Low-temperature hcp-to-monoclinic structural transition in solid C_{70}: Ephemeral nature of the intermediate phase

G. Ghosh, V. S. Sastry, C. S. Sundar, Surajit Sengupta, and T. S. Radhakrishnan

Materials Science Division, Indira Gandhi Centre for Atomic Research, Kalpakkam 603 102, India

(Received 17 August 1998)

We follow the structural transformation in solid C_{70} from the high-temperature hcp to a low-temperature monoclinic phase using detailed x-ray diffraction studies at controlled cooling rates from 0.0033 to 0.42 K/min. Rapid cooling of the sample gives the signature of a two-step transformation that disappears when the system is transformed quasistatically. These experimental results can be rationalized using a simple mean field, Langevin dynamical theory using a free-energy functional with minima corresponding to the parent, and two competing product phases such that one of these product phases remains metastable throughout. The implication of our results on the existence of the intermediate phase in the sequence hcp-dhcp-monoclinic, of structural transitions in solid C_{70} with the lowering of temperature is discussed. [S0163-1829(98)02346-7]

Following the pioneering work of Heiney *et al.*[1] on relating the structural transition at low-temperature (260 K) in solid C_{60} to the development of orientational correlations between rotating C_{60} molecules, there have been extensive studies on fullerene molecular crystals, both solid C_{60} and C_{70}. However, unlike in solid C_{60}, the low-temperature structural transitions in the next higher fullerene C_{70} are not unambiguously established. The situation is exacerbated by the complicated orientational dynamics of the lower symmetry (D_{5h}) molecule, associated sluggishness of the transition, and complications due to intercalated solvent effects, etc. Solid C_{70} is observed to crystallize in both fcc and ideal hcp structures, corresponding to close packing of rapidly rotating spherically averaged molecules. The fcc solid C_{70} is first seen to transform at ≈ 280 K to a rhombohedral structure and subsequently to a monoclinic structure at 200 K (Ref. 2) with the lowering of temperature; both these transitions are associated with considerable hysteresis of ≈ 50 K. A widely accepted viewpoint on the nature of structural transitions in hcp solid C_{70} involves two transitions: one from the ideal hcp ($c/a \approx 1.63$) to the deformed hcp ($c/a \approx 1.82$) at 337 K (dhcp) and a second transition to the monoclinic structure at 276 K.[3–5] Data from differential thermal analysis,[6] differential scanning calorimetry,[7] and dilatometry measurement[8] also lend support to this scenario. The occurrence of a two-step transition is rationalized in terms of successive freezing of molecular orientations, first along the short C_2 axis and then along the long C_5 axis, the structural transitions being produced by the coupling of these orientational degrees of freedom to the lattice strain.

Several experiments, however, see a single-step transition from hcp to monoclinic phase, and there are others[9] that have reported three structural transitions with the variation of temperature. For example, Dennis *et al.*[10] observed a single-step orientational ordering of C_{70} molecules, over the temperature range of 270 to 160 K in their muon spin resonance (μSR) experiments. In our earlier work,[11] using high-quality samples prepared by the solution route we observed (1) the equilibrium room-temperature structure of solid C_{70} to be ideal hcp and (2) a broad (270 to 170 K) single-step transi-

tion from the ideal hcp to a monoclinic structure implying a simultaneous freezing of all the orientational degrees of freedom. It is of interest to know if the differences in the structural sequence are related to the different (often uncontrolled) cooling rates employed in the earlier experiments. If an *equilibrium* intermediate phase actually exists then it would be seen during controlled slow cooling of the system from the ideal hcp structure.

With a view to investigate this, x-ray diffraction (XRD) experiments at various controlled cooling rates (varying over two orders of magnitude) have been carried out, and the evolution of the monoclinic phase at low temperature followed. Contrary to our initial expectations, though the transformation proceeds through a single step (starting at ≈ 270 K) when a slow cooling rate (0.0033 K/min) is used, it has a two-step sequence on cooling rapidly (0.42 K/min). Our experimental results (Fig. 2) strongly suggests that the intermediate phase reported earlier[3–5] is likely to be an artifact of the kinetics of the transformation process and *not* a true equilibrium phase. We show that qualitative aspects of our data for the temparature evolution of the fraction of the retained hcp phase during the hcp-to-monoclinic transition can be understood within a simple phenomenological kinetic theory employing a general free-energy functional with minima corresponding to the parent and two product phases such that one of the product phases is always metastable.

Chromatographically separated C_{70} powder was heated in vacuum at 250 °C for 24 h to get rid of trapped solvents. The x-ray diffraction (XRD) study at low temperatures was carried out using a Siemens D-500 powder diffractometer with a continuous flow cryostat. The sample holder was a (911)-cut silicon wafer,[12] attached to the cold tip of the cryostat using a thin layer of GE vernish. The sample displacement errors due to thermal contraction were corrected by simultaneously using a small quantity of NIST 640a silicon powder as internal d-spacing standard. The XRD patterns were recorded at 10 K steps over the temperature range of 300 to 77 K. The sample was cooled at controlled rates. Experiments were carried out at four different cooling rates varying over two orders of magnitude, viz. 0.0033 K/min, 0.22 K/min, 0.31 K/
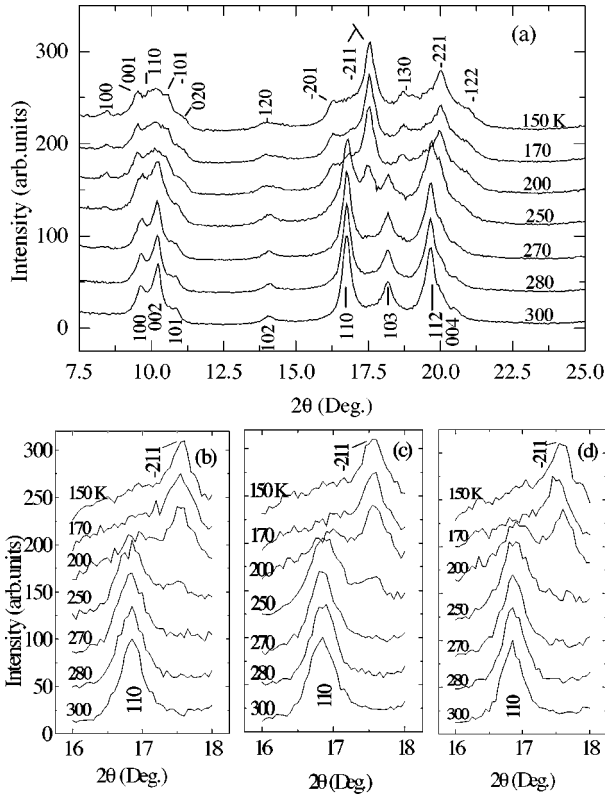
FIG. 1. XRD patterns showing the temperature evolution of the monoclinic phase from the parent hcp at different cooling rates. (a) 0.0033 K/min; the lowest cooling rate employed in this experiment (b) 0.22 K/min, (c) 0.31 K/min, and (d) 0.42 K/min.

min, and 0.42 K/min. Before commencing a fresh cooling cycle we carried out a detailed XRD run at room temperature to ensure that the sample had regained its original hcp structure.

As shown in Fig. 1(a), the room-temperature XRD pattern can be indexed to the ideal hcp with lattice parameters $a = 10.593$ Å, $c = 17.262$ Å, and space group $P6_3mmc$.[13] The low-temperature pattern can be indexed to a monoclinic structure, space group $P2_1/m$, with lattice parameters $a = 10.99$ Å, $b = 16.16$ Å, $c = 9.85$ Å, $\beta = 107.75°$. At a slow cooling rate of 0.0033 K/min, it is seen that the hcp phase transforms to the monoclinic structure without the intervening dhcp phase, consistent with the results reported earlier.[10] At higher cooling rates of 0.22, 0.31, and 0.42 K/min, XRD patterns in the 2θ range of 16° and 18°, corresponding to the most intense peaks of the hcp (110) and the monoclinic ($\bar{2}11$) phases,[11] have been measured, and these results are shown in Figs. 1(b)–1(d).

The change in the fraction of the hcp phase with temperature has been calculated from these patterns as the area ratio of the 100% hcp (110) reflection to the sum of the areas of the (110) reflection of the hcp and ($\bar{2}11$) reflection of the monoclinic phase, and these results are plotted in Fig. 2. It is seen that at a cooling rate 0.0033 K/min the hcp fraction decreases in a single step, within a temperature range of about 100 K. The structural change commences at ≈ 270 K, and by ≈ 170 K the transformation to the monoclinic phase is complete. While *a priori*, such a broad transition could be attributed to impurity effects (presence of intercalants), the
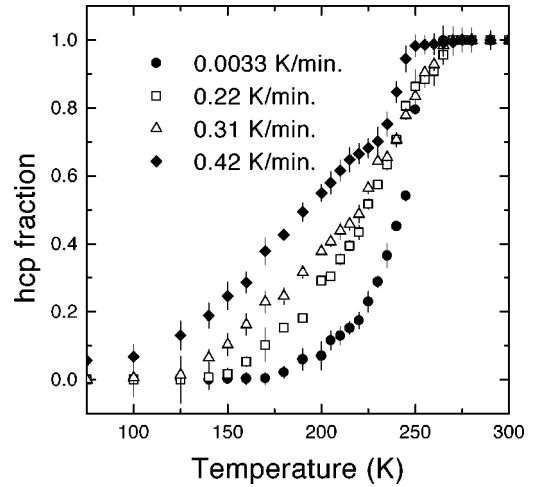

FIG. 2. Change in the fraction of the retained parent hcp phase with temperature at different cooling rates as indicated.

observation of a ≈ 80 K coexistence region even in the sublimed sample[2] suggests that this feature is intrinsic. It is seen from Fig. 2 that the width of the transition increases with the increase in cooling rate (e.g., 0.22 K/min) implying that the width is related to the sluggishness of transition in solid C_{70}. The kinetic model proposed in this paper (see below) accounts for the broad hcp to monoclinic transition in solid C_{70} (cf. Figs. 2 and Fig. 3).

The interesting aspect of Fig. 2 is that with increasing the cooling rate further, one obtains a step in the transformation region, which can be seen as a distinct plateau for the cooling rate of 0.42 K/min, the fastest controlled cooling rate possible with our present experimental setup.
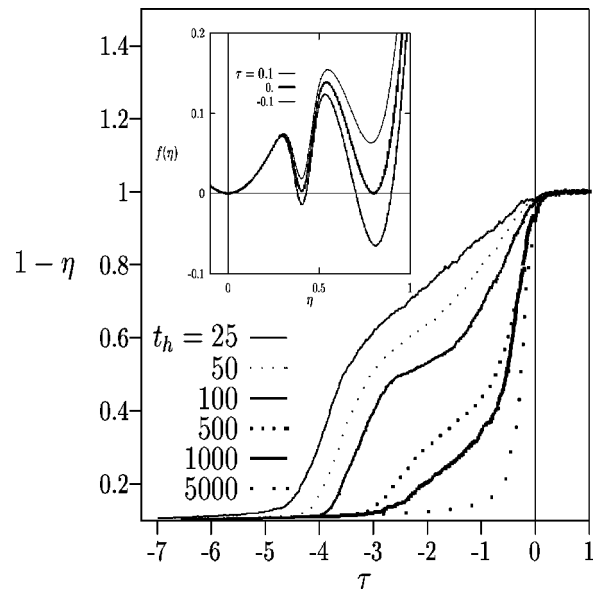

FIG. 3. The time- and noise-averaged order parameter $1 - \eta$ plotted as a function of the dimensionless temperature τ for various cooling rates obtained by holding the system for t_h steps as τ is reduced from $\tau = 1$ in steps of 0.01. The order parameter η is obtained by numerically solving the stochastic differential equation Eq. (3). (inset) Plot of the free energy $f(\eta)$ as a function of the order parameter η for $\tau = 0.1$, 0 and -0.1. Note that the intermediate minimum at $\eta = 0.4$ is always metastable.

We argue below that this plateau is a signature of the formation of an intermediate dhcp phase during the hcp-to-monoclinic transition. The dhcp phase has been reported[8] to have lattice parameters of $a = 10.11$ Å, $c = 18.50$ Å. The (103) reflection of this structure occurs at 17.59, very close to the ($\bar{2}$11) line of the monoclinc phase occurring at 17.61, and has an intensity that is only $\approx 30\%$ intensity of the strongest (110) reflection.[8] Thus, the formation of the dhcp phase will result in a decrease (increase) in the estimated monoclinic (hcp) fraction, leading to the plateau. The interesting aspect of Fig. 2 is that this plateau, corresponding to the dhcp phase, is seen during fast cool. If the intermediate dhcp phase were an equilibrium phase, we should have observed it in the slow cool experiments. This suggests that intermediate phase is metastable, and the feature seen in Fig. 2 is a reflection of kinetic effects—a model for which is developed as follows.

Being a large and somewhat asymmetric molecule, C_{70} possesses a rich energy landscape with many closely competing local minima with the possibility of the system getting trapped in metastable phases influencing the equilibrium phase transitions in this system. A Landau theory for the hcp-monoclinic transition in C_{70} can, in principle, be constructed along the lines worked out in Ref. 14 for the fcc-rhombohedral transition. In this case, the free energy would have three nonequivalent minima corresponding to the three (hcp, dhcp, and monoclinic) phases described above and is expected to have either one (hcp-monoclinic) or a sequence of two (hcp-dhcp-monoclinic) first-order transitions depending on the relative stability of the dhcp and the monoclinic phases. The question of relative stability is, unfortunately, tricky since it depends on the actual magnitudes of the various coefficients in the Landau expansion. The uncertainty in the values of these coefficients, which have to be obtained experimentally or from accurate microscopic calculations, makes it difficult in practice to settle this question convincingly.

We therefore choose a simple, phenomenological approach to understand the *qualitative* features of the kinetics of the hcp-monoclinic transition as depicted in Fig. 2 without trying to derive them with any amount of numerical accuracy. Consider a general free energy $f(\eta)$ with three minima obtained by adding inverted Gaussians at $\eta = \eta_1$ and η_2 with widths $\alpha 1$ and $\alpha 2$ representing the product phases, to a parabolic potential centered at $\eta = 0$, representing the parent phase,

$$f = \eta^2 \{1 - (1 - \tau)(\delta e^{-\alpha_1(\eta - \eta_1)^2} + e^{-\alpha_2(\eta - \eta_2)^2})\}. \quad (1)$$

The depth of these minima relative to the one at $\eta = 0$ is determined by the dimensionless ''relative temperature'' $\tau \propto (T - T_c)/T_c$ (defined for $\tau < 1$ with T_c the equilibrium transition temperature) and δ controls the relative stability of the products for η_1 and η_2; we have chosen δ to be such that the minimum at η_1 is always metastable throughout the range of τ considered. At $\tau = 0$ we have a single first-order transition from the parent to the product corresponding to $\eta = \eta_2$. Using the (arbitrary) set of parameters $\eta_1 = 0.4$, $\alpha_1 = 200$, $\eta_2 = 0.8$, $\alpha_2 = 10$, and $\delta = 0.78$ we have plotted the free energy $f(\eta)$ for $\tau = 0.1, 0$, and -0.1 in Fig. 3 (inset). Note that the parameter δ has been so chosen that the intermediate minimum is always slightly metastable compared to
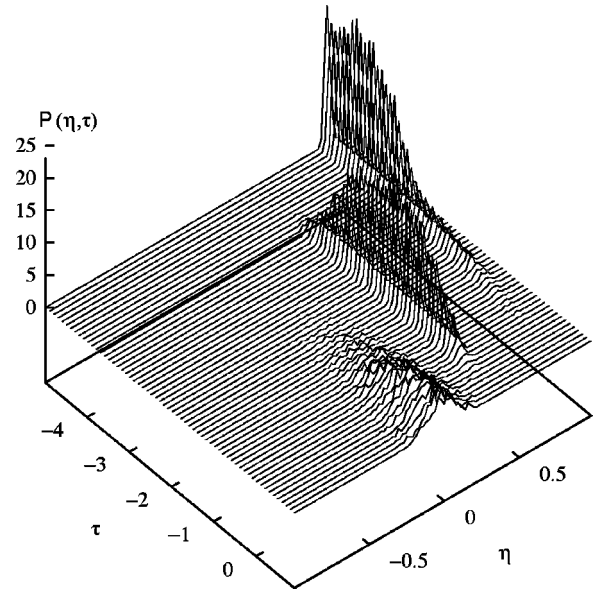

FIG. 4. The normalized probability distribution $P(\eta, \tau(t))$ of the order parameter η as a function of η as τ is reduced from $\tau = 1$ with a holding time of $t_h = 100$ steps (curve number 3 in Fig. 3).

the other two minima. While our order parameter η has no direct connection to actual order parameters for orientational transitions of C_{70} it may be thought of as a ''distance'' along a ''minimum free-energy'' path connecting the parent minima to the two nonequivalent product minima in the true high-dimensional order parameter space.

We now investigate the dynamics of this transition and especially the effect of the metastable minimum at $\eta = \eta_1$. The dynamics is governed by a Langevin equation[15] for the order parameter η (we neglect all spatial fluctuations) evolving in the free-energy landscape $f(\eta)$ and is given by

$$d\eta/dt = -\Gamma df(\eta)/d\eta + \xi(t). \quad (2)$$

The friction coefficient Γ is related to the variance of the Gaussian white noise γ by the usual fluctuation-dissipation relation $\gamma = \langle \xi(t) \xi(t') \rangle = 2k_B T \Gamma \delta(t - t')$, where k_B is the Boltzmann constant and T the actual temperature. The value of Γ can, in principle, be obtained from the libron line shape obtained from Raman[16] and neutron[17] scattering experiments. The angular brackets signify an average over various realizations of the random noise.

We simulate Eq. (2) using a straightforward Euler discretization scheme with a time step of $\Delta t = 0.01$. The dimensionless temperature τ is reduced from 1 in steps of 0.01. At each temperature step the system was held for t_h steps (a larger value of t_h implies slower cooling). The order parameter η averaged over t_h steps and over various realizations of the random noise (typically 300–700) is plotted as a function of τ in Fig. 3 [for the above set of parameters for $f(\eta)$ and $\gamma = 1.8$]. The resemblance with the cooling curves of Fig. 2 is remarkable. Both extremely fast and slow cooling obtains a single-step transformation—the transformation becoming sharper as the cooling rate is reduced. For intermediate values of the cooling rate a plateau develops. The plateau results when the system is trapped, temporarily, in the intermediate

phase as it evolves from the parent to the product structure. This can be illustrated as follows.

In Fig. 4 we have plotted the probability distributions $P(\eta, \tau(t))$ as a function of $\tau(t)$ for a collection of 500 independent systems cooled from $\tau = 1$ to $\tau = -4.0$ with $t_h = 100\Delta t$. Starting from a delta function at the origin at $t = 0$ the $P(\eta, t)$ spreads out with time and eventually evolves into a strong peak centered at the equilibrium value of η. However, we observe that the system spends a considerable amount of time in the secondary metastable minimum near η_1, which roughly corresponds to the plateau observed in Fig. 3 (curve 3). In other words, at slow cooling rates the system gets enough time to relax to the global minimum. For very fast quenches, on the other hand, by the time the system relaxes from the parent to the metastable intermediate phase, τ decreases to the extent that the barriers are no longer sufficient to trap it there. Similar qualitative behavior is seen over a broad range of values for our parameters as long as the intermediate minimum lies sufficiently close to the true global minimum and it is sharp enough to trap the system effectively. This behavior is quite general and is analogous to that in ferroelectrics where a similar kinetic stabilization of the metastable paraelectric state produces double hysteresis loops.[18]

To paraphrase, the low-temperature structural transformation of solid C_{70} exhibits interesting kinetic effects, as evidenced by XRD experiments carried out at various cooling rates. At extremely slow cooling rates (0.0033 K/min), rarely employed in the studies so far, the transformation to the monoclinic phase proceeds through a single step. This implies that the equilibrium transformation corresponds to the simultaneous freezing of all orientational degrees of freedom, and recently[19] a structural model for the low-temperature monoclinic structure has been proposed. At high cooling rate the transformation from ideal hcp-to-monoclinic phase proceeds through an intermediate phase. With support from a theoretical model, we show that such a situation can arise if the intermediate phase is metastable. In the light of present investigations theoretical calculations on the stability of dhcp phase need to be reexamined.

[1] P. A. Heiney *et al.*, Phys. Rev. Lett. **66**, 2911 (1991).

[2] C. Christides, I. M. Thomas, T. J. S. Dennis, and K. Prassides, Europhys. Lett. **22**, 611 (1993).

[3] G. B. M. Vaughan *et al.*, Science **254**, 1350 (1991).

[4] M. A. Verheijen, H. Meekes, G. Meijer, P. Bennema, J. L. de Boer, S. van Smaalen, G. van Tendeloo, S. Amelinckx, S. Muto, and J. Landuyt, Chem. Phys. **166**, 287 (1992).

[5] G. van Tendeloo, S. Amelinckx, J. L. de Boer, S. van Smaalen, M. A. Verheijen, H. Meekes, and G. Meijer, Europhys. Lett. **21**, 329 (1993).

[6] T. Tanaka and T. Atake, J. Phys. Chem. Solids **57**, 277 (1996).

[7] J. Sworakowski, K. Palewska, and M. Bertault, Chem. Phys. Lett. **220**, 197 (1993).

[8] C. Meingast, F. Gugenberger, G. Roth, M. Haluska, and H. Kuzmany, Z. Phys. B **95**, 67 (1994).

[9] S. K. Ramasesha, A. K. Singh, Ram Seshadri, A. K. Sood, and C. N. R. Rao, Chem. Phys. Lett. **220**, 203 (1994).

[10] T. J. S. Dennis, K. Prassides, E. Roduner, L. Cristofolini, and R. DeRenzi, J. Phys. Chem. **97**, 8553 (1993).

[11] G. Ghosh, V. S. Sastry, C. S. Sundar, and T. S. Radhakrishnan, Solid State Commun. **105**, 247 (1998).

[12] G. V. Narasimha Rao, V. S. Sastry, M. Premila, A. Bharathi, C. S. Sundar, Y. Hariharan, V. Seshagiri, and T. S. Radhakrishnan, Powder Diffr. **11**, 5 (1996).

[13] G. V. Narasimha Rao, V. S. Sastry, H. S. G. K. Murthy, V. Seshagiri, and T. S. Radhakrishnan, Powder Diffr. **11**, 200 (1996).

[14] R. Sachidanandam and A. B. Harris, Phys. Rev. B **49**, 2878 (1994); A. V. Nikolaev and K. H. Michel, *ibid.* **54**, 12 733 (1996).

[15] P. M. Chaikin and T. C. Lubensky, *Principles of Condensed Matter Physics* (Cambridge University Press, Cambridge, 1997).

[16] P. H. M. van Loosdrecht, M. A. Verheijen, H. Meeks, P. J. M. van Bentum, and G. Meijer, Phys. Rev. B **47**, 7610 (1993).

[17] K. Prassides, in *Physics and Chemistry of Fullerenes*, edited by K. Prassides (Kluwer Academic Press, 1994), p. 203.

[18] See, for example, T. Mitsui, I. Tatsuzaki, and E. Nakamura, *An Introduction to the Physics of Ferroelectrics* (Gordon and Breach, New York, 1976).

[19] G. Ghosh, V. S. Sastry, and T. S. Radhakrishnan, Phys. Rev. B **57**, R13 969 (1998).