Low Frequency Elastic Properties of the Structural and Freezing Transitions in Single-Crystal C$_{60}$

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(Received 18 February 1993)

We present the first low frequency (0.1–50 Hz) measurements of the complex elastic constant on C$_{60}$ single crystals. We have measured a negative dip anomaly of 25% at $T_1 = 261$ K, which did not show up in previous elastic studies at 10$^4$ Hz. The slow relaxation observed near $T_1$ is supposed to be due to the very slow dynamics of the order parameter fluctuations. In addition it is shown that the elastic anomalies observed at 10$^4$ Hz and 160 K originate from the same physical process as the “glass” transition at 80 K observed in thermal expansivity.

PACS numbers: 62.20.Dc, 05.40.+j, 64.70.Kh, 64.70.Pf

The synthesis of the icosahedral carbon molecule C$_{60}$ [1], the preparation of large quantities of material [2], and the growth of single crystals [3,4] have enabled a number of investigations revealing exciting results even for the undoped material. At room temperature the crystal structure is face centered cubic with space group $Fm\bar{3}m$ [5], and the nearly spherical C$_{60}$ molecules are orientationally disordered with a reorientational correlation time of 9.2×10$^{-12}$ s [6]. At $T_1 = 260$ K a $\lambda$-type order-disorder transition [7] leads the crystal to a simple cubic phase $Pa\bar{3}$. Below $T_1$ the reorientational correlation time increases abruptly to 2×10$^{-8}$ s [6]. Detailed neutron scattering studies [8] have shown that between 90 and 260 K the C$_{60}$ molecules shuffle between two nearly degenerate orientations differing in energy by $\mu_2 = 11.4$ meV and separated by an energy barrier of $\mu_1 = 290$ meV. With decreasing temperature the population of the energetically less favorable orientation decreases, but it does not vanish completely. Below $T_{11} = 90$ K 16.7% of the molecules were found to be frozen in the energetically less favorable minority orientation [8]. This freezing of the misoriented molecules was shown to be strongly time (or equivalently frequency) dependent and is reflected in different quantities, like specific heat [9], thermal expansion [8], thermal conductivity [10], and dielectric permittivity [11]. Sound velocity measurements [12,13] performed in the kHz region exhibit anomalies around 260 and 160 K; the latter was shown to be consistent with a strong temperature dependent relaxation process. At 260 K an 8% upwards jump was observed in the Young’s modulus $E$. This appears surprising, since the Pippard-Buckingham-Fairbank relationship [14] $E^{-1}(T) \propto \alpha(T) \times (dT/dP)$ ($\alpha$ is the thermal expansivity [7])—which also holds in the presence of the third order invariant of the order parameter in the free energy—yields a negative jump of the elastic modulus at $T_1$.

In this Letter we report the first low frequency (0.6–50 Hz) elastic constant measurements on single-crystal C$_{60}$ performed in a temperature range between 100 and 300 K. Two characteristic results are obtained which are essential for the understanding of the transitions at $T_1$ and $T_{11}$. The low frequency elastic relaxations observed above $T_1$ may originate from the appearance and growth of short-range ordered clusters of the low symmetry phase (order parameter fluctuations) with a characteristic relaxation time $\tau_\eta = 0.2$ s just above $T_1$. In addition, frequency dependent anomalies were also observed near the $T_{11}$ transition. Since the time scale used in our experiments was intermediate between the thermal expansivity measurements in [7] and the vibrating reed measurements in [12], our results bridge the two previous results. The perfect agreement with the low frequency data on the thermal expansivity and the reasonably good agreement with dielectric [11] and sound velocity [12] data on the high frequency side prove that in all cases the same activated relaxation process controls the freezing transition at $T_{11}$.

The C$_{60}$ single crystals were grown by a sublimation-condensation method in a closed evacuated glass tube [3]. The source material was purified from residual solvents by heating in a vacuum of 10$^{-7}$ torr and by a successive threefold sublimation process. The typical size of the crystals was 0.6 mm × 0.6 mm × 1 mm. The temperature dependences of the real and imaginary parts of the elastic response to a time dependent stress were measured using a commercial dynamical mechanical analyzer (DMA 7, Perkin Elmer) in the frequency range between 0.6 and 50 Hz. With this apparatus one can measure the static and dynamic strain in response to a static or dynamic stress with a resolution of 3 and 20 nm, respectively. The stress was applied by parallel plates. To obtain a detectable strain amplitude (0.3–1 μm) a rather high force of 500 mN was applied. From stress strain scans we proved that we were still operating in the linear response regime. As-grown crystals with parallel [111] faces were used and a longitudinal stress perpendicular to these faces was applied, resulting in an effective complex elastic constant $C_{eff} = C''' + iC''$. In Fig. 1 we show the temperature
dependence of $C_{\text{eff}}$ and $C_{\text{eff}}''$ for 1 and 50 Hz around the first order phase transition at $T_1$. The most important features are the negative jump in $C_{\text{eff}}$ at $T_1$ and $T'_1$ and the corresponding maximum in $C_{\text{eff}}''$ appearing somewhat higher in temperature (see inset of Fig. 1). The magnitude of the jump decreases with increasing measurement frequency. The thermal hysteresis of 3 K is comparable to previous findings [7,12] and demonstrates the first order nature of the phase transition, in agreement with recent theoretical results [15]. To account for the temperature dependence of the elastic constants near the phase transition it is necessary to add the coupling terms between the order parameter $\eta$ and the strains $\epsilon$ to the free energy [15], which in a simplified notation are of the type $a\eta^2\epsilon + b\eta^2\epsilon^2$ [16]. Using a relaxational behavior of the order parameter fluctuations $\delta \eta(t) - \eta(0)$, the complex elastic constant at applied frequency $\omega$ takes the well-known form [17]

$$C_{\text{eff}}(\omega, T) = C_{\text{eff}}^0(T) - (C_{\text{eff}} - C_{\text{eff}}^0)[1 + i\omega \tau_\eta]^{-1} + b\eta^2(T),$$

(1)

where $\tau_\eta$ is the characteristic time for the response of the order parameter to a suddenly applied external strain and $\eta_0$ is the equilibrium value of the order parameter. The second part of Eq. (1) is due to the coupling term $a\eta^2\epsilon$ and depends on the measurement frequency $\omega$ through the frequency dependence of the order parameter susceptibility. If $\omega \tau_\eta \gg 1$ the coupling $a\eta^2\epsilon$ becomes ineffective because the applied stress varies too fast for the order parameter fluctuations to follow, and $C_{\text{eff}}(\omega) = C_{\text{eff}}^0 + b\eta^2$, where $C_{\text{eff}}^0$ is the background value of the elastic constant obtained at room temperature (Fig. 1). In the limit $\omega \tau_\eta \ll 1$ the system has time to relax to its equilibrium state, resulting in $C_{\text{eff}}(\omega) = C_{\text{eff}}^0 + b\eta_0^2$. In our model as well as in the theory of Lamoen and Michel [16], the difference $(C_{\text{eff}} - C_{\text{eff}}^0)$ is proportional to the square of the order parameter strain coupling coefficient, i.e., $a^2$, which in the limit $\omega \tau_\eta \ll 1$ leads to a negative jump in the elastic constant at $T_1$. The third term in Eq. (1) is due to the coupling $b\eta^2\epsilon^2$ in the free energy and is independent of the applied frequency.

According to Eq. (1) any temperature dependence of the elastic constant and damping should appear only below $T_1$ where $\eta_0 < 0$. The observation of a nonlinear temperature dependence of the elastic constant and damping above $T_1$ is remarkable (Fig. 1). In contrast, the thermal expansion data recorded simultaneously showed a very sharp transition ($< 1.5$ K). Because of the high quality of the sublimation grown crystals an influence from residual solvents can be excluded. The other straightforward interpretation of this precursor effect is based on the assumption of intrinsic order parameter fluctuations with a characteristic lifetime of $\tau_\eta$ [17]. Since the phase transition at $T_1$ is of first order, there is a coexistence region, i.e., a temperature range where nuclei of the ordered low temperature phase (short-range ordered clusters) are embedded in the disordered high temperature phase. These nuclei are metastable above $T_1$ and can be formally described by order parameter fluctuations, $\delta \eta(t) - \eta(0)$, where the homogeneous order parameter $\eta_0 = 0$ for $T > T_1$ [17].

The temperature dependence of $\tau_\eta$ as calculated from Eq. (1) and the corresponding formula for the fluctuation contribution [17] are shown in Fig. 2. At $T_1 + 1$ K the relaxation time is about 0.16 s, which implies $\omega \tau_\eta = 1$ for 1 Hz, and it increases further with cooling, reaching its maximum at $T_1$. This slow motion we are probing near
$T_1$ may be connected with the formation and growth of the nuclei of the ordered phase, i.e., with the movement and merging of their boundaries, involving the correlated motion of C$_6$O molecules. Quite recently the existence of orientational correlations has been demonstrated by x-ray diffuse scattering photography [18]. In contrast to our long relaxation time, the short relaxation time measured by NMR [6] corresponds to the single particle relaxation time governed by the rotational fluctuations of the individual molecules within a short-range ordered cluster (ordered nucleus).

In our model the overshoot in the elastic constant obtained on cooling is due to the precursor of the $n \eta^2$ anomaly which becomes effective because of the large relaxation time in this temperature region. Just below $T_1$, $\tau_\eta$ drops down to 0.0075 s implying $\omega \tau_\eta \ll 1$ and the $\eta^2 \epsilon$ term induces a negative jump. Using Eq. (1) we find that at 50 Hz the anomaly is reduced to about $1/2$ with respect to 1 Hz, in agreement with the experimental data (Fig. 1). According to these results the absence of the negative jump in the sound velocity measurements of Shi et al. [12] is due to their high measurement frequency of $10^4$ Hz.

To get further information about the low-temperature freezing transition at $T_\Pi$ we have measured the temperature and frequency dependence of the complex elastic constant at low temperatures. Figure 3 shows the results for measurement frequencies between 0.6 and 50 Hz, which are characteristic for a relaxational process. With decreasing measurement frequency the knee in $C_{\text{eff}}$ and the corresponding maximum in $C_{\text{eff}}^0$ are shifted to lower temperatures and the anomaly in the elastic constant increases from 7% at 50 Hz to 27% at 0.6 Hz. This behavior can be phenomenologically described by Eq. (1) with an activated behavior for the relaxation time $\tau = \tau_0 \exp(\mu_1/kT)$, which is characteristically different from the relaxation time $\tau_\eta$ used to describe the order-disorder phase transition at $T_1$. Similar to Gugenberger et al. [7], we find no significant distribution of relaxation times (Fig. 3) in the temperature range covered by our measurements. The best fits for all curves of Fig. 3 yielded $\tau_0 = (4 \pm 2) \times 10^{-14}$ s and $\mu_1 = 300 \pm 10$ meV. Thus by cooling the sample at constant measurement frequency we pass from $\omega \tau \ll 1$ at $T_\Pi$ to the limit $\omega \tau \gg 1$ at $T \ll T_\Pi$, and the resulting elastic constant crosses over from the equilibrium value $C_{\text{eff}}^0$ to the frozen value $C_{\text{eff}}^\ast$, respectively. The freezing temperature $T_\Pi$ is defined through $\omega \tau(T_\Pi) = 1$. In Fig. 4 we show the frequency dependence of the freezing temperature $T_\Pi$. The dots are obtained from the fits to our data. The triangles denote the phase transition temperatures as measured by high resolution dilatometry [7] on samples of the same laboratory as ours. In these measurements the cooling rate $q$

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**FIG. 3.** Measured (○) and calculated (---; , , ) elastic constant $C_{\text{eff}}$ and $C_{\text{eff}}^0$ vs temperature at six frequencies between 0.6 and 50 Hz. Different units are used at different frequencies for clarity. The solid lines represent a least squares fit of a Debye relaxational response function with a thermally activated single relaxation time. The dashed line was calculated with a Gaussian distribution of activation energies and a width of $W = 40$ meV, as it was found in Ref. [11]. Inset: $\Delta C_{\text{eff}} = C_{\text{eff}}(T \ll T_\Pi) - C_{\text{eff}}(T \gg T_\Pi)$ as a function of $T_\Pi$ follows a straight line.

**FIG. 4.** $\ln(\omega^{-1})$ vs $T_\Pi^{-1}$ for different measurement frequencies. The points represent our data. The triangles, full squares, and open circles are taken from thermal expansivity [7], dielectric [11], and sound velocity [12] measurements, respectively.
was varied resulting in a shift of $T_{1\text{H}}$ which is defined through $q\tau(T_{1\text{H}})/T_{1\text{H}} = 1$. To compare these results with our data we have formally related the quantity $q/T_{1\text{H}}$ to the measurement frequency $\omega$. Inserting also the data from dielectric [11] and sound velocity [12] measurements, we obtain that the frequency shift of the phase transition temperature $T_{1\text{H}}$ can be quantitatively described by an Arrhenius law for the relaxation time over a frequency range of 11 decades in the temperature range between 180 and 80 K (Fig. 4). This clearly shows that the anomalies observed around 160 K in sound velocity [12] and around 80 K in thermal expansion [7,8] measurements are of the same microscopic origin.

A widely adopted microscopic picture for the behavior of C$_{60}$ molecules below the first order transition at 260 K is based on the two-state model of David et al. [8]. If the cooling rate (or measurement frequency) is smaller than the time $\tau$ for reaching thermal equilibrium, the two states are occupied according to their equilibrium values, but if the cooling rate exceeds the critical value of $1/\tau(T)$, the molecules become frozen in their positions corresponding to the two energy minima. Assuming a linear dependence of the elastic constant on the probability $n(t)$ of misorientations, the frequency dependence of the elastic response is given by the Debye equation (1), where $C_{\text{eff}} = C_{\text{eff}}(T \gg T_{1\text{H}})$ and $C_{\text{eff}} = C_{\text{eff}}(T \ll T_{1\text{H}})$ are linearly related to the thermal equilibrium value $n(t \to \infty)$ and the frozen value $n(T = \omega^{-1})$ of misoriented C$_{60}$ molecules. Thus in this model the decrease of the elastic anomaly with increasing frequency (inset of Fig. 3) is due to the increase of frozen misorientations at higher measurement frequencies.

In summary, very slow elastic relaxations have been found by low frequency elastic measurements around the first order phase transition at $T_{1} = 260$ K and the freezing transition at $T_{1\text{H}}$ on single crystals of C$_{60}$. Around $T_{1}$ they may be attributed to the formation and growth of nuclei of the ordered phase within the matrix of the disordered high-temperature phase. However, since our measurement is a macroscopic one, further experiments are required to clarify the microscopic origin for these low frequency relaxations around $T_{1}$.

From our data on the frequency dependent freezing transition at $T_{1\text{H}}$ and the data of the thermal expansivity [7], dielectric permittivity [11], and sound velocity [12] measurements we find that the frequency shift of the freezing temperature from 180 to 80 K can be described by a simple Arrhenius behavior over a frequency range of 11 decades. The fact that there is no finite Vogel-Fulcher temperature at least down to 80 K and there is no significant distribution of relaxation times indicate that below $T_{1\text{H}}$ a quenched disorder occurs rather than an equilibrium glass phase.

The present work was supported by the Österreichischer Fonds zur Förderung der wissenschaftlichen Forschung under Project No. P. 8285 and by the Bundesministerium für Wissenschaft und Forschung Project GZ 45.212/2-27b91. P.D. is grateful for support from the Austrian BuMiWuF (GZ 45.223/2-27b/91).

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