Anomalous Thermal Conduction in Polydiacetylene Single Crystals

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The thermal conductivity of high-quality polymer single crystals has been measured for the first time. The expected conductivity maximum observed in good single crystals was absent and replaced by a weak ($\sim T^{1/2}$) temperature dependence between 2 and 40 K. This anomalous behavior is attributed to scattering of acoustic phonons by low-energy optical phonons with a coupling matrix element of 40 cm^{-1}.

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In this Letter we present for the first time measurements of the thermal conductivity of polydiacetylene (PDA) single crystals. Polydiacetylenes are the only polymers to form macroscopic crystals of sufficiently high quality to carry out x-ray topographic studies[1] and to produce direct lattice images in the electron microscope.[2] Electrical-conduction measurements also have indicated a very low concentration of defects in the polymer crystals.[3,4] Crystalline specimens of low defect concentration are almost always characterized by a well defined peak in the thermal conductivity arising from the exponential decay of umklapp processes with decreasing temperature and the onset of boundary scattering at very low temperatures.[5] Thus observation of a broad plateau in the thermal conductivity for single crystals of two different polydiacetylenes between $\theta_D/25$ and θ_D, such as might be expected for an amorphous material, was at first surprising.

We have been able to show, however, that this behavior can be attributed to an unusual lattice dynamical property; the massive side groups attached to the polymer backbone give rise to optical phonons with energies compatible to those of the acoustic phonons responsible for heat transport. It has been possible to obtain a good theoretical fit to the measured thermal conductivity by incorporating available experimental data and a single adjustable parameter, the average optical-acoustic phonon interaction energy.[6,7] Such an interaction has not previously been observed in low-temperature thermal conduction, as in most crystals studied the optical phonons lie at too high an energy for such scattering processes to be important.

The PDA crystals were prepared by the solid-state polymerization of monomer crystals of the two diacetylenes, the *bis*(*p*-toluene sulfonate) of 2,4-hexadiyne-1,6-diol (TS) and the 1,6-di-(N-carbazolyl)-2,4-hexadiyne-1,6-diol (DCH). Both crystals are monoclinic, $P2_1/c$, with two polymer chains per unit cell extending in the crystallographic b direction. PDA-TS undergoes a second-order phase transition at 195 K; the space group remains the same but the unit cell is doubled in size and contains two different species of polymer chain.[8] Since thermodynamic and lattice-dynamic data are much less extensive for PDA-DCH than for PDA-TS, the analysis of the results will be concentrated on those of PDA-TS.

We have carried out thermal conductivity measurements from 1 to 40 K on PDA-TS and PDA-DCH. Two samples of each material were used having typical dimensions of 10×2×1 mm, the largest being the polymer chain direction. Epoxy was used to attach the crystals to the variable-temperature heat sink of a standard low-temperature steady-state potentiometric thermal conductivity apparatus. The temperature gradient was applied in the direction of the polymer chains and, at a temperature T, had a maximum value of approximately $2\times10^{-3}T$ mm^{-1}.

The measured thermal conductivities of the two polymers are shown in Fig. 1. The thermal conductivities of the two different specimens of each polymer were the same to within experimental error and so we show the data for a single specimen. The absolute thermal conductivity of the PDA-DCH is some three times higher than that of the PDA-TS and both show a very weak temperature dependence, $\sim T^{1/2}$, with some evidence for the onset of a higher-power dependence at the lowest temperatures.

To describe the PDA-TS data we use the usual expression for thermal conductivity,[5]

$$K=\frac{k_B}{2\pi^2 V}\left(\frac{k_B}{\hbar}\right)^3 t^3\int_0^{\theta_D/T}\tau_T(x)\frac{x^4e^x}{(e^x-1)^2}dx,$$

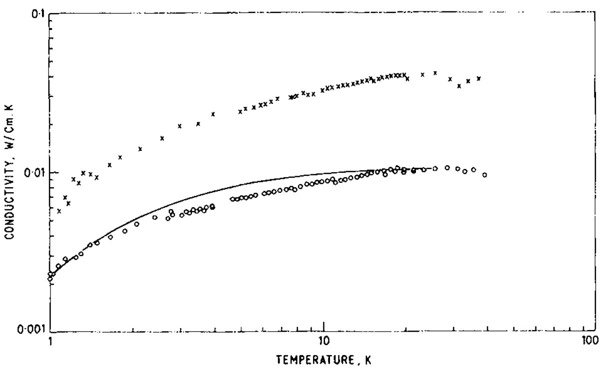

FIG. 1. The thermal conductivity of PDA-DCH (crosses) and PDA-TS (circles). The solid curve shows a theoretical fit to the PDA-TS data using a Rayleigh-scattering mass-defect relaxation rate having $\Delta M = 0.4\bar{M}$.

where $x = \hbar\omega / k_B T$, with a total scattering rate given by

$$\tau_T^{-1} = \tau_B^{-1} + \tau_s^{-1},$$

where τ_B^{-1} is a frequency-independent geometric scattering rate and τ_s^{-1} is a frequency-dependent term. The measured heat capacity for this material[9] has two distinct regions of different temperature dependence. Below 8 K the usual T^3 behavior is observed while above 50 K the temperature dependence becomes almost linear. From a Debye-model fit to the specific-heat data below 8 K, θ_D is estimated to be 49.6 K. Sound-velocity measurements[10] for propagation parallel to the polymer chains of PDA-TS, at temperatures below the phase transition, give values

$$V_L = 5.5 \times 10^3 \text{ m s}^{-1},$$

$$V_{T1} \simeq V_{T2} = 0.86 \times 10^3 \text{ m s}^{-1},$$

with the polymer density $\rho = 1422$ kg m^{-3}. Therefore, the average sound velocity we use is

$$\bar{V} = \sqrt[3]{3}\,[V_L^{-3} + 2V_T^{-3}]^{-1/3} = 1.0 \times 10^3 \text{ m s}^{-1}.$$

With these parameters a good fit to the data is obtained for $\tau_B^{-1} = 4.8 \times 10^7$ s^{-1} and $\tau_s^{-1} = (1.2 \times 10^{-39}\text{ s}^3)\omega^4$ as shown in Fig. 1. The geometric scattering rate is ~ 50 times greater than the Casimir limit appropriate to the dimensions of these crystals and corresponds to a phonon mean free path ~ 10 μm which is equivalent to $\sim 10^4$ polymer chain separations. This mean free path is consistent with an estimate for the mean separation of stacking faults in PDA-TS.[11]

The excellent fit to the data obtained by a phonon-relaxation time inversely proportional to the fourth power of the frequency strongly suggests that a Rayleigh-type scattering mechanism is involved. Initially we consider the frequency-dependent scattering rate to be Rayleigh-type mass-defect scattering.[5] As the crystal volume is largely determined by the polymer side groups, we assume that these are the origin of this mass-defect scattering. Taking the side groups to be rigid units that are statically displaced, or are dynamic with frequencies much lower than the phonon frequencies under consideration, and assuming that every side group contributes to the scattering and has a volume ~ 100 Å^3, we obtain a mass defect $\Delta M = 0.4\bar{M}$, where $\bar{M}$ is the average side-group mass. This figure is so large that crystal perfection would be low and we would expect x-ray diffraction patterns to be characteristic of an amorphous material rather than the single-crystal structure observed.

Another mechanism of acoustic-phonon scattering which has an ω^4 dependence arises from the interaction between optical and acoustic phonons; this phenomenon is peculiar to this type of material. In PDA-TS there is experimental evidence for several optical modes involving motion of the polymer side groups which have energies sufficiently low to interact strongly with acoustic phonons. For PDA-TS these side groups have a mass of approximately 15 carbon atoms. Far-infrared spectroscopy[12] has shown the existence of a number of low-energy modes down to ~ 15 cm^{-1} in PDA-TS. Recent neutron-scattering data[13] for TS monomer have shown the existence of optical modes down to energies ~ 3 cm^{-1}; these should be similar in character for both the monomer and the polymer since modes primarily involving motion of the side groups should not be strongly affected by the formation of the polymer chain. The available data show strong evidence of coupling between acoustic and optical phonons. The difference between the monomer and polymer heat capacities above 50 K (Ref. 9) could be explained by a 10% shift to higher frequency of the optical-phonon modes. We consider scattering by these optical modes to be a linear Raman-type process in which each optical mode is described as a two-level system.[6,7] We do not consider the quadratic Raman process as it is generally weaker. Unlike in amorphous materials, however, these two-level systems are regularly situated within the crystal lattice and at $T = 0$ we would expect no acoustic-phonon scattering. This follows since at $T = 0$ the two-level systems are in their ground state and any scattering will be coherent. Renormalization to include these two-level systems in their ground state results in new normal modes of the system that experience no scattering. However, if one two-level system is excited the symmetry of the two-level system array is removed and the possibility of acoustic-phonon scattering exists. For this reason a linear Raman-type scattering term must include an excitation term $1-\tanh^2[\beta\omega_0/2]$, where ω_0 is a particular two-level system splitting energy and $\beta=\hbar/k_BT$. Therefore, we describe the overall scattering rate by the low-energy side-group modes as[6]

$$\tau_{\mathrm{TLS}}{}^{-1}=\frac{3}{2\pi\hbar^2}\sum_{\substack{\text{optical}\\ \text{modes}}}|M|^4\frac{C(\omega_0)}{\rho^2\bar{V}^7}\omega^4\left(\frac{2\omega_0}{\omega_0{}^2-\omega^2}\right)^2\left(1-\tanh^2\frac{\beta\omega_0}{2}\right),$$

where $C(\omega_0)$ is the number of modes per unit volume and M is the optical-acoustic phonon matrix element. The value of M will only be significantly greater than zero for optical modes which would cross the dispersion curve for the acoustic phonons if there were no interaction between them. Further, we really need only consider those which interact with the transverse modes since the longitudinal velocity is 6.4 times greater than the transverse velocity giving a transverse density of states ~500 times that of the longitudinal phonons; almost all of the heat is transported via the transverse phonons. If we assume a nearest-neighbor interaction model and hence a sinusoidal shape for the transverse phonon dispersion curves, the acoustic-phonon energy at the zone boundary is estimated to be 20 cm^{-1}, so that in the Raman scattering rate above we only need to consider optical modes below this energy.

The far-infrared data reveal modes at 13.9 and 18.8 cm^{-1}. A fit to the data with these mode energies is shown in Fig. 2. The neutron-scattering data suggest three additional modes of energies 4, 8, and 12.5 cm^{-1} and a fit to the data with all five modes is also shown in Fig. 2. It is clearly seen that the fit using all five modes is appreciably better than that with the two infrared-observed modes alone. The sensitivity of the model to the number and frequency of the low-lying optical modes provides a strong incentive for inelastic neutron-scattering experiments to be carried out on the polymer. Taking the matrix element to be frequency independent up to 20 cm^{-1}, we obtain $|M|=40\ \mathrm{cm}^{-1}$. The gap $\Delta(\omega_0)$ that opens in the dispersion curves when the optical and acoustic modes couple is given by[7]

$$\Delta(\omega_0)=\left[\left(\frac{12M^4\omega_{\mathrm{D}}^3C(\omega_0)}{\pi^2\hbar^2\rho^2\bar{V}^7}\right)^{1/2}\omega_0\tanh\frac{\beta\omega_0}{2}\right]^{1/2},$$

with $\omega_{\mathrm{D}}=(k_{\mathrm{B}}/\hbar)\theta_{\mathrm{D}}$, from which we estimate $\Delta(\omega_0)=(1.5\times10^5\ \mathrm{s}^{-1/2})\omega_0^{1/2}$ at temperatures such that $\beta\omega_0=1$. The values of Δ obtained for the five modes considered are in the range 3 to 8 cm^{-1}; they are slightly larger than but consistent with the gaps observed in TS monomer by neutron scattering. We believe that any overestimation arises from the approximation that the matrix element is frequency independent; any dispersion of the optical modes has been neglected as it is as yet unknown.

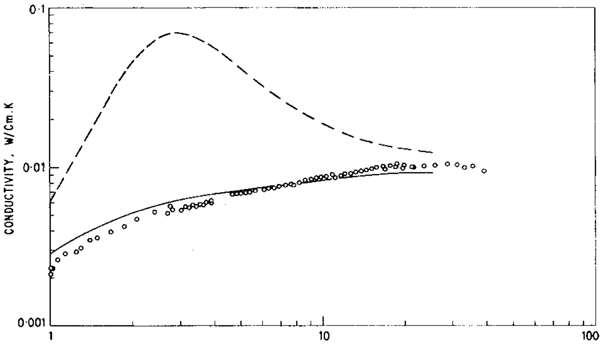

FIG. 2. Comparisons of fits to the PDA-TS data using a linear Raman-type relaxation rate to include the far-infrared–observed modes (dashed line) and the far-infrared modes plus neutron-scattering–observed modes (solid line).

Dislocation densities in PDA-TS crystals grown by solvent evaporation have been estimated to have an upper limit of $10^{13}\ \mathrm{m}^{-2}$.[14] Using the measured room-temperature heat capacity per unit volume, a compressibility $5.3\times10^{11}\ \mathrm{m}^2\ \mathrm{N}^{-1}$,[15] a thermal expansion coefficient $1.15\times10^{-4}\ \mathrm{K}^{-1}$,[16] and a Burgers-vector magnitude 0.491 nm,[13] we estimate a maximum dislocation strain field scattering rate of $\tau^{-1}=9\times10^{-4}\omega$.[5] From a dominant phonon argument this scattering rate is lower than that of the linear Raman term at all temperatures considered. Core scattering is generally weaker than strain-field scattering and dynamic-dislocation scattering does not explain the observed temperature dependence.[17] From considerations such as this we do not believe that mass-defect scattering by the side groups or dislocation scattering is responsible for the observed thermal conductivity.

Finally, we note that the above optical modes together with the higher-energy infrared- and Raman-observed modes[18,19] give an Einstein specific-heat contribution of $C_E = 3.2T$ J kg^{-1}K^{-1} which, combined with the Debye contribution having $\theta_D = 49.6$ K, provides a good fit to the specific-heat data.[9]

In summary, single crystals of PDA exhibit a thermal conductivity in the temperature range 1 to 40 K akin to that of amorphous materials. The scattering process responsible for this anomalous thermal conductivity has been identified as acoustic-phonon scattering by the low-energy optical modes involving motion of the polymer side groups. It should be possible to observe this phenomenon in other crystals, not necessarily polymeric, which have large molecular groups in the unit cell.

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