Anisotropic Heat Conduction in Diacetylenes

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We report measurements of the low-temperature thermal conductivity of diacetylene single crystals. Monomer samples show little anisotropy and display the temperature dependence of a crystalline dielectric. In polymerized samples, heat is conducted up to 60 times better parallel to the chains than perpendicular to them. Dislocations can account for this anisotropy at the lowest temperatures. Quasi one dimensionality of the polymer crystals induces anisotropy at higher temperatures and strongly suppresses anharmonic phonon interactions.

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Much interest has recently been generated by conjugated polymers as one-dimensional conductors. Diacetylenes are particularly interesting because they are the only conjugated polymers to form nearly perfect single crystals. Very little is known, however, about the thermal transport properties of these systems in either their monomer or polymer forms. The only reported measurements of the thermal conductivity of diacetylenes are those of Wybourne and co-workers$^{1-3}$ on polymer *bis*(*p*-toluene sulfonate) of 2,4 hexadiyne-1,6-diol (PTS) and polymer 1,6-di-(N-carbazoyl)-2,4-hexadiyne-1,6-diol (PDCH) in the polymer chain direction.

We report measurements of the thermal conductivity of monomer (TS) and polymer (PTS) diacetylene, both in the chain direction and perpendicular to the chains, from 2 K up to at least 30 K. The results not only yield important information on the nature of defects in this material, but also raise fundamental questions regarding the thermal conductivity of low-dimensional dielectric systems.

TS was synthesized and crystallized by use of the method described by Wegner.^{4} The resulting crystals were of the characteristic diamond shape and pink in color. Polymerization was achieved by annealing the samples for 72 h in an argon atmosphere at 65 °C. The thermal conductivity of six different samples was measured by a four-probe steady-state technique in a standard ^{4}He cryostat. Heat losses set the high-temperature limit of our measurement range. We estimate the relative uncertainty in our data as 5%; as a result of nonuniform cross section, the absolute uncertainty in the reported values is as much as 20%.

Figure 1 shows the thermal conductivity K of both TS (measured here for the first time) and PTS from 2 K to at least 30 K, and in some cases as high as 80 K. For comparison, the results of Wybourne and co-workers$^{1-3}$ are indicated by a dashed line. We point out a number of interesting features: First, the monomer crystals show a typically dielectric behavior, with a maximum in $K(T)$ around 10–12 K. Below the peak, $K(T)$ decreases as T^n with $n > 1$, while above it $K(T) \sim T^{-1}$. The magnitudes of $K(T)$ parallel and perpendicular to the "chain" direction (i.e., the direction in which chains would form upon polymerization) are within a factor of 2. This seems to indicate that TS can be considered, for the most part, an isotropic three-dimensional crystalline dielectric material. In comparison, the thermal conductivity of the polymerized samples is quite different in both magnitude and temperature dependence. In the chain direction (sample P1), $K(T)$ exhibits a broad maximum from 10–20 K. Across the chains (samples P2 and P3) $K(T)$ flattens above 10 K. While this behavior appears glass-like, x-ray topographic studies^5 and a cubic temperature dependence of the specific heat^6 below 10 K indicate that these diacetylenes are in fact crystalline. Interestingly, heat conduction across the carbon chains is a factor of 30–60 times less than conduction in the chain direction. Thus, polymerization of TS changes not only the temperature dependence of $K(T)$ but its anisotropy as well: The conductivity perpendicular to the chains decreases, while that parallel to them increases. The latter behavior is a curiosity. The dashed line labeled "$\perp$" in Fig. 1 represents the data reported in Ref. 3 for PTS perpendicular to the chains. They

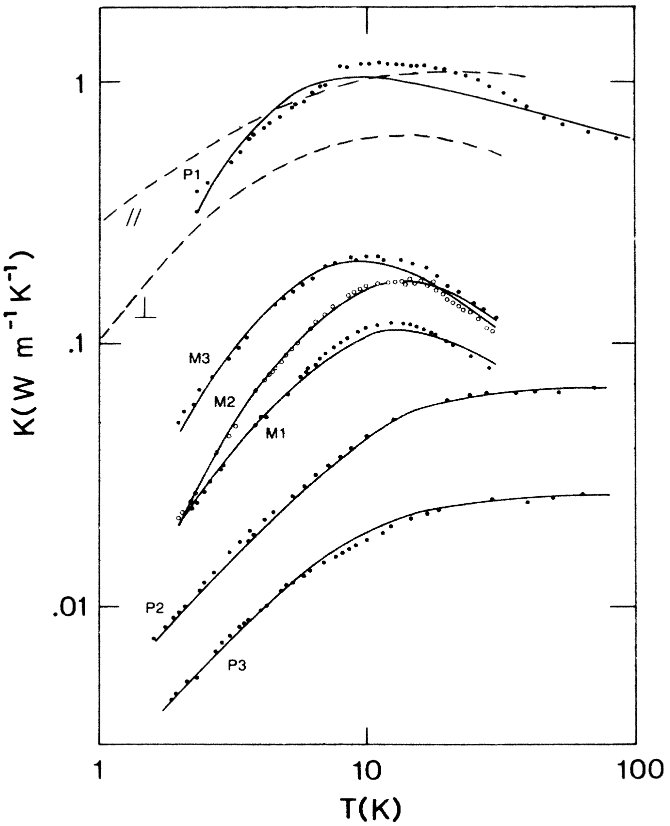

FIG. 1. Thermal conductivity of several monomer and polymer diacetylene single crystals. M1, monomer, || chain; M2 and M3, monomer, ⊥ chain; P1, polymer, || chain; P2 and P3, polymer, ⊥ chain. Each measurement was made on a different sample. The solid lines are the calculated thermal conductivity; the dashed lines represent results previously reported (Refs. 1–3) for heat conduction parallel and perpendicular to the chain axis.

contradict ours, though microscopy analysis of our samples shows a defect density similar to that of the type of samples used by Wybourne and co-workers.[1-3] While the anisotropy ratio we report here has been recently confirmed independently,[7] we note that the value in Ref. 3 for PTS, which has a ratio of elastic constants C_{22}/C_{11} of 8, is actually lower than that for hexagonal selenium,[8] where the thermal conductivity parallel to the c axis is 5–10 times larger than perpendicular to it over the entire umklapp regime, although the ratio of elastic constants is only $C_{33}/C_{11} = 4.3$.

On the basis of their data, Wybourne and coworkers[1,2] modeled the rather anomalous thermal conductivity of PTS by a scattering of acoustical phonons (responsible for carrying the heat) by low-energy optical phonons associated with vibrations of the massive side groups dangling from the carbon chains. If this model were to be relevant, the thermal conductivity of the monomer and polymer forms should be at least qualitatively similar since, upon polymerization, the side chains are left virtually unaffected. The data of Fig. 1, however, seem to indicate that this is not the case. An acoustic-optic phonon coupling model can neither fit the observed monomer data nor account for the larger (~ 10 times) increase in conduction along the chain direction upon polymerization. While we cannot explicitly rule out the possible existence of acoustic-optic phonon scattering in this material, we believe, in view of our data, that the defect nature and the known phonon spectrum of the monomer and polymer can account for the observed results.

Numerous studies have shown that while both TS and PTS show a regular crystalline order, they also possess a prominent dislocation structure which, in fact, is thought to play an important role in the polymerization process. Dudley *et al.*[5] have shown that TS contains both edge and screw dislocations distributed essentially isotropically throughout the crystal, but did not indicate the density of these dislocations. They suggest that the defect structure of the polymer is identical to that of the monomer, being in a sense "frozen in" during polymerization. Young, Read, and Petermann,[9] however, using transmission electron microscopy (TEM), found that in polymer samples stacking faults with spacing on the order of 1 μm are formed parallel to the chain direction. Young and Petermann,[10] also using TEM, estimated the dislocation density in a PTS crystal at $\lesssim 10^{13}$ m^{-2}. This is about 2 orders of magnitude higher than dislocation densities in other dielectric systems whose thermal conductivity has been shown to be limited by dislocation scattering.[11-13] We thus believe that phonon-dislocation scattering is one of the two ingredients in the understanding of our data.

Second, both TS and PTS possess anomalously anisotropic phonon spectra. Because the interchain spacing is about 3 times greater than the interatomic spacing along the chain, the Brillouin zone extends a factor of 3 further out in k space in the chain direction compared with perpendicular to the chains. This is characteristic of both TS and PTS. In the latter, however, an additional anisotropy arises from anisotropic phonon velocities: Longitudinal phonons propagate along the chain about 6.5 times faster than perpendicular to it.[14] As a result, the anisotropy of the cutoff *frequencies* of phonons, which depend on the product of the Brillouin-zone-edge wave vector and the phonon velocity, can be as high as a factor of 20 in PTS; in TS the maximum anisotropy is on the order of 5. Physically, this means that at temperatures below the lower cutoff frequency the system is essentially three dimensional while between the lower and upper cutoff frequencies it acts quasi one dimensional. In fact, heat-capacity (C) studies[6] on both TS and PTS indicate that below 10 K $C \sim T^3$, but above about 50 K C is *linear* in temperature, characteristic of a one-dimensional system. From heat-capacity studies, the cutoffs, in temperature, occur roughly at $\theta_{3D}=50$ K and $\theta_{1D}=2400$ K. The thermal conductivity of a one-dimensional phonon system is expected to differ from that of a three-dimensional system in two major ways: (1) There will be no umklapp processes, nor indeed any anharmonic processes at all,[15] because if there is any dispersion whatsoever in the phonon spectrum, conservation of energy and momentum cannot be simultaneously achieved. This condition implies a high-temperature thermal conductivity *independent* of temperature. (2) Because in one dimension the phonon density of states depends on velocity as $g \sim v^{-1}$ (as opposed to a v^{-3} dependence in three dimensions), the thermal conductivity $K = Cv^2\tau$ (τ is the scattering time) is *proportional* to v, rather than inversely proportional to v as in the ordinary case. This implies that the faster modes carry most of the heat in a one-dimensional material. Thus in the one-dimensional regime the thermal conductivity of a polymer can be highly anisotropic because of the anisotropy in the longitudinal (fast) modes, whereas in the monomer the conduction of heat would be much more isotropic. These one-dimensional effects disappear exponentially below θ_{3D} but are important for temperatures above about 50 K in PTS.

In the low-temperature regime, where most of our data are reported, we shall assume an isotropic three-dimensional Debye spectrum and a relaxation-time approximation. We follow the treatment of Berman[16] for imperfect crystals, allowing for scattering of phonons by boundaries, umklapp processes, and dislocations. While boundary scattering is important below 1 K, where it leads to a cubic temperature dependence of the conductivity,[2] it will in fact play little role at higher temperatures in comparison to scattering by the other two processes. In TS, dislocations are distributed isotropically so that the dislocation scattering rate will take the same form for all three samples. If scattering from dislocation strain fields dominates, then[16]

$$\tau_D^{-1} \sim A_1\omega$$

for all TS samples. In PTS, many of the dislocations become preferentially aligned parallel to the chain direction upon polymerization, forming stacking faults which are capable of scattering phonons propagating perpendicular to the carbon chains. Klemens[17] has analyzed this type of process and finds

$$\tau_D^{-1}(\mathrm{PTS}, \perp) \sim A_2\omega^2.$$

A finite number of dislocations with lines perpendicular to the chain remain in PTS and will scatter phonons propagating along the chain. It has been suggested[10] that, as a result of the extreme elastic anisotropy of PTS, the cores of these dislocations may extend over as many as thirty lattice spacings. Thus for conduction along the chain it is necessary to include core as well as strain-field scattering:

$$\tau_D^{-1}(\mathrm{PTS}, \|) \sim A_3\omega + A_4\omega^3.$$

Using these forms of the dislocation scattering rates together with an umklapp scattering rate $\tau_u^{-1} = u\exp(-\theta/2T)$, we fitted all our data using the phonon-dislocation (A_i) and phonon-phonon (u) coupling constants as adjustable parameters, with θ in the range 35–140 K. The fits are indicated by solid lines in Fig. 1 and are of quite good quality for all samples. What remains to be discussed is whether the values of the parameters used in the fits are in reasonable agreement with what is expected.

For samples P2 and P3 the stacking-fault scattering rate yields stacking-fault spacings of 2.5 and 0.5 μm, respectively. This is consistent with TEM observations which indicate that stacking faults are aligned parallel to the chains with average separation ~ 1 μm.[9] This stacking-fault spacing is greater than the maximum dominant phonon wavelength (approximately 1300 Å for longitudinal phonons in the polymer at 2 K), indicating that they indeed appear to incident phonons as large-scale defects. For the other four samples we calculate [using Eq. (8.3) in Ref. 16] apparent dislocation densities N_D of 3.9×10^{19}, 3.1×10^{19}, and 1.4×10^{19} m^{-2} for samples M1, M2, and M3, respectively, and 2×10^{17} m^{-2} for P1. There have been no independent determinations of dislocation densities in TS; for PTS, TEM experiments[10] estimate $N_D \simeq 10^{13}$ m^{-2}. Thus our value is about 10^4 higher. Such a large discrepancy between dislocation densities calculated from thermal-conductivity data and observed densities is not unusual for dielectric systems.[11-13] A number of considerations must be made which, acting independently or in unison, can account for the difference: (1) TEM studies can identify only those dislocations emerging from the faces of the crystal. Dislocations which begin and end away from any sample surface, which may be significant in number, will go undetected by TEM observations. (2) Dislocations may not be distributed uniformly but rather may be associated. Dudley *et al.*[5] have in fact reported observations of "bundling" of dislocations in this system. The result here is that the effective Burgers vector B of an associated dislocation may be substantially larger than one lattice spacing. This will be particularly important since the scattering rate goes as B^2. (3) A significant number of dislocations in both TS and PTS may be glissile.[10] The scattering of lattice waves by mobile dislocations has been shown[18] to be significantly stronger than that for static dislocations. However, for such processes a $T^{3.5}$ law is expected and this is not consistent with our data. In light of these considerations we believe that the observed strength of dislocation scattering is not in disagreement with what should be expected for this material.

A rather fundamental result is the fact that umklapp scattering is 2 orders of magnitude weaker in PTS than in TS. We think that the reason for this lies in the one-dimensional nature of the polymer around 50 K which, as discussed previously, prohibits anharmonic phonon interactions.[15]

In conclusion, we have measured the thermal conductivity of monomer and polymer diacetylene, both perpendicular and parallel to the chain axis, from 2 K to at least 30 K. Whereas heat conduction in monomer samples is practically isotropic, $K(T)$ parallel to the chain direction in the polymer is about 30–60 times greater than that perpendicular to the backbone. The results can be understood by a model in which phonons are scattered by dislocations which are distributed isotropically in the monomer but become preferentially aligned along the chain direction upon polymerization, forming stacking faults of spacing on the order of a micron. The dislocation densities in the polymer calculated from our thermal conductivity curves are about 10^4 times higher than those determined by TEM studies. This indicates that the dislocations may be associated and/or partially mobile in either (or both) the monomer or polymer. Umklapp processes are strongly attenuated in PTS, and this is ascribed to the one-dimensional nature of these solids.

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[1] M. N. Wybourne, B. J. Kiff, and D. N. Batchelder, Phys. Rev. Lett. **53**, 580 (1984).

[2] M. N. Wybourne, B. J. Kiff, D. N. Batchelder, D. Greig, and M. Sahota, J. Phys. C **18**, 309 (1985).

[3] M. N. Wybourne, B. J. Kiff, D. N. Batchelder, D. Greig, and M. Sahota, in *Proceedings of the Second International Conference on Phonon Physics,* edited by J. Kollar, N. Kroo, N. Meynhard, and T. Siklos (World Scientific, Singapore, 1985), p. 738.

[4] G. Wegner, Macromol. Chem. **145**, 85 (1971).

[5] M. Dudley, J. N. Sherwood, D. J. Ando, and D. Bloor, Mol. Cryst. Liq. Cryst. **93**, 223 (1983).

[6] I. Engeln and M. Meissner, J. Poly. Sci., Polym. Phys. Ed. **18**, 2227 (1980).

[7] M. Meissner, private communication.

[8] A. R. Adams, F. Baumann, and J. Stuke, Phys. Status Solidi **23**, K99 (1967); K. Vedam, D. L. Miller, and R. Roy, J. Appl. Phys. **37**, 3432 (1967).

[9] R. J. Young, R. T. Read, and J. Petermann, J. Mater. Sci. **16**, 1835 (1981).

[10] R. J. Young and J. Petermann, J. Polym. Sci., Polym. Phys. Ed. **20**, 961 (1982).

[11] R. L. Sproull, M. Moss, and H. Weinstock, J. Appl. Phys. **30**, 334 (1959).

[12] A. C. Anderson and S. C. Smith, J. Phys. Chem. Solids **34**, 111 (1973).

[13] S. G. O'Hare and A. C. Anderson, Phys. Rev. B **9**, 3730 (1974).

[14] W. Rehwald, A. Vonlanthen, and W. Meyer, Phys. Status Solidi (a) **75**, 219 (1983).

[15] R. Peierls, Ann. Phys. (Liepzig) **3**, 1055 (1929).

[16] R. Berman, *Thermal Conduction in Solids* (Clarendon, Oxford, 1976).

[17] P. G. Klemens, *Solid State Physics* (Academic, New York, 1958), Vol. 7, p. 1.

[18] J. A. Garber and A. V. Granato, J. Phys. Chem. Solids **31**, 1863 (1970).