Molecular Dynamics and the Phase Transition in Solid C_{60}

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We characterize the molecular reorientational dynamics in two phases of solid C_{60} with ^{13}C NMR measurements. A change in the nature of the dynamics, indicated by a change in kinetic parameters extracted from spin-lattice relaxation data, occurs at the phase transition at 260 K. Above the transition, the molecules appear to execute continuous rotational diffusion; below the transition, they appear to jump between symmetry-equivalent orientations. This interpretation is consistent with the x-ray-diffraction results of Heiney *et al.* as well as our NMR relaxation and spectral data.

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The recent demonstration of a method [1] for producing large quantities of solid C_{60} (buckminsterfullerene) has catalyzed an explosion of interest in the chemical and physical properties of this new molecular form of carbon. A variety of spectroscopic [2–7] and diffraction [8] measurements have confirmed the predicted truncated icosahedral (soccer ball) structure [9] of the C_{60} molecule. Even more recently, interest in the physical properties of C_{60} in the solid state has received impetus from the discovery that C_{60} becomes a conductor [10] and a superconductor [11] upon doping with alkali-metal atoms.

Pure C_{60} adopts a crystal structure in which C_{60} molecules are positioned with their centers of mass on an fcc lattice [12]. ^{13}C nuclear-magnetic-resonance (NMR) spectra of solid C_{60} have shown unequivocally that individual C_{60} molecules reorient rapidly and isotropically in the solid state at room temperature [5,6,13]. This reorientational motion shows up as orientational disorder in room-temperature x-ray-diffraction measurements [12, 14]. As expected, the NMR spectra show that the motion becomes very slow at low temperatures; i.e., large-amplitude reorientations of C_{60} molecules become infrequent on the time scale of the NMR measurements. These observations lead to an important question regarding the structure of solid C_{60} at low temperatures: Do C_{60} molecules order orientationally or do they form an orientational glass? One might predict an orientationally disordered (glass) structure simply because it is not immediately obvious how icosahedral molecules would order orientationally on an fcc lattice. Surprisingly, a recent x-ray-diffraction and calorimetry study by Heiney *et al.* [14] has revealed a phase transition at about 250 K in solid C_{60} that they interpret as a transition to an orientationally ordered low-temperature structure. This interpretation is particularly remarkable because the earlier NMR studies showed that rapid reorientations persist well below the reported transition temperature.

In this Letter, we present ^{13}C NMR measurements that elucidate the nature of the molecular dynamics in both phases of solid C_{60}. We report the temperature dependence of the ^{13}C nuclear spin-lattice relaxation rate and the ^{13}C NMR spectrum of highly crystalline C_{60} powder. Our results show that the nature of the molecular dynamics changes at the phase transition, which we see at 260 K, but that rapid, large-amplitude reorientations of C_{60} molecules occur down to about 140 K. Our results are consistent with a transition from a phase in which the molecules execute isotropic rotational diffusion to a phase in which they execute jumps between symmetry-equivalent orientations.

NMR measurements were carried out in a 9.39-T field (100.5-MHz carrier frequency) using Bruker MSL and Chemagnetics CMX consoles and a home-built variable-temperature probe. Reported temperatures are accurate to within 1°. ^{13}C spin-lattice relaxation times (T_1) were determined using the saturation-recovery technique. NMR spectra were obtained from free-induction-decay (FID) signals following a $\pi/2$ pulse. Background signals from the probe were suppressed by applying a π pulse before alternate signal acquisitions and alternately adding the subtracting FIDs. Polycrystalline C_{60} was prepared from carbon soot by extraction with toluene at room temperature and chromatography in 5% toluene and 95% hexane on an alumina column followed by heating for 18 h at 170 °C in vacuum. The proton NMR spectrum in $CS_{2(l)}$ indicated a residual solvent content of ≤ 1 mole%. The sample for solid-state NMR measurements was sealed in a glass tube with 1 atm He(g) after evacuation. This material was substantially more crystalline than samples used in previous NMR experiments [5,13], as indicated by a tenfold increase in the intensity of the x-ray powder-diffraction peaks. The NMR properties were correspondingly different. In preliminary measurements on less-crystalline material, we observed substantial variations and hysteresis in the temperature dependence of T_1 which we attribute to the dissolution of O_2 into the solid sample upon equilibration with air at room temperature and the loss of O_2 at low temperatures and in vacuum. The highly crystalline sample used in the measurements described below did not show these effects, suggesting that the ability of C_{60} to dissolve O_2 increases with the defect concentration.

Figure 1 shows the results of T_1 measurements between 163 and 323 K. A break in the temperature depen-

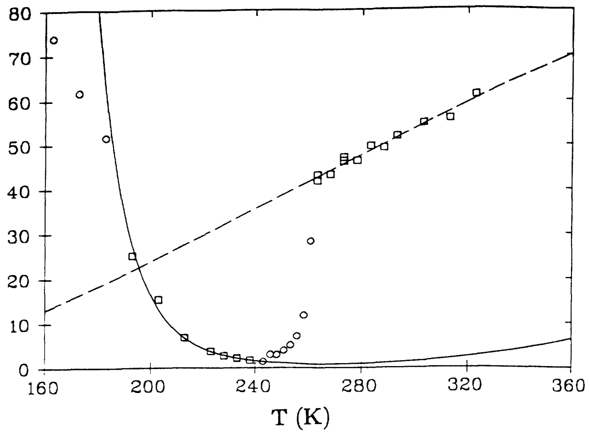

FIG. 1. Temperature dependence of the ^{13}C nuclear spin-lattice relaxation time T_1 in solid C_{60}. The phase transition occurs at 260 K. The solid line is a least-squares fit to the data in the low-temperature phase between 193 and 243 K, based on the model for relaxation driven by molecular reorientations described in the text. The dashed line is a fit to the data in the high-temperature phase above 263 K. T_1 values represented by squares are obtained from single-exponential saturation-recovery curves; values represented by circles are the average T_1 from a biexponential curve.

dence of T_1 at 260 K $= T_c$ is apparent. We associate this feature with the first-order phase transition described by Heiney *et al.* [14]. Their x-ray-diffraction data show the onset of the transition at 249 K, while their calorimetry data show a heat capacity peak at 260 K. The data in Fig. 1 combine measurements taken both on heating and on cooling. No hysteresis was observed. Between 190 and 240 K and above 260 K, our saturation-recovery curves could be fitted by the form $M(1-e^{-t/T_1})+N$. The relative uncertainty in T_1 values is ± 10%. Between 240 and 260 K and below 190 K, the curves were distinctly biexponential and were fitted by the form $M_a(1-e^{-t/T_{1a}})+M_b(1-e^{-t/T_{1b}})$. The T_1 values in Fig. 1 are then the average values, $(M_aT_{1a}+M_bT_{1b})/(M_a+M_b)$. We attribute the biexponential behavior to residual inhomogeneity in the sample. The transition temperature, and the T_1 value at temperatures where $|(d/dT)T_1|$ is large, appears to be sensitive to the presence of defects or impurities. A less-crystalline sample showed a more gradual decrease in T_1, rather than an apparent transition, centered at 240 K. In earlier work [6], Yannoni *et al.* observed a T_1 minimum at 233 K (in a 7.04-T field), although they did not report a phase transition.

Figure 2 shows ^{13}C NMR spectra as a function of temperature. A sharp (2.5-ppm-wide) line is observed down to 190 K. No shift in the resonant frequency is observed between 190 and 323 K. Below 190 K, the line gradually broadens and develops the structure characteristic of a chemical-shift-anisotropy (CSA) powder pattern with CSA tensor principal values $\delta_{11}=213$ ppm, $\delta_{22}=182$ ppm, and $\delta_{33}=33$ ppm, in good agreement with earlier results [5,6]. The development of a powder-pattern line shape below 140 K indicates that (for most molecules) the rate of large-amplitude molecular reorientation has become slow compared to the CSA width (18.2 kHz at 9.39 T). The residual peak at 143 ppm in Fig. 2(g) indicates that a small fraction (roughly 5%) of the C_{60} molecules are still reorienting rapidly at 113 K, probably due to a comparatively low barrier to reorientation in noncrystalline regions of the sample. In measurements on less-crystalline samples [5,13], the powder-pattern line shape developed at temperatures about 30 K lower than in Fig. 2.

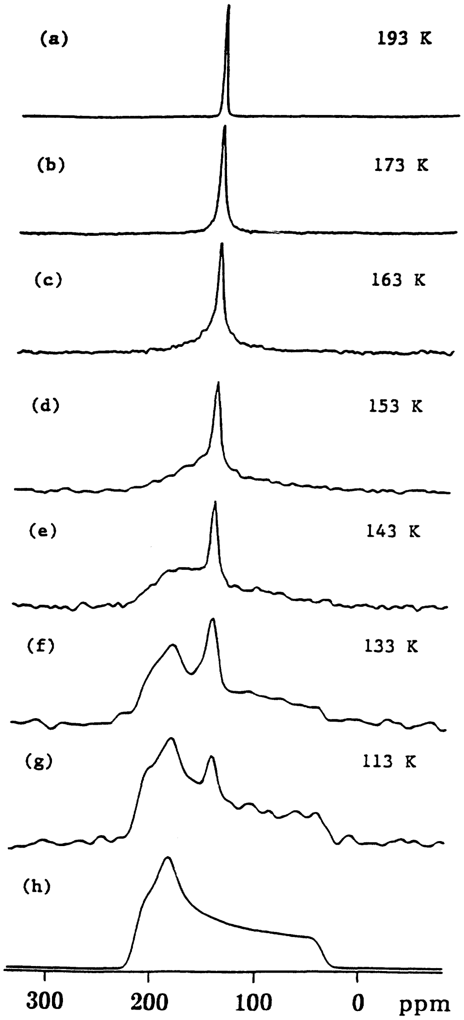

FIG. 2. (a)-(g) ^{13}C NMR spectra of solid C_{60} at indicated temperatures. Frequencies are in ppm with respect to tetramethylsilane. (h) Simulated powder-pattern line shape for rigid molecules with anisotropic ^{13}C chemical shielding (principal values $\delta_{11}=213$ ppm, $\delta_{22}=182$ ppm, $\delta_{33}=33$ ppm).

We expect a phase transition to produce a discontinuity in the temperature dependence of T_1 if the molecular motions that drive spin-lattice relaxation change abruptly at the transition temperature. In the case of C_{60}, the dominant spin-lattice relaxation mechanism in the temperature range in Fig. 1 is provided by the CSA, i.e., the fact that magnitude and direction of the magnetic field at a ^{13}C nucleus depends slightly on the orientation of the molecule as a result of anisotropic magnetic shielding by the electrons of that molecule [15]. A simple model that relates the spin-lattice relaxation to the molecular dynamics is constructed by assuming that large-amplitude molecular reorientations produce fluctuating local transverse magnetic fields $\delta B_\alpha(t)$ $(\alpha=x,y)$ with autocorrelation time τ and that the temperature dependence of τ follows an Arrhenius law:

$$\langle \delta B_\alpha(0)\delta B_{\alpha'}(t)\rangle = \delta B_{\rm rms}^2 e^{-|t|/\tau}\delta_{\alpha,\alpha'}\,, \tag{1}$$

$$1/\tau = A e^{-E_a/kT}\,. \tag{2}$$

Since the fluctuating fields arise from CSA, τ is essentially the molecular orientational correlation time (for second-rank tensors). The relaxation rate $(1/T_1)$ is proportional to the spectral density of the fluctuating fields at the NMR frequency ν_0 [16,17] leading to

$$T_1 = T_1^{\rm min}\cosh\left[\frac{E_a}{kT^{\rm min}} - \frac{E_a}{kT}\right]. \tag{3}$$

The minimum value of T_1 and the temperature at which the minimum occurs are given by

$$T_1^{\rm min} = 2\pi\nu_0/\gamma^2\delta B_{\rm rms}^2\,, \tag{4}$$

$$T^{\rm min} = E_a/k(\ln A - \ln 2\pi\nu_0)\,, \tag{5}$$

where γ is the ^{13}C gyromagnetic ratio (10.705 MHz/T). $T^{\rm min}$ is the temperature at which $\tau^{-1} = 2\pi\nu_0$.

Using Eq. (3), we fitted the experimental relaxation data to extract the kinetic parameters A and E_a and the NMR parameter $\delta B_{\rm rms}$. It is not possible to fit the data over the entire temperature range with a single set of parameters, indicating that the kinetic parameters change across the phase transition. The solid line in Fig. 1 is a least-squares fit to the data between 193 and 243 K, achieved with $A = 3.21\times10^{13}$ s^{-1}, $E_a = 250$ meV, and $T_1^{\rm min} = 0.806$ s ($T^{\rm min} = 268$ K). The corresponding value of $\delta B_{\rm rms} = 2.62$ mT (or $\delta B_{\rm rms}/B_0 = 279$ ppm) is in rough agreement with the CSA width $(\delta_{11} - \delta_{33})$ in Fig. 2. At 200 K, $\tau = 64$ ns. The dashed line in Fig. 1 is a least-squares fit to the data between 263 and 323 K, with the constraint that $T_1^{\rm min} = 0.806$ s. This constraint is motivated by the physical consideration that $\delta B_{\rm rms}$ induced by large-amplitude molecular reorientations should be the same in both phases. The kinetic parameters in the high-temperature phase derived from the fit are $A = 4.22\times10^{11}$ s^{-1} and $E_a = 42$ meV ($T^{\rm min} = 74.6$ K). At 300 K, $\tau = 12$ ps. The observed T_1 values in the low-temperature phase are much shorter than those predicted by the fit to our model below 190 K. This is not surprising since small-amplitude molecular motions will begin to dominate the spin-lattice relaxation once large-amplitude reorientations become too slow to cause efficient relaxation.

Using the kinetic parameters of the low-temperature phase, we find $\tau = 32$ μs at 140 K. This value is in good agreement with the observed development of a powder-pattern line shape at about 140 K. In addition, we can estimate the contribution to the NMR linewidth from dephasing due to fluctuating longitudinal magnetic fields:

$$1/T_2 \approx \gamma^2 B_0^2(\delta_{11} - \delta_{33})^2\tau\,. \tag{6}$$

In Fig. 2, a broadening of about 300 Hz is observed at 173 K. The linewidth $1/\pi T_2$ estimated from Eq. (6) is 300 Hz at 158 K. The fact that a single set of parameters gives good agreement with NMR data from somewhat below 140 to 240 K indicates that there is no additional phase transition in this temperature range.

We estimate the relative uncertainty in the values of E_a derived from the T_1 data to be $\pm20\%$. Because of the limited temperature range of the data in the low-temperature phase, there is substantially greater uncertainty in the values of A and $T_1^{\rm min}$. With the requirement that $T_1^{\rm min} \geq 0.08$ s (otherwise $\delta B_{\rm rms}$ must be unrealistically large), values of A as small as 2×10^{12} give satisfactory fits to the data in the low-temperature phase. Assuming $T_1^{\rm min} = 0.08$ s, the best fit to the data in the high-temperature phase yields $A = 6.6\times10^{12}$.

Heiney *et al.* report that the four C_{60} molecules in the fcc cell become inequivalent below T_c, an observation that they attribute to orientational ordering [14]. Our NMR spectra show that the molecules undergo rapid large-amplitude reorientations well below T_c. A narrow NMR line will be observed whenever the motion is of sufficiently high symmetry and sufficiently rapid that

$$\int_0^{\tau'} dt\, D_{mm'}^{(2)}[\Omega(t)] \approx 0 \tag{7}$$

for all second-rank Wigner rotation matrix elements $D_{mm'}^{(2)}(\Omega)$, where $\Omega(t)$ represents the Euler angles that specify the orientation of an individual molecule and τ' is the time scale given by $(\delta_{11} - \delta_{33})\gamma B_0\tau' \ll 1$. Motion that can be approximated by a thermally activated jumping of C_{60} molecules among their sixty symmetry-equivalent orientations satisfies Eq. (7) and is consistent with the observation of orientational ordering in diffraction measurements. Librational motion, without large-amplitude reorientations, is insufficient to cause the observed motional narrowing of the NMR line above 140 K. The dramatic change in kinetic parameters reflects a change in the nature of the molecular dynamics at the phase transition. The relatively small value of E_a above T_c suggests that the motion in the high-temperature phase approximates continuous rotational diffusion with a temperature-dependent diffusion constant. Rotational diffusion would appear as orientational disorder in diffraction measurements. The energy barrier to reorientation of a particular molecule depends on the orientation of its neighbors, so that a disordered structure may lead to a lower average barrier above T_c. A slight lattice expansion at T_c (so far unobserved [14]) may also contribute to the decrease in E_a above T_c.

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