Glass Transition in Single-Crystal C_{60} Studied by High-Resolution Dilatometry

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The thermal expansion of single-crystalline C_{60} is studied using high-resolution capacitance dilatometry. In addition to the orientational-ordering transition at 261 K, we observe a transition at $T_g \approx 90$ K due to the freezing in of orientational disorder, which has the character of a glass transition. The relaxation near T_g is studied by varying the heating (cooling) rate over more than two decades. It is found to obey an Arrhenius behavior with $E_a = 288 \pm 5$ meV within a simple glass-transition model.

Investigations of solids built of the truncated icosahedral molecule C_{60} have shown many interesting physical and chemical properties. At room temperature the C_{60} molecules occupy face-centered-cubic lattice sites and undergo rapid and nearly uncorrelated rotations, resulting in complete orientational disorder [1-4]. An orientational-ordering transition to a simple-cubic $Pa\bar{3}$ structure is observed at ≈ 260 K [1,5]. However, detailed structural refinements have indicated that a significant amount of orientational disorder persists even at low temperatures [5-7]. In addition, other structural anomalies have been observed below 260 K by thermal expansion measurements at ≈ 90 K [8] and by neutron diffraction at ≈ 90 and 155 K [5], the origins of which remain uncertain. Sound velocity [9], thermal conductivity [10], and dielectric measurements [11], on the other hand, point to relaxation processes in this temperature range. Recent calculations [12] predict a "glassy transition" at 90-130 K due to the freezing in of orientational disorder.

In this Letter we present high-resolution thermal expansion data of single-crystal C_{60} from 5 to 300 K, which clearly demonstrate that the structural anomaly at ≈ 90 K results from a glass transition (we use the term "glass transition" in a very general sense for describing any freezing-in process, as described in Ref. [13]). Moreover, a simple phenomenological model is applied, which reproduces this anomaly very well.

The C_{60} single crystal ($\approx 0.6 \times 1 \times 1$ mm^3) was grown by a sublimation technique [14]. The shiny faces of the sample indicated a high degree of crystallinity. The linear thermal expansion was measured using a capacitance dilatometer [15], where the temperature is varied continuously at constant rates between ± 0.15 and ± 20 mK/s. Errors in absolute temperature are less than 0.3 K, even at the highest heating (cooling) rates. The relative length resolution was $\Delta L/L \approx 5 \times 10^{-8}$.

In Fig. 1 we present the temperature dependence of the relative linear thermal expansion $\Delta L/L(T)$ [Fig. 1(a)] and the thermal expansivity $\alpha(T) = \partial \ln L/\partial T$ [Fig. 1(b)] obtained upon heating at a rate of $q = 6$ mK/s (after cool-

ing with $q = 25$ mK/s). The overall behavior of the expansion is very similar to what is found in the change in lattice parameter derived from x-ray [16] and neutron diffraction [5]. Two anomalies, at 261 and ≈ 90 K can be observed. There is no indication for further anomalies between 5 and 300 K. The length of the crystal increases almost discontinuously by $(0.325 \pm 0.025)\%$ at the upper transition and also shows a marked thermal hysteresis [≈ 1.5 K, see inset of Fig. 1(a)], both consistent with a first-order transition. This is in agreement with recent experimental [5,16] and theoretical [17,18] results. The magnitude of the discontinuity is comparable to the re-
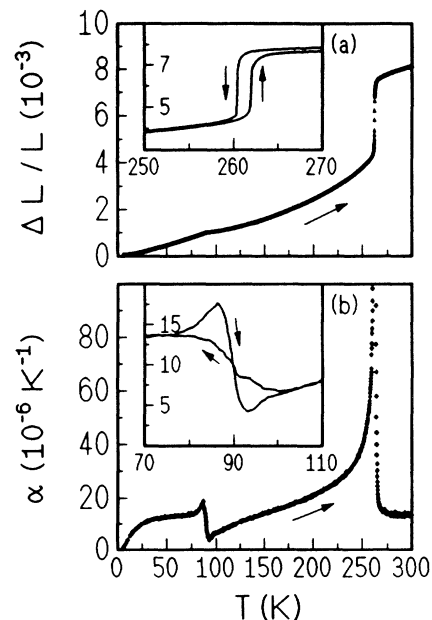

FIG. 1. Temperature dependence of (a) relative linear thermal expansion $\Delta L/L(T)$ and (b) thermal expansivity $\alpha(T)$. The data were obtained upon heating at a rate of 6 mK/s (after cooling at a rate of 25 mK/s). Inset (a): Heating and cooling curves at the 261-K transition. Inset (b): Heating and cooling curves at the 90-K anomaly.
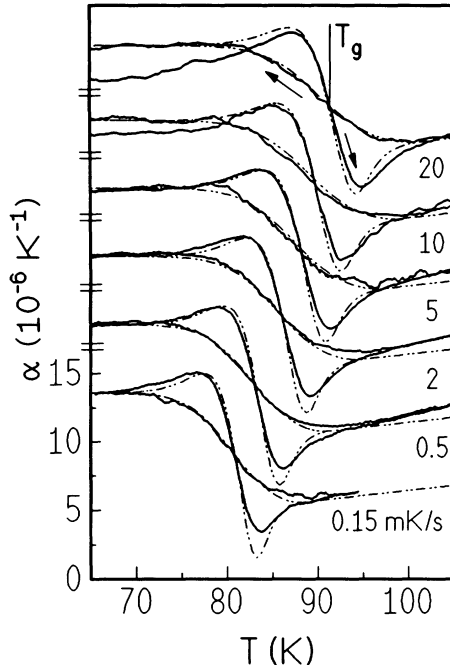
FIG. 2. Thermal expansivity vs temperature at the 90-K anomaly. The data (solid lines) were taken at six different heating (cooling) rates ($q = \pm 0.15$ to ± 20 mK/s). The curves for $q \geq 0.5$ mK/s are vertically offset for clarity. Noticeable is the shifting of the transition to lower temperatures with decreasing q and the large hysteresis, both of which are common features of glass transitions. Also plotted are the results from a simple glass-transition model (dot-dashed lines), which reproduce both the hysteresis and the shifting of the transition quite well. T_g is defined as the crossover of heating and cooling curves at each rate, respectively.

ported jumps in the lattice parameter of 0.344% [5] and 0.311% [16]. The remarkable sharpness of the transition (< 1 K) points to the high quality of our single crystal. Significant precursor effects are seen in the expansivity data [Fig. 1(b)] below the 261-K transition, which in this figure has a λ shape. We note that the peak in $a(T)$ ($\alpha_{max} \approx 6000 \times 10^{-6}$ K^{-1}) is cut off.

The high resolution of the expansion measurement allows a detailed study of the slope change at ≈ 90 K [Fig. 1(a)]. This slope change appears as a discontinuity in $a(T)$ with strong overshoots and undershoots [Fig. 1(b)] which, however, occur only upon heating [see inset of Fig. 1(b)]. The cooling curve has a completely different shape and looks like a broad (≈ 20 K) second-order anomaly. On the other hand, heating and cooling curves are identical above and below the transition region. Such a hysteresis is not characteristic of an ordinary phase transition, but is very typical of a glass transition [19–21] and, therefore, gives rise to a closer look at the time-dependent behavior of the system.

In Fig. 2 we show expansivity data taken at six different cooling (heating) rates where in each case
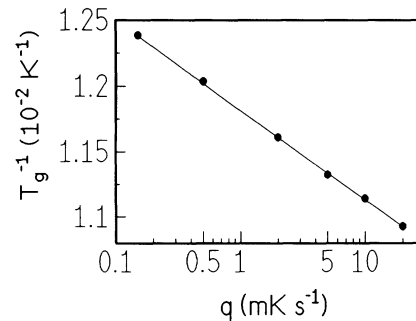

FIG. 3. Dependence of the inverse glass-transition temperature T_g^{-1} on the heating (cooling) rate (logarithmic scale). The solid line is a linear regression of the data. The slope yields an activation energy $E_a = 288 \pm 5$ meV.

$|q_{heating}| = |q_{cooling}|$. The anomalies in both heating and cooling curves are shifted to lower temperatures with decreasing rate, whereas their shapes remain nearly unchanged [22]. Such a behavior is also characteristic of a glass transition where a plot of T_g^{-1} vs $\ln q$ allows one to extract an activation energy of the relaxation process [21]. Such a plot of our data is shown in Fig. 3. Very good linear behavior is seen and the slope, determined by linear regression (solid line), yields an activation energy $E_a = 288 \pm 5$ meV.

It is well known that glass transitions are not limited to supercooled liquids, but also occur in plastic (i.e., orientationally disordered) crystals, indicating a freezing in of orientational degrees of freedom [13,20]. Therefore it is tempting to relate the 90-K anomaly in C_{60} to the observed orientational disorder in the low-temperature phase. To gain more insight into the nature of this disorder, we analyze our data within a simple two-state model (a similar model was recently used by Yu et al. to describe the thermal conductivity of C_{60} [10]).

We assume that the orientational disorder is connected with local structural excitations, where the excited (disordered) state has a higher energy (Δ) and is separated from the ground (ordered) state by an energy barrier E_a. To be able to influence thermal expansion these excitations must change the volume of the crystal. We assume a linear relation between the lattice parameter $a(T)$ and the occupation probability of the excited states $c(T)$,

$$a(T) = a_0(T)[1 + \eta c(T)] . \qquad (1)$$

$a_0(T)$ corresponds to the lattice constant in the absence of disorder and η is a constant. Hence it follows that

$$a(T) = a_a(T) + \eta \frac{1}{1 + \eta c(T)} \frac{\partial c(T)}{\partial T} , \qquad (2)$$

where $a_0(T) = \partial \ln a_0(T)/\partial T$. In thermal equilibrium the occupation probability is given by

$$c_\infty(T) = (e^{\Delta/k_B T} + 1)^{-1} . \qquad (3)$$

$c(T)$ depends on the details of the relaxation process.

For exponential relaxation it is determined by the differential equation

$$\frac{\partial c(T)}{\partial T} = -\frac{1}{qt_r(T)}[c(T) - c_\infty(T)], \qquad (4)$$

where $q = \Delta T/\Delta t$ is a *constant* cooling (heating) rate and the relaxation time t_r obeys an Arrhenius law, i.e.,

$$t_r^{-1}(T) = v e^{-E_a/k_B T}. \qquad (5)$$

It is useful to discuss two limiting cases of Eq. (4). At high temperatures the relaxation time t_r is very short, allowing the system to stay in equilibrium $[c(T) \approx c_\infty(T)]$. At low temperatures t_r is very large, resulting in a temperature-independent (frozen-in) occupation of excited states $[\partial c(T)/\partial T \to 0]$. The glass transition occurs when $qt_r(T)/T|_{T_g}$ is a constant of order 1. Using Eq. (5) one can derive (in first approximation) the relation $\ln q \propto -E_a/k_B T_g + \text{const}$, which was already found to be well obeyed (see Fig. 3).

To calculate the contribution to $\alpha(T)$ arising from the structural excitations, Eq. (4) was solved by iteration using the following procedure. The simulation of the cooling process ($q < 0$) was started at 150 K assuming thermal equilibrium $[c(T) = c_\infty(T)]$. The temperature was lowered to 50 K in steps of 0.5 K. Then, the reheating simulation is carried out with the (rate-dependent) frozen-in concentration of the cooling process $c(T = 50$ K) as the starting value.

Because we are only interested in the behavior of $\alpha(T)$ in the vicinity of T_g, we approximate $\alpha_0(T)$ by a T-independent value. Because $\partial c/\partial T \approx 0$ for $T < T_g$, it follows that $\alpha_0 \approx \alpha(T < T_g)$. From Fig. 2 we obtain $\alpha_0 = 13.6 \times 10^{-6}$ K^{-1}. $E_a = 288$ meV is taken from Fig. 3. The free fitting parameters are v, η, and Δ, and were determined by a visual comparison of simulation and data.

The data are equally well described by several different sets of parameters, which makes a unique determination of v, η, and Δ impossible. Nevertheless, for a given Δ value, both v and η can be determined. Good fits are obtained for all $\Delta \le 20$ meV. In Fig. 2 we show, as an example, the fit with $\Delta = 13$ meV, $v = 5.4 \times 10^{13}$ s^{-1}, and $\eta = -0.0032$ (dot-dashed lines) in comparison to our data (solid lines). Both the shapes of cooling and heating curves as well as the $T_g(q)$ dependence are reproduced very well by the model. The only deviation (which seems to increase with decreasing q) occurs at the undershoot of the heating curves. This may be due to more complex relaxation behavior, e.g., a weak nonexponential relaxation function [23], or a distribution of activation energies as proposed in Ref. [11]. Simulation with a Gaussian distribution function showed that the width W must be extremely narrow ($W \le 5$ meV) to retain the sharp structure of the heating curves, in contrast to the wide distribution ($W \approx 40$ meV) of Ref. [11] which, however, was obtained at higher temperatures. Here we emphasize

that the E_a value is determined quite exactly, since even a slight deviation from 288 meV does not reproduce the correct shift in $T_g(q)$. This can be compared to other values determined from thermal conductivity (240 ± 30 meV) [10], sound velocity (241 and 293 meV) [9], dielectric (270–280 meV) [11], and NMR (250 ± 50 meV) [3] measurements.

A lower limit for Δ can be estimated from a comparison of the calculated contribution to the specific heat due to a change in occupation of the excited state,

$$C_v^{\text{exc}}(T) = \Delta f N_A \, \partial c(T)/\partial T, \qquad (6)$$

with experimental results from polycrystalline samples [8]. N_A is Avogadro's number and f the fraction of excitation centers per C_{60} molecule. Figure 4(a) shows $C_v^{\text{exc}}(T)$ as calculated for five different values of Δ and with $f = 1$. Note that the jump height shows a maximum for $\Delta \approx 20$ meV. In the inset of Fig. 4(a) we show the measured $C_p^{\text{exc}}(T)$. To obtain as large a jump in C_v^{exc} from the model as observed experimentally, two requirements must be fulfilled. First, f cannot be significantly smaller than 1 and, second, $\Delta \ge 10$ meV. Thus, although a distinct value of Δ is not ascertainable, we can specify lower and upper bounds of 10 and 20 meV, respectively, in agreement with [10], where Δ is found to be ≈ 12 meV. Within these limits $v = 10^{13} - 10^{14}$ s^{-1}, which agrees well with other reported values [3,9–11]. We fur-
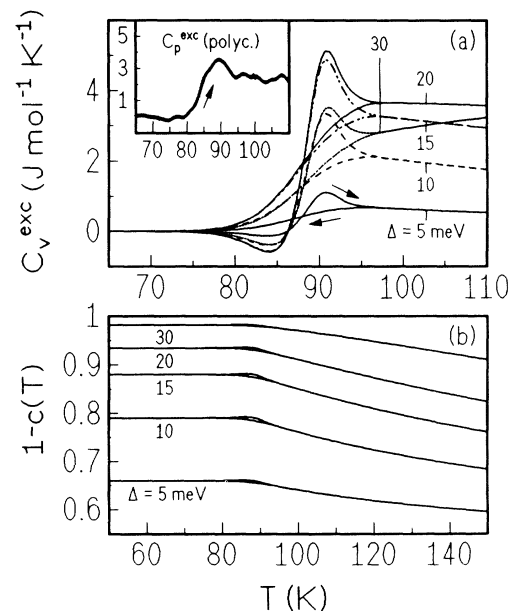

FIG. 4. Calculated temperature dependence of (a) the specific-heat contribution from the two-state system $C_v^{\text{exc}}(T)$ and (b) fraction $c(T)$ of excited states for five different values of Δ and with $f = 1$ ($q = 5$ mK/s). The slope change at ≈ 90 K in (b) corresponds to the glass transition, below which $c(T)$ is nearly constant. Inset (a): Measured contribution $C_p^{\text{exc}}(T)$ on powdered C_{60} from Ref. [8], after subtraction of a suitable background.

ther obtain $-0.004 \le \eta \le -0.0025$.

We now discuss possible microscopic origins of the structural excitations. Since, as we just argued, the density of two-level systems must be about equal to the density of C_{60} molecules, extrinsic effects (e.g., twin boundaries) can be excluded. Orientational disorder of the C_{60} molecules, as predicted by Lu et al. [12] and observed by David et al. [5], is the most likely explanation. The latter proposed a model where the molecules can occupy either a ground state or one misoriented state in which hexagons (instead of pentagons) face C-C double bonds of adjacent molecules. The fraction of misoriented molecules was found to be nearly constant ($\approx 18\%$) below ≈ 90 K (i.e., frozen in) and to increase up to 260 K. In Fig. 4(b) we show the temperature dependence of our calculated concentration $c(T)$ for different values of Δ. The overall shape of these curves is very similar to the data from David et al. Additionally, their amount of frozen-in disorder is also consistent with our predictions [(7-21)%] within the estimated range of Δ. This good agreement, thus, strongly suggests that this is the correct microscopic interpretation of the presently observed transition.

Finally, we discuss the significance of the parameter η, which determines the effect of the misorientations on the volume [see Eq. (1)]. Its negative value implies a volume decrease with an increasing amount of disorder, a feature not common of typical glasses. In terms of the David model, a simple geometrical explanation may be that a C-C double bond finds more room when facing a hexagon instead of a pentagon thereby decreasing the intermolecular distance.

In summary, solid C_{60} undergoes a transition to a glasslike state at ≈ 90 K due to the freezing in of orientational disorder. This disorder strongly affects the volume, and, thus, the transition is very pronounced in the thermal expansion. The good agreement between a simple glass-transition model and the measured expansivity shows that the relaxation is essentially exponential. Further, if one includes the relaxation data obtained from sound velocity [9] and dielectric measurements [11] at ≈ 150 K, the relaxation time is found to nearly follow an Arrhenius behavior over a large temperature range. This is typical of the "strong" (versus "fragile") category of glasses [20], where the divergence of the relaxation rate is expected to occur well below T_g. Our case differs from an ordinary glass because the disorder above T_g is an equilibrium property and not a metastable state of a supercooled liquid [13], and also the Kauzmann paradox, which provides a "thermodynamic basis" for a divergence above $T=0$ K, does not apply [20]. This, however, does not rule out a divergence at finite temperature or even a kinetically hindered phase transition below T_g as has recently been seen by Suga [13] in hexagonal ice.

Note added.— After submission of the manuscript, we became aware of an article by Matsuo et al. [24] who measured the specific heat of C_{60}. They found "orientational glass behavior" with a glass transition at 86.8 K, in good agreement with our results.

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