Thermal Conductivity of Single Crystal C60

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We report the first measurement of the thermal conductivity of single crystal C_{60}. We observe that orientational disorder significantly reduces the thermal conductivity, evidenced by a large jump in the thermal conductivity at the 260 K orientational-order transition. The temperature and time dependences of the thermal conductivity below 260 K are shown to be described by a phenomenological model that involves thermally activated jumping motion between two nearly degenerate orientations, separated by an energy barrier of $\sim$260 meV.

The discovery of C_{60} and the subsequent development of techniques that permit its large-scale production [1,2] stimulated tremendous interest in the physical and chemical properties of fullerenes and their derivatives. For solid C_{60} it has been shown that the C_{60} molecules rotate freely at very high frequency above 260 K [3]. Upon cooling, the solid changes from a face-centered-cubic (fcc) to a simple-cubic (sc) structure at about 260 K accompanied by a reduction of orientational disorder, although significant disorder persists to low temperature [4,5]. The orientational disorder in C_{60} is not only of interest in its own right, but may also have profound effects on the electronic structure [6].

The Debye temperatures of C_{60} intermolecular phonon modes are quite low, $\theta_D \sim 75$ K, presumably due to the weak van der Waals bonding of C_{60} [7,8]. Above the Debye temperature the specific heat due to propagating modes is independent of temperature. Consequently, the thermal conductivity κ is an ideal probe of the phonon mean free path—and hence the ordering of the C_{60} molecules—through the kinetic expression

$$\kappa = \tfrac{1}{3} C_v v l , \tag{1}$$

where C_v is the specific heat, v is the sound velocity, and l is the phonon mean free path. In this Letter, we report thermal-conductivity measurements on single crystal C_{60}. We find that $\kappa \sim 0.4$ W/mK and is nearly temperature independent above 260 K. The thermal conductivity increases abruptly by 25% at 260 K, which accords with the previously observed first-order transition [4]. Upon further cooling, the thermal conductivity increases. At about 85 K, the thermal conductivity shows a shoulder-like structure. A remarkable time-dependent thermal conductivity was observed at several temperatures in the vicinity of 85 K.

The C_{60} single crystals were prepared at Illinois by subliming 99.5% pure C_{60} powders from SRI [9]. The typical dimensions of C_{60} crystals are about $0.4 \times 0.2 \times 0.2$ mm^3. The thermal conductivity was measured by the static method. One end of the sample was mounted to a

quartz-crystal block. A miniature thin-film resistor was attached to the other end of the crystal, serving as the heater. The two junctions of a 12-μm Chromel-Constantan differential thermocouple were attached to the sample by silver paste. The typical separation between the two junctions was $\sim$0.2 mm. The temperature gradient was measured with the heater on and off after a typical delay time of 30 to 55 s after the onset of the heat pulse. The heat-pulse manipulation and data acquisition were controlled by a personal computer. The heat loss due to the heater leads and the thermocouple is negligible. The radiation loss is also insignificant.

In Fig. 1, we show the temperature dependence of the thermal conductivity from 300 to 30 K. We can see that
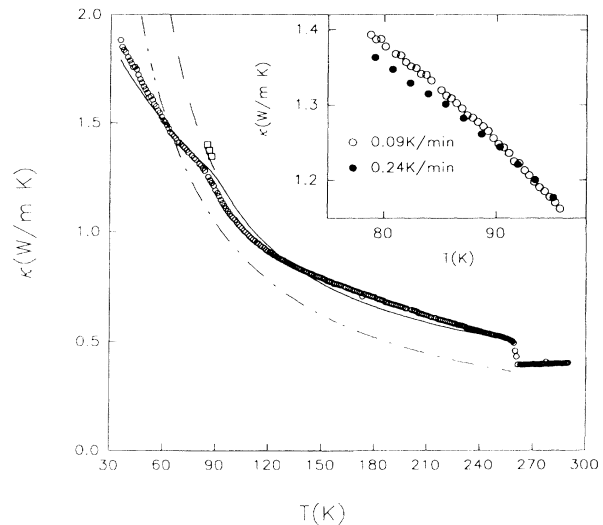

FIG. 1. Temperature dependence of the thermal conductivity of C_{60} single crystal. O, the temperature-dependent experimental data; $\square$, κ_f at 87.5, 86, and 85 K. The dot-dashed line is the best fit from A/T form for data below 260 K; the solid line, the fit from Eq. (3); the dashed line, Eq. (3) in the limit of $t \to \infty$. Inset: Thermal-conductivity data for two different cooling rates.

the thermal conductivity is about 0.4 W/mK, and almost flat above 260 K. The thermal conductivity changes abruptly at 260 K from 0.4 to 0.5 W/mK, with a transition width of $\sim$2 K. Upon further cooling, the thermal conductivity increases monotonically down to 30 K. There is a reproducible shoulderlike structure at about 85 K. The cooling rate for this run is about 0.15 K/min. With decreasing cooling rate, we observe enhancement of the thermal conductivity below some characteristic temperature in the vicinity of 90 K. In the inset of Fig. 1, we show two sets of data in the vicinity of 85 K taken with different cooling rates of 0.09 and 0.24 K/min. We see that below 90 K the slower cooling rate results in a larger thermal conductivity.

To explore the time dependence, we measured the thermal conductivity at several fixed temperatures using the following procedure. First, we held the temperature at 130 K for a few minutes, followed by cooling the sample to the target temperature for about 30 min. Then we continuously took data until the thermal conductivity was saturated, while the temperature was held constant. The temperature fluctuations were controlled to less than 1%. In Fig. 2, we plot the time dependence of the thermal conductivity at 87.5, 86, and 85 K. The thermal conductivity increases with time and saturates with a different relaxation time at each temperature.

To understand these unusual observations, we express the phonon mean free path $l = v\tau$, where τ^{-1} is the scattering rate, and $\tau^{-1} = \sum_i \tau_i^{-1}$ with i denoting different scattering mechanisms. At high temperatures, one important determinant of the thermal conductivity is the phonon-phonon scattering via umklapp processes [10]. This scattering rate is proportional to temperature,
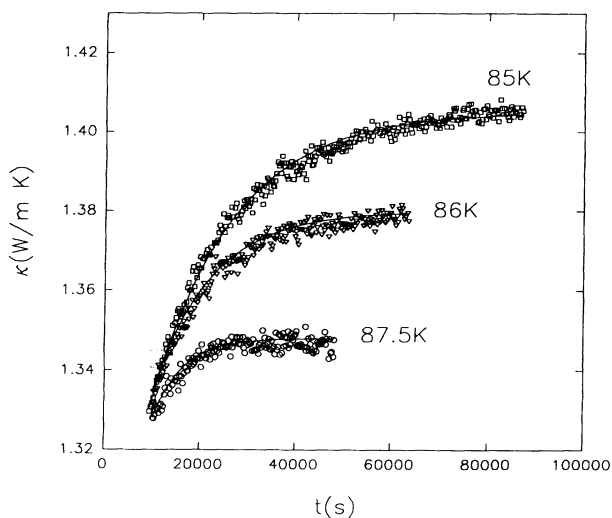
$$\tau_U^{-1} \propto T. \qquad (2)$$

FIG. 2. Time dependence of thermal conductivity of C_{60} at temperatures 87.5, 86, and 85 K. The solid lines are plots of Eq. (6) using parameters κ_f and $\ln C$ obtained from Fig. 3.

While a $1/T$ dependence qualitatively describes the thermal-conductivity behavior, there are significant deviations. In Fig. 1, we show the best fit of data below 260 K by E/T (with E the fitting parameter). The discrepancy between the data and the fit is substantial.

At 260 K, the thermal conductivity jumps by 25%, yet the sound-velocity measurements show only a 4% jump [11], and the lattice constant, a 0.4% change [5]. The large jump in thermal conductivity can only be attributed to a sudden increase of the phonon mean free path. From NMR experiments, we know that the orientational motion of the C_{60} molecules changes dramatically at the 260-K transition [3]. This suggests that the orientational ordering of C_{60} molecules has a significant effect on the phonon mean free path.

The orientational disorder of C_{60} above 260 K has been characterized as a continuous diffusive rotational motion of C_{60} molecules [3,12]. The complete orientational disorder causes strong phonon scattering. The small and nearly temperature-independent thermal conductivity suggests that this phonon scattering due to orientational disorder is the major limiting factor in the phonon mean free path. If we take the thermal conductivity $\kappa = 0.4$ W/mK, $C_v \sim 50$ J/K mol [7], and $\bar{v} \sim 2000$ m/s [8], we can calculate the phonon mean free path $l \sim 50$ Å, which is only a few times the lattice spacing $a \sim 14$ Å. It is worth noting that this room-temperature value of the thermal conductivity of C_{60} is much lower than that of graphite in the direction perpendicular to the layer, presumably due to the low phonon density, weak molecular bonding, and the orientational disorder in C_{60}.

At 260 K, C_{60} undergoes a first-order transition from a fcc to a sc structure, and C_{60} orientation dynamics change from continuous rotational diffusion to a jumping motion between discrete orientations [3]. The observed jump of thermal conductivity at 260 K can be explained by the substantial reduction of orientational disorder in the sc phase [13]. While Tycko et al. suggested from their NMR experiments that the molecular orientational dynamics in the sc phase involve a jumping motion between symmetry equivalent orientations [3], we require that the jumping motion involves accessible inequivalent orientations separated by finite-energy barriers. In fact, several recent calculations [8,14] suggest that important intermolecular Coulomb interactions arise from the charge transfer accompanying the bond-length difference. In the sc phase, these interactions lead to unique C_{60} molecule orientations that minimize the short-range Coulomb energy and energy-unfavorable "misorientations" [14]. At finite temperature, there will be a finite population of molecules at these misorientations. Because of the energy barriers separating the ground-state orientations and misorientations, the number density of misoriented molecules is time dependent if the starting number density is away from the thermal equilibrium value. If the phonon scattering rate depends on the orientational disorder, the thermal conductivity will also be time dependent.

In order to describe the temperature and time dependence of the thermal-conductivity data quantitatively, we adopt a phenomenological model in which the scattering rate τ_{OD}^{-1} due to orientational disorder is proportional to the occupation probability of the misorientations n_D, $\tau_{OD}^{-1} \propto n_D(T)$. For simplicity, we assume that the temperature dependence of the τ_{OD}^{-1} is due entirely to that of n_D. Since $\tau = (\tau_{OD}^{-1} + \tau_U^{-1})^{-1}$, then we have

$$\kappa = A/[n_D(T) + BT],\qquad(3)$$

where A and B are constants.

To proceed, we assume that each C_{60} molecule has a single misorientation separated from the ground-state orientation by an energy barrier u_1; the energy difference between these two orientations is u_2, and $u_1 \gg u_2$. If v is the average librational frequency of C_{60} molecules, and the interactions between C_{60} molecules are ignored, the rate at which the C_{60} molecule jumps from one orientation to the other is

$$t_r^{-1} = v e^{-u_1/k_B T}.\qquad(4)$$

The occupation probability of misorientations is then

$$n_D(t) = [n_D(0) - n_D(\infty)]e^{-t/t_r} + n_D(\infty),\qquad(5)$$

where $n_D(0)$ is the occupation probability at $t = 0$, and $n_D(\infty) = 1/[1 + \exp(u_2/k_B T)]$ is the thermal equilibrium value as $t \to \infty$. From Eqs. (3) and (5) we have

$$\kappa = [C \exp(-t/t_r) + \kappa_f^{-1}]^{-1},\qquad(6)$$

where

$$C = [n_D(0) - n_D(\infty)]/A$$

and $\kappa_f = A/[BT + n_D(\infty)]$ is the thermal conductivity as $t \to \infty$. Hence we have

$$\ln(\kappa^{-1} - \kappa_f^{-1}) = \ln C - t/t_r.\qquad(7)$$

From Fig. 2, we take the saturated κ in the limit of $t \to \infty$ as κ_f, then plot $\ln(\kappa^{-1} - \kappa_f^{-1})$ versus time t in Fig. 3. They conform to straight lines quite well. By least-squares fits, we extract the relaxation times t_r corresponding to different temperatures. In the inset, we plot $\ln t_r$ vs $1/T$. By least-squares fit with a straight line, we obtain the energy barrier $u_1 = 240 \pm 30$ meV and the librational frequency $v = 10^{12 \pm 2}$ Hz from the slope and the intercept, respectively. These fitting parameters are
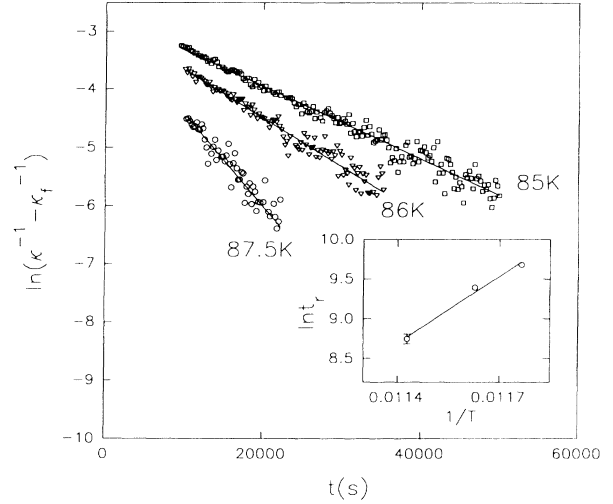

FIG. 3. $\ln(\kappa^{-1} - \kappa_f^{-1})$ vs time for data at temperatures 87.5, 86, and 85 K. The solid lines are the linear least-squares fits. Inset: $\ln t_r$ vs $1/T$. The solid line is the linear least-squares fit.

all presented in Table I. Using κ_f and $\ln C$ (the intercept of linear fit from Fig. 3), we plot Eq. (6) against the data in Fig. 2, and the agreement is quite satisfactory.

In order to fit the temperature-dependent thermal conductivity, we must take into account the finite time spent at each temperature, especially for data points below 90 K. The typical time scale for each data point is ~ 300 s. We use $n_{D,i}(0)$ at each point i as $n_{D,i-1}(t_{i-1})$, where t_{i-1} is the time taken at point $i - 1$. We adjust v and u_1 within the range of values obtained from Fig. 3, and also adjust u_2, A, and B to obtain the best representation of the experimental data. The solid line in Fig. 1 was obtained by using $v = 10^{12}$ Hz, $u_1 = 262.5$ meV, $u_2 = 11.9$ meV, $A = 0.42$ W/mK, and $B = 0.0018$ K^{-1}. All the fitting parameters, as well as those from Fig. 3, are presented in Table I. The κ_f data are also plotted in Fig. 1. The dashed line is the $t \to \infty$ limit of Eq. (6) using the same set of parameters. This represents the thermal equilibrium value of the thermal conductivity κ_f. The overall temperature dependence of the thermal conductivity, as well as the shoulderlike structure at 85 K, is quite nicely reproduced. Our obtained value of $u_1 \sim 262$ meV is comparable to $u_1 = 240$–280 meV from the sound-velocity measurement [11], and $u_1 = 250$ meV from NMR data [3].

The 85-K feature is due to the limitation imposed where the practical time scale is comparable to the

TABLE I. The fitting parameters.

T (K)	t_r (10^4 s)	κ_f (W/mK)	u_1 (meV)	u_2 (meV)	v (s^{-1})	A (W/mK)	B (K^{-1})
87.5	0.63 ± 0.04	1.348	240 ± 30	~ 12	$10^{12 \pm 2}$	~ 0.42	~ 0.0018
86.0	1.2 ± 0.2	1.38					
85.0	1.6 ± 0.2	1.405					

thermal equilibrium relaxation time. For $T \leq 85$ K, the occupation probability of misoriented molecules is essentially frozen at a value of 17%, which means that orientational disorder is always present at low temperatures. Indeed, a recent neutron-scattering experiment by David *et al.* indicated that about 18% static orientational disorder persists down to low temperatures [5].

Our phenomenological model considers only two nearly degenerate orientations, and may be too simple, but the qualitative description of the orientational glassy behavior revealed by this experiment will not change. As for the microscopic origin of the phonon scattering mechanism due to orientational disorder, one possibility may involve phonons scattering off librons due to the coupling between phonon strain field and librational coordinates, similar to the case of the orientational glass KBr:KCN [15]. In our model, we neglect other possible scattering mechanisms, such as phonon scattering from structure defects, etc. We also take the sound velocity and the heat capacity to be independent of temperature. A more complete model should take these effects into account.

In summary, we measured the thermal conductivity of single crystal C_{60} and observed a time-dependent phonon mean free path which is interpreted as evidence for orientational disorder freezing. A simple phenomenological model that involves a thermally activated jumping motion between two nearly degenerate orientations separated by ~ 12 meV and an energy barrier of ~ 262 meV was developed to describe the temperature and time dependence of the thermal conductivity.

[1] H. W. Kroto *et al.*, Nature (London) **318**, 162 (1985).

[2] W. Kräschmer *et al.*, Nature (London) **347**, 354 (1990).

[3] R. Tycko *et al.*, Phys. Rev. Lett. **67**, 1886 (1991).

[4] P. A. Heiney *et al.*, Phys. Rev. Lett. **66**, 2911 (1991).

[5] W. F. David *et al.* (to be published).

[6] Martin P. Gelfand and Jian Ping Lu, Phys. Rev. Lett. **68**, 1050 (1992).

[7] T. Atake *et al.*, Physica C (to be published).

[8] X.-P. Li *et al.* (to be published).

[9] R. L. Meng *et al.* (to be published).

[10] J. M. Ziman, *Electrons and Phonons* (Clarendon, Oxford, 1963), p. 296.

[11] X. D. Shi *et al.*, Phys. Rev. Lett. **68**, 827 (1992).

[12] D. A. Neumann *et al.*, Phys. Rev. Lett. **67**, 3808 (1991).

[13] A similar jump of thermal conductivity due to molecular orientational ordering can be found in a ferroelectric material KH_2PO_4. See Yasutaka Suemune, J. Phys. Soc. Jpn. **22**, 735 (1967).

[14] Jian Ping Lu *et al.* (to be published).

[15] Eric R. Grannan *et al.*, Phys. Rev. Lett. **60**, 1402 (1988); Mohit Randeria and James P. Sethna, Phys. Rev. B **38**, 12607 (1988).