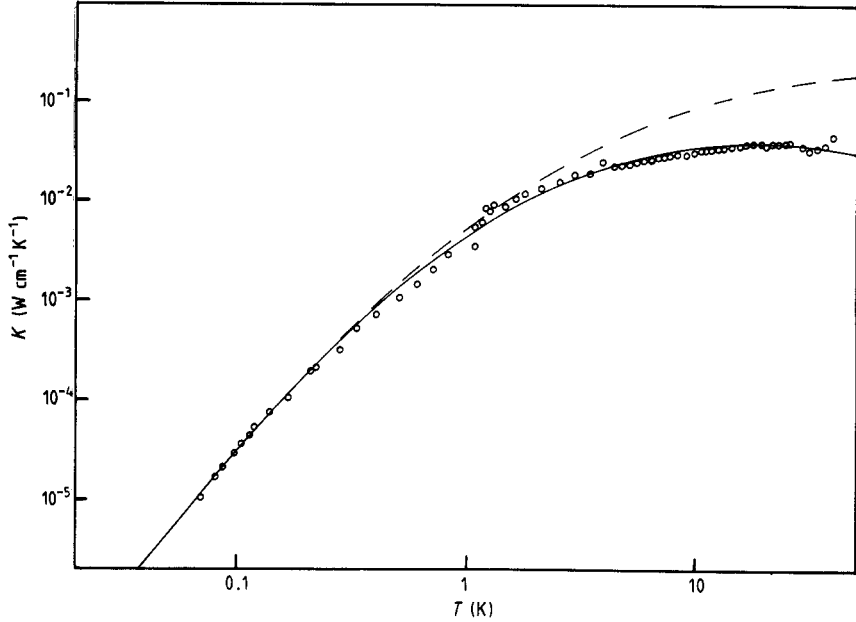


Figure 3. The best fit to the DCH polymer data (Wybourne *et al* 1985a) using the resonant frequencies, measured by far-infrared spectroscopy, in the resonance term of the Raman scattering. The broken curve shows the fit using the stacking fault term alone.

$$\tau_{\text{TLS}}^{-1}(\omega) = \frac{3}{2\pi\hbar^2} \sum_{\omega_0} \frac{|M|^4 C(\omega_0) \omega^4}{\rho^2 v_T^7} \left(\frac{2\omega_0}{\omega_0^2 - \omega^2} \right)^2 \left(1 - \tanh^2 \frac{\beta\omega_0}{2} \right) \quad (4)$$

where ω_0 are the optical mode frequencies determined from the far-infrared spectrum. $C(\omega_0)$ is the number of modes at frequency ω_0 per unit volume, M is the matrix element that describes the coupling between the optical and the acoustic modes, the density $\rho = 1350 \text{ kg m}^{-3}$ for the DCH polymer and $\beta = x/\omega$. The rate of scattering by stacking faults is described by

$$\tau_{\text{SF}}^{-1}(\omega) = 0.7(a^2/\bar{v})\gamma^2 N_S \omega^2. \quad (5)$$

where we have taken a to be 14 \AA , the interchain separation, and the Grüneisen constant $\gamma \approx 1.5$, as for pTS. N_S is the stacking fault density to be determined from the best fit to the data.

Performing the integration in equation (1) over all acoustic phonon frequencies, we obtain the best fit of the DCH polymer data shown in figure 3. Above 10 K the thermal conductivity is dominated by the optical phonon scattering, as demonstrated in figure 3 where the omission of this scattering process gives the broken curve. This temperature range is precisely the one over which the monomer and polymer data are the same which indicates that the mechanism of optical–acoustic phonon scattering is effective in both forms of the material. From the fit to the data we estimate the magnitude of the coupling constant for DCH to be $M \approx 6.3 \text{ meV}$ which is 25% greater than the value for pTS.

The frequency independent boundary scattering rate, $\tau_{\text{B}}^{-1} = \bar{v}/l$ which dominates at the lowest temperatures provides a measure of the MFP l which is limited by the crystal geometry. The best fit to the DCH polymer data yields an effective MFP of 0.2 mm which

is close to the smallest crystal dimension of 0.25 mm. This result is consistent with the absence of macroscopic defects within the DCH polymer crystal. In contrast, pTS exhibited a frequency independent MFP that was an order of magnitude less than the smallest crystal dimension, evidence for the existence of macroscopic planar defects.

The stacking fault density determined from the fit to the data is $N_s \approx 10^5 \text{ m}^{-1}$ which is one third the value found in pTS crystals. The lower stacking fault density of DCH is supported by electron microscopy of DCH which shows little evidence of such defects (Young 1985). We suggest that the difference between polymer and monomer data in the temperature range 2.8–8 K (figure 1) is most probably due to a higher stacking fault density in the monomer crystal since, in this temperature range, scattering by stacking faults has the maximum influence on the data. We note the monomer may have more stacking faults because of passing through the phase transition.

Finally, we have also considered scattering by point defects which would add an extra scattering rate proportional to ω^4 to $\tau_s^{-1}(\omega)$. Electrical conductivity measurements provide indirect evidence that DCH polymer crystals contain a considerably higher density of point defects than pTS polymer crystals (Donovan *et al* 1985). Since DCH is polymerised by irradiation with γ -rays whereas pTS is thermally polymerised, this result is not surprising. However, the point defect density in DCH is relatively low, approximately 10^{22} m^{-3} and, in the presence of optical phonon scattering, which is also proportional to ω^4 away from resonance, we find that point defect scattering has no effect on the best fit to the data. Experimentally, unirradiated monomer and irradiated polymer conductivities are very similar above 10 K, which supports this observation.

In conclusion, we have measured the thermal conductivity of DCH monomer and have found it to be very similar to that of DCH polymer. The similarity between the polymer and monomer data is evidence for coupling between acoustic phonons and optical modes being the dominant phonon scattering process at temperatures above 8 K. Describing the coupling by a linear Raman-type process we have shown that using the optical mode energies of the side groups, a good fit to the thermal conductivity of the polymer is obtained. From the fitting parameters we estimate the magnitude of the acoustic–optical mode coupling constant to be about 6.3 meV. We have also determined the boundary limited phonon MFP and have found it to be in excellent agreement with other studies that suggest DCH contains virtually no planar defects.

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