Thermal Conductivity of C₆₀ and C₇₀ Crystals

N. H. Tea¹, R.-C. Yu¹*, M. B. Salamon¹, D. C. Lorents², R. Malhotra², R. S. Ruoff²

¹ Department of Physics, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA
² SRI International, 333 Ravenswood Avenue, Menlo Park, CA 94025, USA

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Abstract. We have performed thermal conductivity measurements on C₆₀ and C₇₀ crystals grown by sublimation. For single crystal C₆₀, the thermal conductivity κ is about 0.4 W/m K at room temperature and is nearly temperature independent down to 260 K. We observed a sharp orientational phase transition at 260 K, indicated by a 25% jump in κ. Below 90 K, κ is temperature dependent, which manifests itself as a shoulder-like structure at about 85 K. The temperature and time dependence of κ below 260 K can be described by a simple model which accounts for the thermally activated hopping of C₆₀ molecules between two nearly degenerate orientations, separated by an energy barrier of about 240 meV. It is found that solvents have a strong influence on the physical properties of C₇₀ crystals. For solvent-free C₇₀ crystal, κ is about constant above 300 K. There is a broad first-order phase transition in κ at 300 K with a 25% jump. We associate this transition with the aligning of the fivefold axes of the C₇₀ molecules along the c-axis of the hexagonal lattice. Upon further cooling, κ increases and is time independent.

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Since the development of efficient techniques [1] for synthesizing C₆₀ and C₇₀, tremendous research activity has been directed toward understanding the physical and chemical properties of the fullerenes and their derivatives. Recent progress has lead to the growth of large (mm-size) C₆₀ crystals [2-3] that are free of solvents.

Experiments and theories have shown many remarkable features in the dynamics of solid C₆₀. X-ray [4-5], nuclear resonance [6], neutron scattering [7], sound velocity [8], dielectric constant [9], and thermal measurements [10-13] on C₆₀ reveal an orientational ordering transition from a room temperature fcc structure to a sc structure at 260 K. Below this transition, the C₆₀ molecules can still jump between nearly degenerate, inequivalent orientations, separated by energy barriers. Furthermore, the orientational order is time dependent, evident as a shoulder-like structure at about 85 K in the thermal conductivity [11]. Theoretical studies [14-15] show that the observed sc structure at low temperature can be understood if the Coulomb interactions between the electron-rich double bonds and the electron-poor single bonds are included in the Hamiltonian in addition to the usual Lennard-Jones potential.

The next higher stable fullerene is C₇₀, which has an elongated “rugbyball” shape. Its geometry suggests that there should be two possible phase transitions. The first corresponds to the locking of the fivefold axes of the C₇₀ molecules along specific crystal directions and the second, to freezing of rotations about that axis. Vaughan et al. [16] reported two reproducible transitions at about 275 K and 335 K from differential scanning calorimetry (DSC) on solvent-free C₇₀ powder which contained less than 20% hcp phase. They also found that the high temperature fcc phase is slightly lower in energy than the hcp phase but that the two phases coexist. However, for single crystals grown by sublimation starting from solvent-free C₇₀ powder, there are two possible crystal structures – fcc and hcp. TEM studies [17] show that crystals with fcc structure have only one phase transition while crystals with hcp structure have more than one. However, mm-size C₇₀ crystals have not been available until now. As a result, little is known about the dynamics of C₇₀.

In this paper, we describe the preparation of mm-size single crystals of both C₆₀ and C₇₀ by sublimation. We then report thermal conductivity measurements on solvent-free C₆₀ and C₇₀ crystals and on C₇₀ crystals containing solvents. For C₆₀, we present a simple model that captures all the essential features in the thermal conductivity. This model takes into account the thermally activated hopping of the C₆₀ molecules between two nearly degenerate orientations separated by a large energy barrier.

1 Sample Preparation

Fullerene-enriched soot was obtained by the arc-method [1]. C₆₀ and C₇₀ were extracted by high-performance liquid-column chromatography. The C₆₀ powder obtained was
99.5% pure. For C\textsubscript{70}, repeated chromatography was necessary to obtain better than 99% purity. The purity of the C\textsubscript{70} powder was determined by SALI (surface-analysis-by-laser-ionization) to be 99.85% pure. The C\textsubscript{60} and C\textsubscript{70} powders were dried under dynamic vacuum for 24 h at 200ºC. This purification process yields highly crystalline C\textsubscript{60}. About 30 mg of dry C\textsubscript{60} powder was loaded in a quartz tube (4 mm ID and 6 mm OD) which was held at a pressure of 10\textsuperscript{-3} Torr for about 12 h after which the quartz tube was sealed under about 20 mTorr of ultra-high purity argon gas. The quartz tube was then placed in a furnace with a linear temperature gradient; the powder was held at 600ºC and the cold end at 500ºC. In about 100 h, mm-sized C\textsubscript{60} crystals were obtained. Shown in Fig. 1 are C\textsubscript{60} crystals about 0.5 × 0.5 × 1.0 mm\textsuperscript{3} with a very flat shiny face. C\textsubscript{60} crystals having a long rectangular shape, about 0.5 mm × 0.3 mm in cross-section ranging from 1 mm to 2 mm long, were also obtained.

C\textsubscript{70} crystals prepared under the same conditions as C\textsubscript{60} have shiny flat faces with dimensions of about 0.5 × 0.4 × 0.4 mm\textsuperscript{3} as shown in Fig. 2a. These C\textsubscript{70} crystals contain solvents and thermal conductivity results were not reproducible. To obtain better C\textsubscript{70} powder, we follow the method used by Vaughan et al. [16]. Residual solvents were eliminated by subliming the C\textsubscript{70} powder at 550ºC in a dynamically pumped quartz tube. Solid C\textsubscript{70} condensed only near the furnace exit and after 20 h, about 15 mg of C\textsubscript{70} powder was collected. The dry C\textsubscript{70} powder was then sealed under about 50 mTorr of argon gas in a quartz tube which was placed in a furnace with a linear temperature gradient. The powder was held at 600ºC and the cold end at 500ºC for 100 h. The temperatures of both ends were slowly cooled to 200ºC and held at 200ºC for two weeks. Crystals with dimension of about 0.5 × 0.5 × 0.9 mm\textsuperscript{3} (see Fig. 2b) were selected for measurements.
X-ray experiments [4-5] show that C\textsubscript{60} undergoes a first-order orientational transition from a fcc structure to a sc structure at about the same temperature. Sound velocity increases with time and then saturates with a different relaxation time at each temperature. The run with a slower cooling rate, 0.09 K/min, results in a larger thermal conductivity than the run with a cooling rate of 0.24 K/min. With decreasing cooling rate, we observed an enhanced \( \kappa \) at a characteristic temperature of about 90 K, as shown in the inset of Fig. 3. The run with a slower cooling rate, 0.09 K/min, results in a larger thermal conductivity than the run with a cooling rate of 0.24 K/min.

To explore this time-dependent property, we measured \( \kappa \) at several temperatures in the vicinity of 90 K as follows. First, the temperature was held at 130 K for a few minutes, followed by rapid cooling to the target temperature in about 1800 s. When the temperature reached the target temperature, we took data continuously until \( \kappa \) saturated. The target temperature was stabilized to better than 1%. Shown in Fig. 4 is the time dependence of \( \kappa \) at three different temperatures. The thermal conductivity increases with time and then saturates with a different relaxation time at each temperature.

### 2 Experimental

The thermal conductivity was measured by the static method. One end of the sample was attached to a block of quartz crystal and a miniature thin-film heater was attached on the other end of the sample. We also mounted a LakeShore silicon diode sensor on the quartz-crystal block. A pair of 12 \( \mu \)m Chromel-Constantan differential thermocouples was mounted on the sample with silver paste. The typical separation between the thermocouple junctions is about 0.2–0.3 mm. The temperature gradient was measured with the heater on and off after waiting for complete saturation of the thermal voltage (a typical delay of 30–60 s). The heat-pulse manipulation and data acquisition were controlled by a personal computer. The heat loss due to thermal conduction via the heater leads and thermocouples and to blackbody radiation is negligible.

### 3 Thermal Conductivity of \( \text{C}_{60} \) Single Crystals

Because \( \text{C}_{60} \) is a van der Waals-bonded molecular solid, its Debye temperature due to the intermolecular phonon modes is low \( \theta_\text{D} \sim 70 \text{K} \) [10]. For \( T \gg \theta_\text{D} \), the specific heat due to propagating modes is constant. The sound velocity of a typical solid is approximately temperature independent, making the thermal conductivity \( \kappa \) an ideal probe of the phonon mean free path through the kinetic expression

\[
\kappa = C v_s \lambda / 3
\]

where \( C \) is the specific heat, \( v_s \) is the sound velocity, and \( \lambda \) is the phonon mean free path. If the orientational disorder in \( \text{C}_{60} \) and \( \text{C}_{70} \) is one of the dominant scatterers of phonons, then measuring \( \kappa \) provides an excellent probe of the orientational order in solid \( \text{C}_{60} \) and \( \text{C}_{70} \).

Shown in Fig. 3 is the temperature dependence of \( \kappa \) for a solvent-free single-crystal \( \text{C}_{60} \). We find that \( \kappa \sim 0.4 \text{W/m K} \) at room temperature and is approximately temperature independent down to 260 K. At 260 K, \( \kappa \) takes a sharp jump from 0.4 to 0.5 W/m K with a transition width of \( \sim 2 \text{K} \). X-ray experiments [4-5] show that \( \text{C}_{60} \) undergoes a first-order orientational transition from a fcc structure to a sc structure at about the same temperature. Sound velocity measurements show only a 4% jump and the lattice constant changes only by \( \sim 0.4\% \). Because the heat capacity due to intermolecular modes is constant at 260 K, the 25% jump in \( \kappa \) must be due to a sudden increase in the phonon mean free path. From NMR experiments [6], the motion of the \( \text{C}_{60} \) molecules was found to be fully dynamic above 260 K while neutron scattering experiments [18] characterized the motion of \( \text{C}_{60} \) as a continuous diffusive rotation. In other words, \( \text{C}_{60} \) molecules rotate essentially freely and isotropically (completely disordered) above 260 K. Below 260 K, the \( \text{C}_{60} \) molecules jump between discrete orientations separated by energy barriers. This suggests that orientational disorder in \( \text{C}_{60} \) causes strong phonon scattering which, in turn, limits the phonon mean free path. As a result, we expect that \( \kappa \) will have a very weak temperature dependence above 260 K, as indeed observed.

Below 260 K, the thermal conductivity increases with decreasing temperature and there is a reproducible shoulder-like structure at about 85 K. Further, the thermal conductivity was found to be time dependent. The cooling rate for the run shown in Fig. 3 is about 0.15 K/min. With decreasing cooling rate, we observed an enhanced \( \kappa \) at a characteristic temperature of about 90 K, as shown in the inset of Fig. 3. The run with a slower cooling rate, 0.09 K/min, results in a larger thermal conductivity than the run with a cooling rate of 0.24 K/min.

### Fig. 3. The temperature dependence of the thermal conductivity of \( \text{C}_{60} \) single crystal. The dot-dashed line is an overlay of E/T for data below 260 K. Inset is a plot of the thermal conductivity for two different cooling rates.
For insulators at high temperature, Umklapp processes dominate and the temperature dependence of the thermal conductivity $\kappa$ goes as $1/T$. Shown in Fig. 3 is an overlay of $\kappa_u = E/T$, where $E$ is an adjustable parameter for data below 260 K. Clearly, there are discrepancies between the experimental data and $\kappa_u$, especially for $T < 90$ K and $T > 150$ K. As shown below, this substantial deviation from $1/T$-behavior arises mostly from the measurement time scale imposed by the experiments.

In order to understand the unusual shoulder-like structure at about 85 K, we must take into account not only the temperature dependence of $\kappa$ but also its time dependence.

We first write $\lambda = v_0 \tau$, where $\tau^{-1} = \sum_{i=1}^{\infty} \tau_i^{-1}$ is the total scattering rate, and $i$ denotes the various scattering mechanisms. At high temperature, phonon-phonon scattering via Umklapp processes play an important role in determining the thermal conductivity. This scattering rate is proportional to temperature, $\tau_u^{-1} \propto T$. Because the phonon scattering rate depends on the orientational disorder, the thermal conductivity will also be time dependent. To account for this time dependence, we introduce the orientational disorder scattering rate $\tau_{od}^{-1}$, which is proportional to the occupation probability of misorientations $n_d(T, t)$. For simplicity, we assume that the temperature dependence of $\tau_{od}^{-1}$ is entirely due to $n_d(T, t)$. Then the total scattering rate is given by

$$\tau = \frac{1}{\tau_{od}^{-1} + \tau_u^{-1}}.$$  

The thermal conductivity $\kappa \propto \tau$ and we can write it as

$$\kappa = \frac{A}{n_d(T, t) + BT}.$$  

To proceed, we need to know $n_d(T, t)$. A recent calculation by Lu et al. [14] shows that below about 270 K, there exist many nearly degenerate orientations separated by potential barriers of order $\sim 300$ meV. For simplicity, we assume two such orientations separated by an energy barrier $E_b$, as shown in Fig. 5. The energy difference between these orientations is $\varepsilon$, where $E_b \gg \varepsilon$. If $\nu$ is the average librational frequency of the C$_{60}$ molecules and the interactions between C$_{60}$ molecules are neglected, then the rate for a C$_{60}$ molecule to thermally jump from one orientation to the other is

$$t_{ij}^{-1} = \nu e^{-E_b/k_BT}.$$  

(4)

The occupation probability of misorientations is given by

$$n_d(T, t) = \frac{[n_d(T, 0) - n_d(T, \infty)] e^{-t/t_\nu} + n_d(T, \infty)}{\nu}.$$  

(5)

and $n_d(T, \infty) = 1/[1 + \exp(\varepsilon/k_BT)]$] is the thermal equilibrium population. By combining (2) and (5), the thermal conductivity can be written as

$$\kappa = \frac{1}{C \exp(-t/t_\nu) + \kappa_f^{-1}},$$  

(6)

where $C = [n_d(T, 0) - n_d(T, \infty)]/A$ and $\kappa_f$ is the thermal conductivity as $t \to \infty$ given by

$$\kappa_f = \frac{A}{n_d(T, \infty) + BT}.$$  

(7)

Taking the logarithm of (6) puts the thermal conductivity in a useful form for analysing the data plotted in Fig. 4. The resulting equation is

$$\ln(\kappa_{\infty} - \kappa_f^{-1}) = \ln C - t/t_\nu.$$  

(8)

In Fig. 4, we take the saturated values of $\kappa$ as $\kappa_f$ and plot the data in the form of (8) in Fig. 6. The data conform to a straight line very well. We extract the relaxation time $t_\nu$ at three different temperatures by a least-squares fit. In the inset, we plot $\ln t_\nu$ versus $1/T$ and a straight line can be drawn through the data. From a least-squares fit, we obtained an energy barrier $E_b = 240 \pm 30$ meV from the slope and $\nu = 10^{12} \pm 2$ from the intercept.

In order to fit the temperature-dependent thermal conductivity, we must account for the finite time spent at each temperature, especially for data points below about 90 K.
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The typical time spent at each data point is about 300 s. We take \( n_{d,i}(T_i, t_i) \) as \( n_{d,i}(T_i, t_i) = n_{d,i-1}(T_{i-1}, t_{i-1}) \), where \( t_{i-1} \) is the time taken at point \( i - 1 \) and we obtained the following relation

\[
n_{d,i}(T_i, t_i) = [n_{d,i-1}(T_{i-1}, t_{i-1}) - n_d(T_i, \infty)] \\
\times e^{-t_i/t_f(T_i)} + n_d(T_i, \infty)
\]  

The adjustable parameters are \( A, B, \varepsilon, \nu \) and \( E_b \). The values obtained from the best representation by (6) in our earlier analysis [11] are \( A = 0.42 \text{ W/m K}, B = 0.0018 \text{ K}^{-1}, \varepsilon = 12 \text{ meV}, E_b = 271 \text{ meV}, \) and \( \nu = 3 \times 10^9 \text{ s}^{-1} \). These parameters together with \( t_f \) and \( \kappa_f \) obtained from Figs. 4 and 6 are presented in Table 1. These parameters were chosen so that \( \kappa_f \) passes through the time-dependent data. As a result of this compromise, the curve only crosses the temperature-dependent data at several points.

Another way to extract \( E_b \) and \( \nu \) is to carry out a least-squares fit of the temperature-dependent thermal conductivity to (6). The inset of Fig. 7 shows a plot of \( \kappa^{-1} \) versus \( T \). Clearly, the thermal conductivity does not follow the \( 1/T \) form, so we carried out a least-squares fit to (6) only for the data below 150 K. The best fit was obtained with \( A = 0.643 \text{ W/m K}, B = 0.0032 \text{ K}^{-1}, \varepsilon = 8.7 \text{ meV}, E_b = 240.5 \text{ meV}, \) and \( \nu = 6.3 \times 10^9 \text{ s}^{-1} \). These parameters are also presented in Table 1. \( E_b = 240.5 \text{ meV} \) obtained from the least-squares fit to our thermal conductivity data is comparable to \( E_b = 240-248 \text{ meV} \) from sound-velocity measurements [8], \( E_b = 250 \text{ meV} \) from NMR experiments [6], \( E_b = 270 \text{ meV} \) from dielectric constant measurements [9], and \( E_b = 230 \text{ meV} \) from heat capacity measurements [13]. Recently, Matsuo et al. [13] reported temperature and time dependence of the heat capacity of solvent-free C₆₀ powder. Their time-dependent measurements are similar to the method used in our thermal conductivity experiments. Our \( \nu \) of \( 6.3 \times 10^9 \text{ s}^{-1} \) agrees very well with their \( \nu = 2.5 \times 10^{10} \text{ s}^{-1} \).

In Fig. 7, we show a plot of \( \kappa \) (dot-dashed line) and \( \kappa_f \) (dotted line), which represents the thermal equilibrium value of the thermal conductivity, from [11]. Also shown in Fig. 7 are \( \kappa \) (solid line) and \( \kappa_f \) (dashed line) generated from the least-squares-fit parameters. Both \( \kappa \)'s reproduce well the temperature dependence of the thermal conductivity data including the shoulder-like structure at 85 K. As a result of our choice of parameters [11], \( \kappa_f \) (dotted line) also goes through the time-dependent data. However, \( \kappa_f \) (dashed line) calculated from the least-squares-fit parameters does not go through the saturated \( \kappa_f \) obtained from time-dependent measurements. This discrepancy is not surprising, given the crudeness of our model. Theoretical model [14] predicts a variety of energy barriers and consequently, a range of relaxation times. Evidently, fits to the short-time behavior represented in Fig. 7 tend to overestimate the ultimate long-time limit of the disorder probed by the data of Fig. 4. Also

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**Table 1. The fitting parameters**

<table>
<thead>
<tr>
<th>( T ) [K]</th>
<th>( t_f [10^4 \text{ s}] )</th>
<th>( \kappa_f [\text{W/m K}] )</th>
<th>( E_b [\text{meV}] )</th>
<th>( \varepsilon [\text{meV}] )</th>
<th>( \nu [\text{s}^{-1}] )</th>
<th>( A [\text{W/m K}] )</th>
<th>( B [\text{K}^{-1}] )</th>
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<tbody>
<tr>
<td>87.5</td>
<td>0.63 ± 0.04</td>
<td>1.348</td>
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<tr>
<td>86.0</td>
<td>1.20 ± 0.2</td>
<td>1.380</td>
<td></td>
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<tr>
<td>85.0</td>
<td>1.60 ± 0.2</td>
<td>1.405</td>
<td></td>
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</tr>
<tr>
<td>Parameters from [11]</td>
<td>271.0</td>
<td>12.3</td>
<td>3.0 × 10⁹</td>
<td>0.420</td>
<td>0.00180</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Least-squares-fit parameters</td>
<td>240.5</td>
<td>8.70</td>
<td>6.3 × 10⁹</td>
<td>0.643</td>
<td>0.00332</td>
<td></td>
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</tr>
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</table>
we assume in our model that \( n_{d,i}(T_i, t_i) = n_{d,i-1}(T_{i-1}, t_{i-1}) \) which does not account for the variation in \( n_d \) between data points. However, the qualitative picture described here should remain valid. This simple model shows that the shoulder-like structure at 85 K is due to the measurement time scale imposed by the experiments.

Our simple model considers only two nearly degenerate orientations and does not include other scattering mechanisms such as defect scattering, four-phonon scattering, phonon-libron scattering, etc. The model also assumes that the sound velocity and the heat capacity are temperature independent and neglects possible phonon scattering from the intramolecular modes. Solid \( C_{60} \) has many nearly degenerate orientations at low temperature and a more complete calculation should take these into account. However, the qualitative description of the glassy behavior is expected to remain unchanged.

Shown in Fig. 8 are plots of the calculated \( \kappa \) and the occupation probability of misorientations \( n_d(T, t) \), using the least-squares-fit parameters with various wait times between data points for the double-well model. Clearly for \( T < 90 \) K, the values of the thermal conductivity approach the equilibrium values as the time taken between data points approaches infinity. For \( T > 90 \) K, the calculated \( \kappa \) is time independent. The occupation probably for temperatures below the shoulder-like structure is essentially frozen due to the long relaxation time \( t_i \) required for the molecules to reorient. This means that orientational disorder is always present at low temperature unless the experimental time scale is infinitely long. Our experimental time scale corresponds to a frozen value of about 22% in the occupation probability shown as the dotted line in Fig. 8. Indeed, a recent neutron scattering experiment by David et al. [7] found that about 18% static orientational disorder persists down to 10 K. Our earlier analysis [11] showed a frozen-in disorder of about 17%.

A theoretical calculation by Lu et al. [14] showed that, because many local energy maxima exist at low temperature, there is a glassy transition between 90 K and 130 K depending on the experimental time scale. Below this transition, the disorder becomes frozen.

5 Thermal Conductivity of \( C_{70} \)

Solid \( C_{70} \) has a “rugbyball” shape; we naively expect that there must be at least two phase transitions. Further, its elongated shape should inhibit rotations; thus, its transition temperature should be higher than \( C_{60} \). Because its shape makes it similar to the classic \((KBr)_{1-x}(KCN)_x \) orientational glass and \( C_{60} \) was shown to be orientationally disordered below 90 K, we wish to explore these possibilities in solid \( C_{70} \).

Shown in Fig. 9 is the temperature dependence of the thermal conductivity of \( C_{70} \) crystals containing solvents. The thermal conductivity varies from run to run and was highly non-reproducible. Further, there is an unusual peak in the thermal conductivity on warming. Unlike solvent-free \( C_{60} \) crystals, the thermal conductivity decreases with decreasing temperature. This type of temperature dependence is similar to amorphous solids and conventional glasses such as vitreous silica where the phonon mean free path increases slowly with decreasing temperature and \( \kappa \) follows approximately the heat capacity. If the pure \( C_{60} \) extract was not dried at 200°C for 24 h, its high resolution ac heat capacity [19] showed an orientational phase transition at 220 K rather than at 260 K for solvent-free \( C_{60} \). In a recent paper by Atake et al. [20], solvents were found to have a strong influence on the orientational phase transition in solid \( C_{60} \).
Shown in Fig.10 is the temperature dependence of the thermal conductance of solvent-free C$_{70}$ crystals. Because the shape of the C$_{60}$ crystals is quite irregular, an accurate calculation of the thermal conductivity is not possible. The thermal conductance is $\sim 0.068 \text{ W/K}$ above about 300 K. At about 300 K, there is a 25% jump in the thermal conductance with a broad transition width of $\sim 15$ K. The size of this jump is the same as in C$_{60}$ crystals. Below this transition, the thermal conductance increases with decreasing temperature, analogous to the thermal conductivity of solvent-free C$_{60}$ crystals. The thermal conductance reaches a maximum at about 25 K and then decreases with decreasing temperature.

Vaughan et al. [16] have performed DSC measurements on solvent-free C$_{70}$ powder and found two reproducible phase transitions at about 275 K and 335 K. They also found coexistence of fcc and hcp phases in their C$_{70}$ powder but that the hcp phase could be reduced by annealing. A recent TEM diffraction experiment by Verheijen et al. on solvent-free C$_{70}$ crystals found that, for C$_{70}$ crystals with an fcc structure, there is a single phase transition while for C$_{70}$ crystals with a hcp structure, there are several transitions. They suggest that the crystals with hcp structure undergo two transitions: alignment of the fivefold axes of the C$_{70}$ molecules with the $c$-axis of the hexagonal lattice somewhat above room temperature and freezing of rotations about the fivefold axis near the ice point. We attribute the jump at about 300 K in our thermal conductance with the alignment of the fivefold axes of the C$_{70}$ molecules along the $c$-axis of the hexagonal lattice. We have also performed high-resolution ac heat capacity measurements on these solvent-free C$_{70}$ crystals and the results together with detailed measurements of the thermal conductance will be reported elsewhere.

In summary, we have measured the thermal conductivity of C$_{60}$ and C$_{70}$ crystals that are free of solvents and C$_{70}$ crystals that contain solvents. At 260 K, C$_{60}$ crystals undergo a first-order phase transition from a fcc structure to a sc structure. Below 90 K, the thermal conductivity of C$_{60}$ is time dependent which is interpreted as freezing of the orientational disorder. A simple model is developed to explain the temperature and time dependence of the thermal conductivity of C$_{60}$. The temperature dependence of the thermal conductivity of C$_{70}$ crystals containing solvents behaves like amorphous solids and is non-reproducible. Solvent-free C$_{70}$ crystals undergo a first-order phase transition at about 300 K. We identify this transition as the alignment of the fivefold axes of the C$_{70}$ molecules along the $c$-axis of the hexagonal lattice.

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