

## Time-Resolved X-Ray Studies of Quenching and Annealing in a Glass-Forming Intercalate, HNO<sub>3</sub>-Graphite

Roy Clarke and Pedro Hernandez<sup>(a)</sup>

*Randall Laboratory of Physics, University of Michigan, Ann Arbor, Michigan 48109*

(Received 9 November 1988)

We report high-resolution x-ray scattering results on the relaxation behavior of a glass-forming intercalate, HNO<sub>3</sub>-graphite. Isothermal annealing following a shallow quench is found to proceed via a sequence of discrete metastable states with modulated structures and appears to be a cooperative process.

PACS numbers: 64.70.Pf, 64.60.My, 81.40.Ef

Quenched structural disorder represents an important class of nonequilibrium dynamical systems.<sup>1</sup> In many cases, such as molecular glasses,<sup>2</sup> random spin systems,<sup>3</sup> and their ferroelectric analogs,<sup>4</sup> competing interactions are responsible for kinetically limited disordered phases. Glass formation, structural relaxation, and annealing are well-known examples of physical processes governed by kinetics, and although such phenomena are ubiquitous they are still quite poorly understood.<sup>5</sup> One would like to know, for example, what is the nature of local correlations and what mechanisms control a system's evolution towards the equilibrium state. The relationship between structural disorder and relaxation dynamics in spin-glasses<sup>6</sup> is also a topic of current interest in trying to understand the role of competing interactions in a more general sense.

While the ensemble-average behavior of nonequilibrium systems has been studied intensively there is little information as yet on the *local* structural correlations and their behavior during the progression to macroscopic long-range order. Real-time x-ray diffuse scattering offers a powerful experimental probe into this question, permitting one to follow the detailed kinetics of nonequilibrium states over length scales from atomic dimensions to several microns. Such high-resolution measurements have only recently been made possible by new developments in the techniques of time-resolved x-ray scattering.<sup>7,8</sup> In particular, the use of multichannel x-ray detectors coupled with very-high-brightness synchrotron x-ray beams has opened up a wide spectrum of nonequilibrium processes to experimental study.

This Letter reports the results of quenching and annealing experiments on a molecular intercalation compound, HNO<sub>3</sub>-graphite, which undergoes a first-order freezing transition at  $T_m \approx 252$  K. The experiments reveal dramatically different structural kinetics depending on whether the quench temperature  $T_q$  is above or below a certain point  $T_g$  which we associate with a glass transition. The case where  $T_g \leq T_q \leq T_m$  is particularly interesting: We are able to follow in real time the process of annealing and have found that the associated kinetics are characterized by the appearance of a series of *discrete metastable states* which lead ultimately to the equilibrium crystalline structure. The microscopic na-

ture of these states and their time dependence is the main focus of the work reported here.

The use of molecular intercalates for these experiments is motivated by earlier structural studies<sup>9,10</sup> showing that the molecular arrangement is determined by competing intermolecular forces.<sup>11</sup> Specifically, the low-temperature, equilibrium structure is dictated by commensurability with the corrugation potential of the graphite host. High stages<sup>12</sup> of intercalation favor the commensurate structure as the interlayer forces are weakened relative to the corrugation interaction. For this reason we chose to work with stage-4 HNO<sub>3</sub>-graphite, which has been reported to have a commensurately ordered equilibrium structure<sup>9</sup> with a relatively large in-plane unit cell ( $9a_0 \times 12a_0$ ) and weak three-dimensional interlayer correlation.<sup>10</sup>

The first indication of nonequilibrium effects in the ordering of HNO<sub>3</sub>-graphite was given by the rotating-anode x-ray scattering data in Fig. 1(a) showing the temperature dependence of the peak x-ray intensity measured at a reciprocal-lattice vector where a peak would appear in the fully ordered state. The x-ray intensity was measured during heating after the sample had first been cooled through the freezing transition at a moderately fast rate ( $\sim 1$  K/min). In this type of measurement one would normally expect the intensity to be constant for  $T < T_m$  (apart from the usual Debye-Waller thermal factor) and to exhibit a sharp drop at the melting point. What we see instead in Fig. 1(a) is not a sharp drop, but rather an *upturn* in intensity which onsets  $\approx 14$  K prior to melting.

The upturn in Fig. 1(a) is found to depend on both the heating rate and the thermal history of the sample. For example, if the sample is cooled very slowly through  $T_m$  ( $\lesssim 0.1$  K/min) only a discontinuous drop in the intensity is observed on subsequent heating. An additional clue is the existence of weak additional peaks [see Fig. 1(b)] in the "unannealed" diffraction pattern of samples cooled moderately fast (but not rapidly quenched). These additional features are not present when the samples are cooled very slowly through the freezing transition. Note also that the position of the peak ( $B$ ) plotted in Fig. 1(a) shifts during heating and does not correspond exactly to the commensurate value.

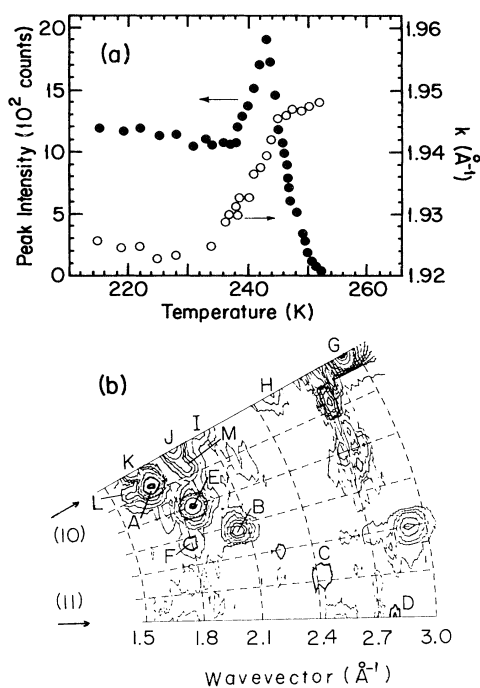


FIG. 1. X-ray scattering data on a single-crystal sample of stage-4  $\text{HNO}_3$ -graphite that had been cooled below the freezing transition at a rate of  $\sim 1 \text{ K min}^{-1}$ . (a) Premelting behavior of ordering peak; data taken on heating slowly ( $\sim 0.2 \text{ K min}^{-1}$ ). Closed circles, peak intensity; open circles, wave vector of peak. (b) Segment of in-plane x-ray scattering contour map at  $T=200 \text{ K}$ .  $G$  is the (100) graphite peak and  $F$ ,  $L$ , and  $M$  are examples of additional features associated with nonequilibrium structure. The ordering peak referred to in (a) is labeled  $B$ . The other labeled peaks are given by the equilibrium structure of the intercalant as described in Ref. 9.

All of these pieces of evidence point to a kinetic mechanism as the origin of the premelting anomaly shown in Fig. 1. Specifically, the ordering process is quite sluggish so that crystallographic order is not fully established unless the cooling rate is extremely slow. On heating, the partially ordered arrangement begins to anneal (i.e., become more ordered) at  $T_g \approx 238 \text{ K}$ , whereupon the x-ray intensity increases. Thus, even moderately slow rates of cooling can lead to frozen-in disorder.<sup>13</sup> In this case  $T_g$  would represent a glass transition temperature<sup>14</sup> below which the frozen-in disorder represents an effectively stable nonequilibrium state.

The intriguing behavior depicted in Figs. 1(a) and 1(b) motivated us to carry out a systematic study of the kinetics of the first-order freezing transition in stage-4  $\text{HNO}_3$ -graphite. Using a position-sensitive linear x-ray detector (resolution  $1.5 \times 10^{-3} \text{ \AA}^{-1}$  FWHM), a small ( $\pm 0.02 \text{ \AA}^{-1}$ ) region of reciprocal space was explored simultaneously in order to monitor the time-dependent structure factor associated with the ordering.<sup>15</sup> Data were accumulated within a 5-sec integration time taking

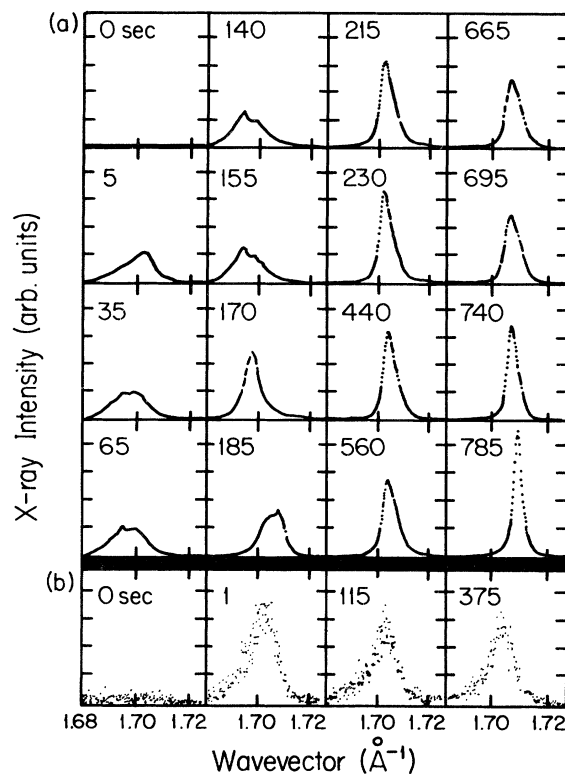


FIG. 2. Time-resolved x-ray scattering data for quenched stage-4  $\text{HNO}_3$ -graphite. (a) Shallow quench,  $T_q = 240 \text{ K}$ , showing annealing behavior. The accumulation time was 5 sec and a typical peak intensity is  $\sim 10^4$  counts; (b) deep quench,  $T_q = 102 \text{ K}$ , showing glassy structure. Accumulation time was 1 sec, giving  $\sim 150$  counts at the peak. Intervals shown refer to time after quenching. The region of reciprocal space around peak  $A$  [see Fig. 1(b)] is shown in each case.

advantage of the high flux available from the eight-pole wiggler beam line at Stanford Synchrotron Radiation Laboratory.

The following results refer to the time-evolution of the structure factor for two different depths of quench,  $T_q = T_m - 12 \text{ K}$  (shallow quench) and  $T_q = T_m - 150 \text{ K}$  (deep quench). Quenching was performed by blowing cooled  $\text{N}_2$  gas over the samples held in a Displex cryostat. Prior to the quench the sample temperature was  $260 \pm 0.2 \text{ K}$ . A small differential thermocouple was used to monitor the sample temperature during and after quenching; the interval required to reach the quench temperature was less than 0.5 sec in both cases.

Figure 2(a) shows a time-resolved sequence of x-ray data for a shallow quench. A cut was made through reciprocal space at the (07) point,  $q \approx 1.7 \text{ \AA}^{-1}$  [through peak  $A$  in Fig. 1(b)]. Immediately after the quench the scattering profile is quite broad ( $6 \times 10^{-3} \text{ \AA}^{-1}$  FWHM) and appears to consist of several overlapping peaks. As isothermal annealing takes place (at  $T_q$ ) the profile narrows and its mean position tends toward higher wave

vector. We have checked carefully that no deintercalation or restaging occurs during these measurements. The most striking aspect of the data is the long interval that elapses before anything resembling a sharp commensurate peak appears (c.f. data at 785 sec after the quench). Another general feature which stands out is that the progression towards ordering is not smooth and continuous but takes place in a series of discrete steps (see also Fig. 3). Between jumps, the line shape and position remain relatively constant. We stress that these diffraction peaks correspond to nonequilibrium structure which has no counterpart in the equilibrium phase: Stage-4 HNO<sub>3</sub>-graphite is accurately commensurate over the whole temperature range below freezing.<sup>9</sup> It appears, therefore, that the structure passes through a series of long-lived metastable states as equilibrium is approached. This is the most important finding of these studies.

What can we say about the nature of the metastable states? Since the detector can sample only a limited portion of reciprocal space in a single run, and only along a single axis at present, a detailed picture of the metastable structure is not yet possible. However, there are some interesting general observations that one can make: First, there is the trend during annealing towards increasing wave vector, as noted above. Second, the peaks are substantially broader than the resolution width throughout the whole sequence of evolution shown in Fig. 2(a). This immediately implies that the structural ordering associated with the metastable states is not long ranged but extends over only a few hundred Å. We will refer to this as "intermediate-range ordering."

One can speculate as to the form of the metastable structures and most likely they consist of domains approximately 100–500 Å in size, of commensurately ordered molecules separated by domain walls, or discommensurations.<sup>11</sup> This picture is supported by the presence of poorly resolved shoulder or split peaks [see Fig. 1(b)], and is also consistent with the shift of the peak position to longer wave vectors as would be given by a de-

creasing density of light domain walls [see also, Fig. 1(a)]. Note that peak splitting and asymmetries on the order of  $\pi/500 \text{ \AA}^{-1}$  are consistent with typical length scales associated with discommensurations. It is also of interest to note that the quasielastic neutron scattering studies<sup>16</sup> of stage-2 HNO<sub>3</sub>-graphite (which has an *equilibrium* incommensurate phase prior to melting) have shown a strong dependence of molecular librations on the discommensuration density.

Further clues as to the nature of the intermediate-range ordering and its time dependence are seen in Fig. 3. Note the overall tendency of the peak intensity to increase with time, together with a complementary trend of decreasing peak width. It is important, however, to notice that these trends are not monotonic and can even be retrograde: For example, the peak width (a measure of the inverse correlation length) shows oscillations (see Fig. 3) before finally turning down towards the resolution limit at very long times. We believe this unexpected behavior is related intimately to the dynamics of annealing, as will be discussed in more detail below.

In contrast to the annealing effects following a shallow quench ( $T_q > T_g$ ), a deep quench produces a frozen-in disorder. This is illustrated in Fig. 2(b); the data show no obvious change in the structure factor from 1 sec after quenching to at least 375 sec. The relaxation after a deep quench is characterized by a very slow ( $\sim \log t$ ) increase in peak intensity (see Fig. 3) reminiscent of a glass. The broad Lorentzian structure factor [see Fig. 2(b)] indicates that the intermediate-range order of the deep-quenched state has a distribution of wave vectors associated with it. At the level of our resolution the distribution seems to be continuous, indicating that the glassy phase is a superposition of many local configurations with similar wave vectors.

We turn now to a discussion of these results in the context of how a disordered dynamical system approaches equilibrium. Very little is known about this question from a statistical mechanical viewpoint, although it has been speculated that the dynamics is controlled by a multidimensional free-energy surface with many hills and valleys.<sup>3,17</sup> In a deep quench many local minima would be occupied simultaneously. Our x-ray data support this type of mechanism. During the process of annealing the evolution seen in Fig. 2(a) might be described in terms of a local restructuring of the disordered system to a configuration favored by a particular local minimum. The system then proceeds to "explore" the free-energy surface in an attempt to find the lowest-energy configuration. Taking a typical value for the dwell time,  $\sim 10^2$  sec, and a characteristic attempt frequency of  $10^{14}$  Hz, we estimate that the rms "roughness" of the free-energy surface is approximately 0.6 eV. This large value reflects the collective nature of the molecular motions involved in the annealing process.

Interestingly, the peak widths are relatively sharp (FWHM  $\lesssim 6 \times 10^{-3} \text{ \AA}^{-1}$ ) during annealing, which im-

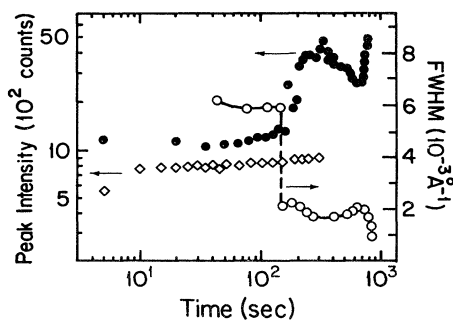


FIG. 3. Time dependence of x-ray data from Fig. 2. Closed circles, intensity of strongest diffraction feature after shallow quench; diamonds, intensity after deep quench; open circles, FWHM of most intense peak after shallow quench.

plies that there are large ( $\geq 500 \text{ \AA}$ ) highly correlated regions within the sample. Moreover, dramatic changes in intensity and peak width (see Fig. 3) show the annealing to be a *cooperative* process such that the whole system transforms from one metastable state to another. This is somewhat surprising given that the x-ray beam illuminates an area of at least  $1 \text{ mm}^2$ . We conclude from these observations that the network of compact domains (of average size  $\geq 500 \text{ \AA}$ ) is correlated dynamically such that, during a transformation, information about the metastable configuration propagates throughout the whole network.

If the picture of a free-energy hyperspace is relevant here, it is not surprising that a system distributed over different sets of local minima at different times would exhibit a highly irregular time dependence of peak widths and intensities. We note also that each time the system is quenched the details of the peak shapes and time intervals between jumps are different but follow the same generic behavior as we have described, for the same depths of quench. This is what one would expect if local minima of very similar depths were controlling the annealing dynamics, which could also explain why a jump occurs when two overlapping intensities become approximately equal. Furthermore, the idea of the progression from one metastable state to another being a cooperative process is consistent with our observation that a unique temperature  $T_g$  exists below which the relaxation is extremely slow.

There are many unanswered questions relating to the behavior described above. However, high-resolution measurements have identified some important features of the dynamics of quenched structural disorder which should be taken into account in future theoretical work. In summary, we find that the annealing process proceeds via a sequence of discrete metastable states. The process seems to be a cooperative one involving long-range correlations but not necessarily long-range structural order. In this respect the analogy with spin-glasses appears to be quite interesting and would be worthwhile to explore in detail.

It is a pleasure to acknowledge the assistance of the staff of the Stanford Synchrotron Radiation Laboratory in the course of this work, and we thank F. Lamelas, S. K. Sinha, P. Dimon, and E. Sirota for their help in the early stages of the experiment. We also benefitted from stimulating discussions with S. K. Sinha and R. Hoogerbeets. The project was supported by NSF Grants No. DMR8404075 and No. DMR8805156.

<sup>(a)</sup>Present address: Universidad Autónoma de Puebla, Puebla, Mexico.

<sup>1</sup>J. Joffrin, in *La Matière Mal Condensée*, edited by R. Balian, R. Maynard, and G. Toulouse (North-Holland, New York, 1979), p. 63.

<sup>2</sup>K. H. Michel, Phys. Rev. Lett. **57**, 2188 (1986); H. Klee, H. O. Carmesin, and K. Knorr, *ibid.* **61**, 1855 (1988).

<sup>3</sup>K. Binder and A. P. Young, Rev. Mod. Phys. **58**, 801 (1986).

<sup>4</sup>E. Courtens, T. F. Rosenbaum, S. E. Nagler, and P. M. Horn, Phys. Rev. B **29**, 515 (1984).

<sup>5</sup>See, for example, *Heidelberg Colloquium on Glassy Dynamics*, edited by J. L. van Hemmen and I. Morgenstern, Lecture Notes in Physics Vol. 275 (Springer-Verlag, New York, 1987).

<sup>6</sup>R. Hoogerbeets, W.-L. Luo, and R. Orbach, Phys. Rev. B **34**, 1719 (1986), and references therein.

<sup>7</sup>See, *Time-Resolved Studies and Ultrafast Detectors*, edited by R. Clarke, P. Sigler, and D. Mills (Argonne National Laboratory Workshop Report No. ANL/APS-TM-2, 1988).

<sup>8</sup>K. F. Ludwig, Jr., G. B. Stephenson, J. L. Jordan-Sweet, J. Mainville, Y. S. Yang, and M. Sutton, Phys. Rev. Lett. **61**, 1859 (1988).

<sup>9</sup>R. Clarke, P. Hernandez, H. Homma, and E. Montague, Synth. Met. **12**, 27 (1985).

<sup>10</sup>E. J. Samuelson, R. Moret, H. Fuzellier, M. Klatt, M. Lelaurain, and A. Hérold, Phys. Rev. B **32**, 417 (1985).

<sup>11</sup>M. J. Winokur and R. Clarke, Phys. Rev. Lett. **54**, 811 (1985).

<sup>12</sup>The "stage" of an intercalation compound is the number of carbon planes separating adjacent intercalant layers.

<sup>13</sup>The *symmetry* of domain vertices plays an important role in ordering kinetics. For example, computer simulations of domain walls on a triangular lattice have been found to favor fast domain growth independent of quench temperature, whereas walls on a square lattice can be frozen-in at low temperatures [see P. S. Sahni, D. J. Srolovitz, G. S. Grest, M. P. Anderson, and S. A. Safran, Phys. Rev. B **28**, 2705 (1983)]. Interestingly, our samples show the presence of an additional commensurate phase which has *triangular* symmetry [peaks  $H-J$  in Fig. 1(b)]. The kinetic behavior of this phase is very similar to that reported by P. Hernandez, F. Lamelas, R. Clarke, P. Dimon, E. B. Sirota, and S. K. Sinha [Phys. Rev. Lett. **59**, 1220 (1987)] and supports the simulation results of Sahni *et al.*

<sup>14</sup>P. W. Anderson, Ref. 1, p. 161.

<sup>15</sup>Hernandez *et al.*, Ref. 13.

<sup>16</sup>I. Rosenman, F. Batallan, A. Magerl, and H. Fuzellier, Synth. Met. **12**, 117 (1985).

<sup>17</sup>J. D. Reger, W. Kinzel, and K. Binder, Phys. Rev. B **30**, 4028 (1984).