

Thermal conductivity of C_{60} at pressures up to 1 GPa and temperatures in the 50–300 K range

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(Received 7 December 1995)

The thermal conductivity λ of C_{60} shows anomalies near 260 K and 90 K which are associated with the well-established phase transition and glass transition, respectively. Both transition temperatures increase with pressure, at the rates 120 K GPa^{-1} and 62 K GPa^{-1} , respectively. With increasing temperature, λ of the simple cubic (sc) phase increased below 170 K (glasslike behavior) but decreased above. The glasslike behavior of λ is probably due to a substantial amount of lattice defects. Possible reasons for the change of sign of $d\lambda/dT$ near 170 K are discussed. In the face centered cubic (fcc) phase ($T > 260 \text{ K}$ at atmospheric pressure) λ was almost independent of temperature, a behavior which is far from that of an ordered crystal ($\lambda \propto T^{-1}$ for $T > \text{Debye temperature}$). This result can be attributed to the molecular orientational disorder of the fcc phase. The relaxation behavior associated with the glassy state and its unusually strong dependence on thermal history are discussed briefly, and data which support a previously reported relaxation model are presented. At room temperature, the density dependencies of λ , $(\partial \ln \lambda / \partial \ln \rho)_T$, were 5.5 and 9.5 for the fcc and sc phases, which are values typical for an orientationally disordered phase and a normal crystal phase, respectively. [S0163-1829(96)00130-0]

I. INTRODUCTION

The properties of buckminsterfullerene, C_{60} , have been studied in numerous investigations,^{1,2} many of these also under high pressure. In the present study, the thermal conductivity λ of C_{60} was measured at high pressure. In general, λ provides information about structural order and phase behavior. For C_{60} , measurements of λ have previously provided fundamental information such as the observation of a glass transition at about 90 K at atmospheric pressure.^{3,4}

C_{60} has two phases which we will refer to as the face-centered-cubic (fcc) phase, which is the stable phase at high temperatures, and the simple-cubic (sc) phase, respectively. The fcc phase is an orientationally disordered crystal (odic) phase. In such a phase, the molecules show translational periodicity of molecular centers but no long-range periodicity of the molecular orientation. A molecule in an odic phase can occupy any one of an often large number of favored orientations. A change of orientation can take place either by occasional jumps, after spending most of the time undergoing librational motions, or by rapid reorientation. The latter behavior is found for the C_{60} molecules in the fcc phase.⁵ The transition fcc phase \rightarrow sc phase occurs at about 260 K at atmospheric pressure. In the sc phase, orientational disorder is still present but to a smaller extent than in the fcc phase. Models based on the assumption that the C_{60} molecules in the sc phase occasionally jump between two orientations, commonly referred to as hexagon and pentagon orientations, fit experimental data very well. The models yield a small energy difference of about 10 meV between the two orientational states and an energy barrier for the reorientational motion of roughly 250 meV. With decreasing temperature, of course, an increasing number of molecules occupy the orientation which corresponds to the low-energy state (pentagon orientation at atmospheric pressure). However, at 90 K this ordering process essentially ceases and the remaining orien-

tational disorder becomes frozen in, because the probability for the thermally activated molecular jumps between the two orientations becomes small. Below about 90 K, the reorientational rate is insufficient to produce the equilibrium molecular orientational state within the normal time scale of an experiment. The resulting state of frozen-in orientational disorder is referred to as a glassy crystal state,⁶ and the associated glassy crystal transition at 90 K is a special case of a glass transition.

The thermal conductivity of C_{60} has been studied at atmospheric pressure in three previous investigations.^{3,4,7,8} Yu and co-workers^{3,4} measured λ for a single crystal prepared by sublimation and found that λ of the fcc phase was almost independent of temperature, a result which agrees well with that found for other odic phases.⁹ The results for the sc phase ($\lambda \propto T^{-1}$) resembled those of crystals which are both positionally and orientationally ordered, which indicates that the C_{60} molecules exhibit (nearly) orientational order. However, as mentioned above, the results for λ also showed evidence for a glassy crystal transition at about 90 K, indicated by a time dependence of λ below 90 K and a sharp change in $d\lambda/dT$ at 90 K. Both these results are consistent with the two orientational state models described above. The other two investigations^{7,8} of λ both concerned polycrystalline C_{60} . In one of these,⁸ the specimen contained substantial amount (15%) of C_{70} . Both investigations^{7,8} showed that λ was almost independent of temperature in the fcc phase, in agreement with the single-crystal data. However, λ of the polycrystalline samples were smaller in magnitude by factors of two⁷ and four,⁸ respectively. Data for λ of the sc phase ($T < 260 \text{ K}$) were recorded only for the C_{60}/C_{70} mixture.⁸ These data exhibited a glasslike temperature dependence for λ (positive $d\lambda/dT$ at constant pressure) in contrast with the dependence $\lambda \propto T^{-1}$ which was obtained for the sc phase of the single crystal. In addition, the data showed no evidence for a fcc \rightarrow sc phase transition or a glassy crystal transition.

II. EXPERIMENT

We used the transient hotwire method to measure simultaneously the thermal conductivity λ and the heat capacity per unit volume ρc_p under pressure.¹⁰ The hotwire probe used was a Ni wire (0.1-mm diameter) placed horizontally in a ring of constant radius within a Teflon cell. The probe, surrounded by the medium under investigation (2 g polycrystalline C_{60} , see below), was heated by a 1.4-s pulse of approximately constant power and the wire resistance was measured versus time. This enabled the temperature rise of the wire to be determined. A theoretical expression for the temperature rise was fitted to the data points, thereby yielding λ and ρc_p . For temperatures above 100 K, the inaccuracy was estimated as $\pm 2\%$ in λ and $\pm 5\%$ in ρc_p assuming perfect thermal contact between the hotwire and the sample.¹⁰ Owing to the decreased sensitivity of the hotwire probe, the inaccuracy increases with decreasing temperature and was $\pm 4\%$ in λ at 40 K. (The inaccuracy in ρc_p was not estimated but is probably substantially larger than 5%.)

Two batches of C_{60} , one of which was purified by sublimation, were supplied by Term USA, Berkeley, CA, and had a stated purity $>99.9\%$. The nonsublimed specimen was identical to that used in a recent study of compressibility¹¹ and all results except those presented in Fig. 7 pertain to this batch. The samples were dried under low dynamic pressure (0.1 Pa) for 1 day at 200 °C and then enclosed in glass tubes. Raman spectroscopy analysis of both batches showed that the amount of solvents was less than the experimental resolution, which is 0.1% by mass. The results for λ of the sublimed specimen were 6% larger at room temperature and 30% larger at 80 K than those of the nonsublimed specimen. To investigate the effect of annealing, we measured λ of two samples (nonsublimed material) which had been subjected to different annealing procedures. One sample was annealed at 200 °C for 2 days whereas the other was annealed at 280 °C for 3 days followed by annealing at 200 °C for 5 days, all at 0.1 Pa. The results for these two samples were the same to within the experimental inaccuracy. The samples were characterized using x-ray (MoK α) analysis and found to exhibit the same x-ray-diffraction pattern. As described below, our data for λ indicate a substantial amount of structural disorder which might be produced by nonhydrostatic pressure conditions in the sample cell. However, the x-ray analysis showed no significant difference in peak width and positions between fresh samples and those subjected to high pressure. There are two possible explanations for this: Either the structural disorder was present already in the fresh sample, or the x-ray pattern did not change sufficiently to enable the observation of increased structural disorder.

The samples were loaded in the sample cells in an atmosphere of dry argon. The cells were mounted in a piston-cylinder type of pressure vessel with an internal diameter of 45 mm and a load was applied using a 5 MN hydraulic press. Temperature was varied by cooling or warming the whole pressure vessel and was measured using an internal Chromel versus Alumel thermocouple which had been calibrated against a commercially available (calibrated) silicon-diode thermometer. Pressure was determined from load-area with an empirical correction for friction which had been established by comparison with directly measured pressure in a

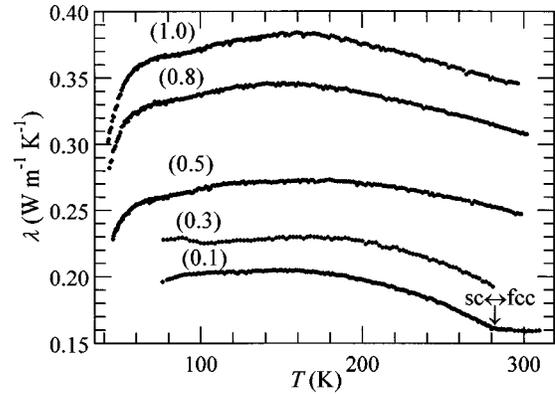


FIG. 1. Thermal conductivity plotted against temperature, at pressures in GPa given in parentheses. All data except at 0.3 GPa are at decreasing temperature.

hydrostatic experiment. The inaccuracy in temperature was estimated as ± 0.5 K and the inaccuracy in pressure as ± 40 MPa. The vessel was cooled with a closed helium gas cycle refrigerator. The apparatus has been described in detail elsewhere.¹²

Measurements were made along either isobars or isotherms. During measurements along isobars, the rate of temperature change was typically in the range 0.1–0.5 K min⁻¹.

III. RESULTS AND COMPARISON WITH PREVIOUS WORK

A. The temperature and pressure dependence of λ

Figure 1 shows the temperature dependence of λ at different pressures. In contrast with ordered crystals, λ of our polycrystalline C_{60} depends weakly on temperature between 70 and 200 K. As is well known, ordered simple crystals such as alkali halides exhibit typically $\lambda \propto T^{-1}$ near and above the Debye temperature, which at atmospheric pressure is roughly 60 K for C_{60} . As mentioned, $\lambda \propto T^{-1}$ was indeed obtained for single crystal C_{60} .^{3,4} In Fig. 2 we show our results, extrapolated to atmospheric pressure, together with literature data for both single-crystal^{3,4} and C_{60}/C_{70} mixture.⁸

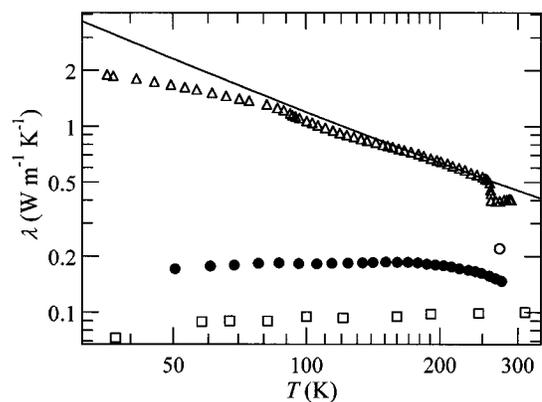


FIG. 2. Thermal conductivity plotted against temperature: present work (●), Yu and co-workers (Refs. 3 and 4) (△), Withers *et al.* (Ref. 7) (○), Olson *et al.* (Ref. 8) (□). The solid line corresponds to $\lambda \propto T^{-1}$.

The significant differences, in both magnitude and temperature dependence, between our results and those for a single crystal can probably be accounted for by a substantial amount of structural disorder in our sample. Polycrystalline samples of complex crystals sometimes exhibit a significantly weaker temperature dependence than $\lambda \propto T^{-1}$.¹³ Generally, various kinds of structural disorder have been suggested to be responsible for the phonon scattering which causes this weaker temperature dependence. Results for $\lambda(T)$ of ordinary glasses provide evidence for such interpretation. In the temperature range considered here (40–300 K), glasses exhibit a λ which in general is almost independent of temperature and, in fact, *increases* slightly with increasing temperature. As seen in Fig. 2 our results for $\lambda(T)$ show an intermediate behavior between those found for glasses and ordered crystals, respectively. At temperatures below about 170 K, λ behaves as in a glass whereas above 200 K the temperature dependence of λ approaches that found for ordered crystals. The latter is verified by least-squares fits in the range 200–260 K, where typically $\lambda \propto T^{-0.5}$ is found as an average in the whole range whereas a fit close to the fcc-sc transition temperature yields $\lambda \propto T^{-0.9}$. As shown in Fig. 2, the change in $d\lambda/dT$ at about 170 K is not a feature which occurs in our sample only. The data for λ of the single crystal show the same tendency, which is most clearly seen by comparing with a line corresponding to $\lambda \propto T^{-1}$ (solid line in Fig. 2). In ordered crystals, the T^{-1} dependence arises due to three phonon umklapp processes but, as we shall explain in the discussion section, it is possible that a phase transition is responsible for the change in $d\lambda/dT$ at about 170 K. If this is the case then our data yield transition temperatures which are only weakly pressure dependent (≈ 20 K GPa⁻¹). It should be noted that the “glassy” behavior of λ discussed above indicates structural disorder in the sample *in addition* to the molecular orientational disorder which is responsible for the glassy crystal transition.

Concerning the transition behavior, our data are in agreement with that of the single-crystal C_{60} .^{3,4} However, as shown in Fig. 2, the temperature dependence of λ below about 170 K is in better agreement with that found by Olson *et al.*⁸ for the *compacted* polycrystalline C_{60} (85%) mixed with C_{70} . The polycrystalline mixed C_{60}/C_{70} sample exhibited values for λ which were glasslike in the whole temperature range 40–300 K (Fig. 2). This glassy behavior is probably partly due to the large amount of C_{70} present. However, as shown in the present investigation, even C_{60} of purity better than 99.9% exhibits glasslike behavior for λ (below 170 K). Our results together with those of Olson *et al.*⁸ show that a substantial amount of structural disorder can be introduced in the lattice of C_{60} . This might be an effect of the method used in applying pressure on the sample. In our case, the pressure transmitting medium is Teflon and it is therefore impossible to obtain perfect hydrostatic pressure. The result might be a breaking of the weak intermolecular van der Waals bonds of C_{60} , leading to crystal imperfections such as stacking faults, interstitials and vacancies. Since the sample which had been pressurized to 1 GPa gave essentially the same results as the fresh sample, this effect must occur mainly during the *initial* pressurization of the sample. Unfortunately, this pressurization cannot be monitored using data for λ since the thermal contact between the solid sample and

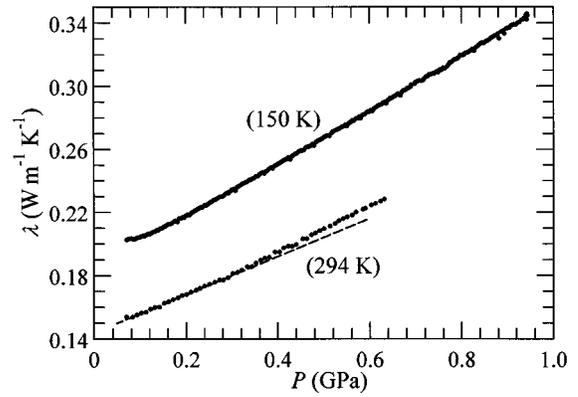


FIG. 3. Thermal conductivity plotted against pressure, at temperatures given in parentheses. The dashed line represents the best fit of a first-order polynomial to the low-pressure data at 294 K.

the hotwire is insufficient during the first pressure increase up to about 0.05 GPa. For other materials we have found good agreement between data for λ of single crystals at atmospheric pressure and those for polycrystalline samples under pressure.¹⁴ However, C_{60} might be a special case since it has been shown to be affected by mechanical grinding. Using DSC measurements, de Bruijn *et al.*¹⁵ found that the peak in the heat capacity, associated with the sc→fcc phase transition, became smeared for a sample which had been subjected to mechanical grinding. In two recent investigations,^{16,17} it has been shown that the peak is less pronounced and can even split into two peaks for samples which exhibit crystal imperfections such as stacking disorder. A probable explanation is therefore that the grinding produces a lot of structural defects which then cause the observed transition behavior. It follows that nonhydrostatic conditions might be responsible, at least partly, for the substantial amount of structural disorder which apparently is present in our C_{60} sample.

Figure 3 shows $\lambda(P)$ both at room temperature and 150 K. The data at room temperature exhibit an increase in $d\lambda/dP$ at about 0.3 GPa, which is shown by the deviation from the linear extrapolation of the low-pressure data (dashed line in Fig. 3). This coordinate corresponds well with that previously observed¹¹ for the fcc→sc phase transition in this sample. We note that the fcc phase has a somewhat weaker pressure dependence of λ than the sc phase. Both phases do, however, show the commonly observed⁹ linear increase of λ with pressure. Using data for $\lambda(P)$ together with data for the compressibility of C_{60} (Ref. 11) for the same specimen it is possible to calculate the density dependence of λ , which is conveniently described using the Bridgman parameter $g = (\partial \ln \lambda / \partial \ln \rho)_T$. At room temperature, we find $g = 5.5$ and 9.5 for the fcc and sc phases, respectively. At 150 K, we obtained $g = 8.7$ for the sc phase. Since ionic phases typically show values for g in the range 4–7 whereas ordered crystals exhibit values in the range 6–10,⁹ the density dependencies of λ are typical for the type of phases that C_{60} exhibits. A simple theory for g (Ref. 9) yields $g = 3\gamma + 2q - 1/3$, where γ is a weighed value of the Grüneisen parameters for the modes contributing to λ and $q = -(\partial \ln \gamma / \partial \ln \rho)_T$. With this theory, the unusually large intermolecular anharmonicity of C_{60} (Ref. 18) should yield a much larger value for g than that

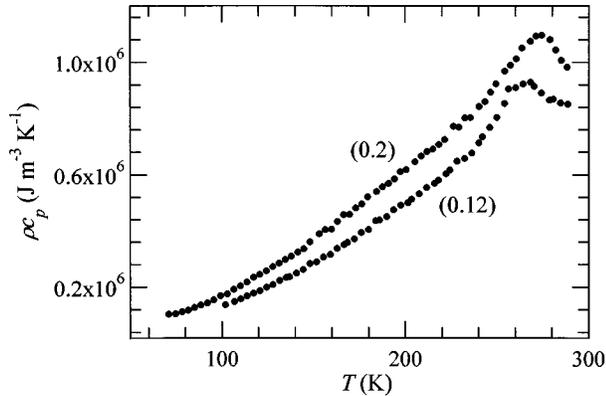


FIG. 4. Heat capacity per unit volume plotted against temperature, at pressures in GPa given in parentheses.

normally observed for crystals. Using a plausible value for q ($=1-2$) (Ref. 19 and 20) together with an estimate for γ of the acoustical modes ($\gamma \approx 5$),¹⁸ gives $g \approx 18$. This difference between theory and experiment might be due to the disorder in our sample since amorphous states normally exhibit $g \approx 1-4$. It is therefore important to note that the results for g given here pertain to our C_{60} sample and might be significantly higher for single crystal C_{60} .

B. The heat capacity per unit volume ρc_p

As mentioned in the experimental section, the hotwire method yields data for both ρc_p (Fig. 4) and λ . However, the data for ρc_p have a much larger uncertainty than those for λ , especially at low temperatures. Our data for ρc_p at 0.2 GPa and room temperature were typically 15% lower than a value calculated using data for heat capacity⁶ and density at atmospheric pressure. We prefer therefore to use these data only to discuss the transition between the sc and fcc phases.

C. The phase transition

The transition between the fcc and sc phases could be detected as a change in the slope of $\lambda(T)$ (Fig. 1) and as a peak in the data for $\rho c_p(T)$ (Fig. 4) at about 270 K at 0.1 GPa. The transition temperatures, defined by the maxima in $\rho c_p(T)$, are 265 and 275 K at 0.12 and 0.2 GPa, respectively. The slope of the transition line calculated from these data is $\Delta T/\Delta P = 120 \text{ K GPa}^{-1}$, which is within the range 100–170 K GPa^{-1} that has been found in other investigations of C_{60} .^{11,21}

Normally λ changes discontinuously at a first-order transition such as that between the fcc and sc phases and this was also observed by Yu and co-workers^{3,4} (Fig. 2). We see no such steplike feature in our data (Fig. 1). Several effects could be the cause of this. Our data for λ indicate the presence of a substantial amount of structural disorder in addition to the molecular orientational disorder. This structural disorder apparently causes the transition to occur over a considerable temperature interval,¹⁵⁻¹⁷ which more or less can remove the discontinuity in λ . Other possibilities are a broadening of the transition region due to nonhydrostatic pressure and a change of the transition to second order at high pressures. In our view, the first two explanations are

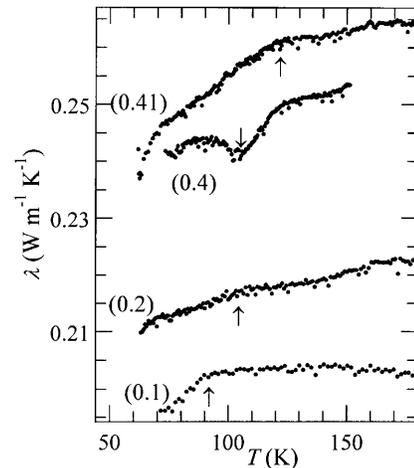


FIG. 5. Thermal conductivity plotted against temperature showing glass transition anomalies (arrows pointing upwards). The arrow pointing downwards indicates the temperature of maximum orientational disorder ($P/H=50/50$) for a sample which has been pressurized from 0.07 to 0.4 GPa below T_g and thereafter heated (see text).

most likely to be valid. We note that Lundin and Sundqvist¹¹ found a continuous broadening or smearing of the transition with pressure.

D. The glassy crystal transition

We associate the rather abrupt changes in $d\lambda/dT$, indicated by arrows pointing upwards in Fig. 5, with the glassy crystal transition. (The results with an arrow pointing downwards are discussed below.) Such an interpretation is supported by previous results for λ near glass transitions. In general, λ does not change much at glass transitions. For instance, at the glass transition temperature T_g of glycerol, λ decreases only slightly on heating.^{22,23} Another sign of a glass transition can be a discontinuous change in the $d\lambda/dT$. For glycerol, $d\lambda/dT$ is weakly positive below T_g but slightly negative above.^{22,23} A transient method, such as that employed here, often indicates an apparent peak in λ and a dip in ρc_p at a glass transition.^{22,23} These two anomalous features are observed when the structural relaxation, associated with the glass transition, causes a pronounced effect on the temperature rise of the probe (hotwire). C_{60} is a so-called strong glass former²⁴ in which the relaxation time changes relatively slowly with temperature and, furthermore, glassy crystal C_{60} should exhibit only a small amount of residual entropy due to the relatively small degree of orientational disorder. Consequently, the *weak* relaxation effects are distributed in a large temperature range and, therefore, the lack of relaxation anomalies in λ and ρc_p at T_g of C_{60} is not surprising. All or some of the phenomena mentioned above *might* be indications of a glass or a glassy crystal transition. For example, it has been shown that the glassy crystal transition in cyclohexanol²⁵ exhibits several of these phenomena, whereas the glassy crystal transitions of cyclooctanol²⁶ can be detected only by a slight decrease in λ .

The observed changes in $d\lambda/dT$ are not very pronounced but since it is well established that a glassy crystal transition occurs in C_{60} , it is sensible to ascribe these to the transition,

especially since a similar behavior of λ has been found at the glassy crystal transition of cyclohexanol²⁵ and the glass transition of glycerol.^{22,23} Furthermore, a sharp change in $d\lambda/dT$ was noticed at 90 K in the data for the single crystal,^{3,4} and an extrapolation to atmospheric pressure of the temperatures for our similar anomalies yields 90.5 K. We have considered the possibility of other explanations for the change in $d\lambda/dT$, for instance, that the melting point of argon is responsible. Argon was used as a protecting gas in the glove box during loading of the C_{60} in the sample cell. However, since the melting point of argon is 84 K at atmospheric pressure and 145 K at 0.3 GPa,²⁷ this seems implausible.

The change in $d\lambda/dT$ can instead be correlated with the orientational order being temperature dependent above T_g but independent of temperature below. The C_{60} orientations are commonly referred to as pentagon (P) and hexagon (H) orientations, in which a double carbon-carbon bond on one molecule faces the electron deficient center of a pentagon or a hexagon of its nearest neighbor. At atmospheric pressure, the P orientation is favored and the P/H occupation ratio and the orientational order increase with decreasing temperature.²⁸ As a result, phonon scattering against orientational disorder decreases. At T_g , the P/H ($=83/17$) (Ref. 28) ratio becomes essentially frozen and the phonon scattering arising from orientational disorder becomes temperature independent which yields the change in $d\lambda/dT$. In this model it is also possible to explain why T_g appears more or less clearly in $\lambda(T)$ at different pressures. As shown in Fig. 5, it is much more difficult to determine T_g at 0.2 GPa than at 0.1 and 0.41 GPa. Furthermore, at high pressures above about 0.7 GPa, it is also difficult to distinguish T_g (not shown). Both these facts can be explained in terms of a temperature-independent P/H ratio both below and above T_g for pressures above about 0.7 GPa as well as at 0.2 GPa. It has been shown²⁹ that the P/H ratio depends very strongly on the pressure. The P orientation, which dominates at low temperatures and pressures, rapidly gives way to the H orientation which permits closer packing.² At 150 K, the P/H ratio changes approximately linearly with pressure, passing through 50/50 at 0.191 GPa.²⁹ Since the two orientations have the same energy at this pressure, the P/H ratio must be 50/50 at all temperatures near 0.191 GPa. This result together with P/H at atmospheric pressure²⁸ can be used to estimate P/H at all pressures and temperatures using the assumption that the P/H ratio varies linearly with pressure. Such an estimate shows that at pressures above about 0.7 GPa, the H orientation is much preferred and $P/H \approx 0/100$ is the equilibrium state up to temperatures well above T_g . (If we assume instead that the difference in free energy varies linearly with pressure we find somewhat higher values for the P/H ratio above 0.5 GPa, and a small fraction of P oriented molecules remains above 0.7 GPa.) It follows that orientational order and, consequently, λ is neither much affected at T_g near 0.2 GPa nor at T_g at high pressures (>0.7 GPa), which explains the difficulties to observe a glassy crystal transition in these pressure ranges. An additional complication at high pressure is that T_g falls very close to the maximum in $\lambda(T)$ at about 160 K (see Fig. 1), and it is thus difficult to say whether the change in $d\lambda/dT$ actually disappears completely or whether there is a small residual cusp due to orientational fluctuations even at high pressures. The

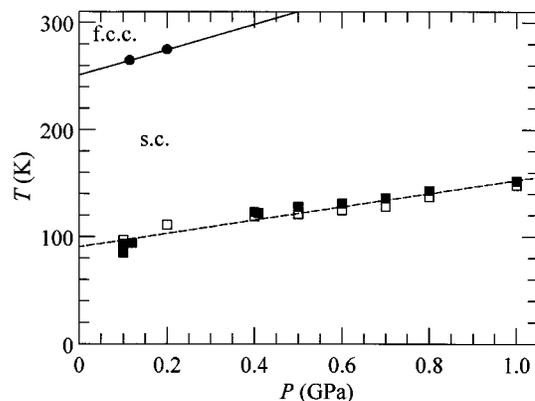


FIG. 6. Phase diagram for C_{60} . (●) fcc \rightarrow sc phase transition, “normal” glass transition (see text) observed on (□) cooling, (■) heating.

results for T_g above 0.7 GPa must therefore be regarded as uncertain even though the extracted transition coordinates appear to agree fairly well with those extrapolated from low pressures as shown by the phase diagram (Fig. 6). Moreover, a few runs for a specimen purified by sublimation (see experimental) yielded more pronounced T_g anomalies above 0.7 GPa (not shown) than those of the nonsublimed specimen (Fig. 1). The P - T coordinates for the transition yield $dT_g/dP = 62$ K GPa⁻¹ (for both specimens). Taking into account the normal curvature of such a transition line this indicates that the glass transition pressure at 293 K is larger than 3.5 GPa.

As described in detail elsewhere,³⁰ the results for λ near T_g depends very much on the thermal history of the sample. The discussion above concerns what we call the “normal” glassy crystal transition, observed when the pressure is the same on heating through T_g as on cooling. If, however, the pressure is changed below T_g then a different situation arises. For instance, if C_{60} is cooled at 0.07 GPa then $P/H = 75/25$ at T_g . Since the molecular reorientation is very slow below T_g , changes in pressure and temperature do not significantly change this ratio once the sample is in the glassy crystal state. If the pressure is increased to 0.4 GPa the P/H ratio remains 75/25, although in the “normal” glassy crystal state it should have been 20/80. The results for a sample with such a thermal history when heated at 0.4 GPa are shown in Fig. 5. In this case, $\lambda(T)$ exhibits a minimum (arrow pointing downwards) which can be explained by P/H relaxation towards the equilibrium value of 20/80. It is reasonable to assume that $\lambda(P, T)$ should exhibit a minimum at maximum orientational disorder, i.e., $P/H = 50/50$. Since we must pass through the maximum degree of orientational disorder during the relaxation from $P/H = 75/25$ to $P/H = 20/80$, a minimum in λ is expected. It is clear from the results in Fig. 5 that the relaxation in this case can be observed at temperatures well below the “normal” T_g at 0.4 GPa. It is therefore apparent that the reorientational relaxation time (and T_g) must be strongly dependent on the P/H ratio and, in particular, increase with a decreasing P/H ratio. This increase can be associated with the volume decrease which accompanies with a decreasing P/H ratio. As a consequence of the smaller intermolecular distances the potential barrier for the reorientational motion increases, which yields a larger reori-

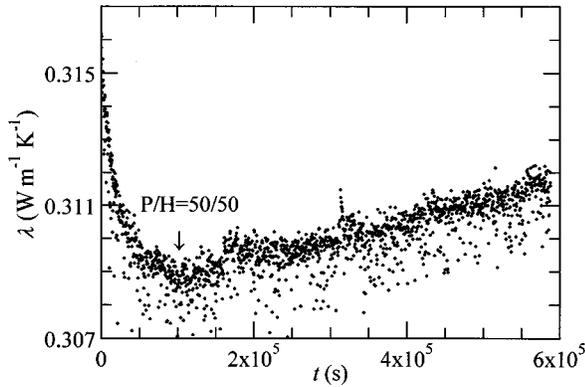


FIG. 7. Thermal conductivity plotted against time at 0.7 GPa and 100 K. Thermal history: sample cooled from room temperature to below T_g at 0.07 GPa, pressurized to 0.7 GPa and, subsequently, heated to 100 K.

entational relaxation time. It follows that the reorientational relaxation time (and T_g) in C_{60} is unusually strongly dependent on the thermal history since the equilibrium P/H ratio varies strongly with pressure and temperature.

An interesting consequence of the model described is that λ can either decrease or increase with time for a nonequilibrium sample kept at constant pressure and temperature, depending on the current and equilibrium values for the P/H ratio. This situation is shown in Fig. 7. The results pertain to C_{60} which has been cooled from room temperature to below T_g at 0.07 GPa, isothermally pressurized to 0.7 GPa at 80 K, and subsequently annealed at 100 K (0.7 GPa). Accordingly, the frozen-in P/H ratio is about 75/25 whereas the equilibrium state should be close to $P/H=0/100$. As can be seen, λ initially decreases following the change of P/H towards 50/50, reaches a minimum ($P/H=50/50$) and thereafter increases as the orientational order improves. Since the decrease is more rapid than the following increase it appears that the initial τ is shorter than that at the end of the annealing, also in good agreement with the model.

IV. DISCUSSION AND CONCLUSIONS

We have argued that our sample of C_{60} exhibits a substantial amount of disorder. An indication of this is given by the phonon mean free path. The mean free path l can be estimated using the simple Debye formula for λ which is given by $\lambda=(1/3)\rho c_v l v$, where v is the phonon velocity and ρc_v is the heat capacity per unit volume of the phonons which are responsible for the heat transport. We associate the vibrating unit with the C_{60} molecule ($c_v=25 \text{ J mol}^{-1} \text{ K}^{-1}$, $\rho=2400 \text{ mol m}^{-3}$) and approximate v with the sound velocity ($\approx 2 \times 10^3 \text{ m s}^{-1}$), which yields $l=50 \text{ \AA}$ at 200 K (about three lattice constants). Although the absolute value for l obtained in this way needs to be treated with caution, the true l is almost certainly rather small. It probably follows that the amount of defects must be substantial but a quantification is not possible without specific knowledge of their ability to scatter phonons.

The results for $\lambda(T)$ can be discussed qualitatively in terms of available models as well as the known behavior for λ at transitions. We will mainly discuss the result for $\lambda(T)$ at

0.1 GPa, but the specific features which occur in the data can be observed at all pressures if shifts in temperature with pressure are accounted for. As shown in Figs. 1 and 5, there are several discontinuities in $d\lambda/dT$. Such behavior is usually due to phase transitions (first or higher order). The well-established glass transition in C_{60} at 90 K and the first-order transition at 260 K explain the discontinuities in $d\lambda/dT$ near these temperatures. (The change in $d\lambda/dT$ at low temperatures, e.g., 60 K at 1 GPa, can be attributed with confidence to the decrease of the heat capacity at roughly constant mean free path.) At about 170 K, we observe another abrupt change in $d\lambda/dT$ which might also be due to a transition. However, before discussing this possibility we will explore the extent to which λ can be modeled below 260 K.

At low temperatures the large amount of structural disorder dominates the phonon scattering, which is reflected in a weak temperature dependence for λ in comparison with that of an ordered crystal. At sufficiently high temperature one expects that three phonon umklapp processes should provide significant additional phonon scattering, yielding $\lambda \propto T^{-1}$. In order to test if umklapp processes together with scattering from structural defects could describe $\lambda(T)$ in the range 100–260 K (above T_g), we employed the commonly used relaxation time model for λ .^{31,32} In addition to the relaxation time τ for umklapp scattering, we introduced a constant τ to roughly account for the scattering from structural defects (a constant τ is normally associated with boundary scattering but is also sometimes used to discuss λ of amorphous materials). However, a fit yielded poor agreement with the experimental data, mainly because of the abrupt change in $d\lambda/dT$ near 170 K. That is, we find that three-phonon umklapp scattering cannot cause a change in $d\lambda/dT$ at 170 K sharp enough to give a fair description of the data. It is possible that the model, which assumes Debye lattice waves, is too simple or even invalid for materials with a substantial amount of structural disorder. A different approach using Einstein oscillators is sometimes employed for disordered materials,^{8,13} but will also fail because it yields a constant λ at high temperatures. We conclude that the most commonly employed models for λ cannot explain the change in $d\lambda/dT$ at 170 K without introducing a scattering mechanism which increases the phonon scattering more abruptly than umklapp scattering, or a phase transition which changes also other properties such as the phonon velocity (see below). A scattering source might be provided by other modes than the acoustical and, in particular, the librational modes of C_{60} . As a consequence of large molecular mass, C_{60} exhibits low-frequency librational branches which overlap those of the acoustical modes.^{33,34} It follows that these modes can be important to phonon scattering and there is experimental evidence for such strong scattering in for example solid N_2 and CO .³⁵ However, a quantification for C_{60} is difficult due to the meagre theoretical knowledge about phonon-libron scattering.

In analogy with the model proposed for $\lambda(T)$ in the single crystals,^{3,4} the anomaly in $\lambda(T)$ at the glass transition can be described qualitatively using the relaxation time model. In the analysis of the single-crystal data, Yu and co-workers^{3,4} introduced a phonon scattering rate associated with the P-H orientational disorder τ_{OD} . Furthermore, they assumed that the three-phonon umklapp process was the only other signifi-

cant scattering source. These assumptions yielded the observed discontinuity in $d\lambda/dT$ at T_g since the P-H disorder decreases and, consequently, τ_{OD} increases down to T_g where it becomes constant. Our data for λ in the range 50–170 K can be described in an analogous way. However, in our case, the dominant scattering mechanism in the sc phase is structural disorder (other than orientational disorder). Consequently, if we exchange the scattering rate for umklapp processes with one associated with structural disorder ($\tau = \text{const}$) then the discontinuity in our data can be reproduced (not shown in the figures).

We return now to the 170-K anomaly and two other possible explanations for this result, besides umklapp and libron scattering described above. One originates from *heat transport* through nonacoustical modes, which therefore is quite the opposite of the one described above in which these modes act only in scattering processes. The other explanation attributes the anomaly to a phase transition.

We first consider the possibility that nonacoustical modes can contribute to a significant extent to λ . Through theoretical calculations, it has been found that the optical vibrations in an alkali halide³⁶ can contribute significantly to λ . In addition, there is experimental evidence that also librational vibrations can take part in heat conduction,³⁷ besides being possible scattering sources.³⁵ When nonacoustical modes are excited, additional paths for the heat transport become available if the modes exhibit a large group velocity. (Otherwise they can serve only as scattering sources for the acoustical modes.) Such modes with large group velocity do exist in C₆₀.³⁴ This contribution is added to that from acoustical modes and, hence, yields an increase in $d\lambda/dT$,³⁶ similar to that observed in the data for the single crystal near 120 K (Fig. 2). At even higher temperature, λ can approach T^{-1} when the nonacoustical modes which contribute to λ are fully excited,³⁶ in agreement with the single-crystal results above about 160 K as well as our results near the sc→fcc phase transition.

Another explanation for the result near 170 K is a structural transition. There are several investigations at atmospheric pressure which suggest the existence of such a transformation. Among these, both Sakaue *et al.*³⁸ and Moret³⁹ found weak evidence for a transition near 160 K in the x-ray-diffraction pattern of C₆₀, and a recent investigation of the photoconductivity⁴⁰ supports this suggestion. Moret³⁹ proposed that the transition might be associated with a change of the nature of the correlated reorientational motion. Such a transition could increase the phonon scattering rate but also affect λ through changes in other properties, e.g., the inter-

molecular forces. In fact, it has been found that the sound velocity decreases more rapidly with temperature above 160 K than below.^{41,42} In the simple Debye formula, λ is proportionally to the sound velocity. Consequently, if we assume that the group velocity of phonons that dominate the heat transport exhibits the same tendency as the sound velocity (despite the fact that their frequencies are much higher than those of sound waves) then this explains the observed discontinuity in $d\lambda/dT$. Furthermore, according to the Debye formula, the change in $(d \log \lambda / d \log T)$ due to a change in phonon velocity would be equally large in our data as in the single-crystal data, which is roughly in agreement with the experimental data (Fig. 2). If instead a scattering source was solely responsible for the 170 K anomaly then it would probably be much more pronounced in the single-crystal data than in our data. This follows from a discussion of l which is much smaller in our (structurally disordered) specimen than in the single-crystal specimen. Consequently, a new scattering mechanism should affect λ of the single crystal much more than that of our specimen, which is in *disagreement* with the experimental results.

There have been several observations¹ of anomalies in the properties of C₆₀ at 160 K. These have usually not been explicitly attributed to a new transition, but instead been referred to as precursor effects of the sc→fcc transition¹ at 260 K, which is associated with the onset of almost isotropic reorientation. If the anomalies observed at 160 K on heating are indeed associated with the onset of an additional mode (or modes) for the reorientational motion then these two models seem to be basically identical.

In summary, our data for $\lambda(T)$ at 0.1 GPa show anomalies at about 90, 170, and 270 K. Those at 90 and 270 K are associated with the well-established glass and phase transitions, respectively. The feature observed at 170 K support previous reports^{38–40} of a transition, which could be associated with the excitation of an additional reorientational mode. However, we cannot completely exclude that our anomaly at 170 K is associated with a strong scattering source (perhaps librions) or even originates from heat conduction through nonacoustical modes, although the latter is less likely.

ACKNOWLEDGMENTS

We are grateful to Dr. Per Jacobsson for the Raman spectroscopy analysis. This work was supported financially by the Swedish Natural Science Research Council (NFR) and the Swedish Research Council for Engineering Sciences (TFR). A.S. acknowledges financial support from NFR.

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