

ORDERING AND KINETICS IN GRAPHITE INTERCALATED WITH NITRIC ACID

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ABSTRACT

Molecular ordering in HNO₃-graphite is studied by X-ray scattering. Two stable in-plane configurations coexist at T ≤ 250K and both appear to be registered with graphite. One configuration is hexagonal and the other oblique, the latter possibly stabilized by a ~12° tilt of the nitrate group. Time resolved X-ray scattering shows that the evolution of the oblique phase is very sluggish.

INTRODUCTION

While nitric acid graphite was the first intercalation compound to be synthesized, more than 150 years ago, its structure is still not well understood [1]. Here, we report on an X-ray study of HNO₃-graphite with the aim of probing the temperature dependence of the molecular arrangement, especially the in-plane structure.

The structure of many molecular graphite intercalation compounds (GICs) can be described in terms of long-period superlattices, either commensurate or incommensurate with the graphite host [2,3]. Our major interest in HNO₃-GIC is the possibility that the intercalant could break the symmetry of the host graphite to produce a non-hexagonal structure which may be quasi-two-dimensional at the higher stages. In particular the behavior can be contrasted with that of the more isotropic, hexagonal, structures; for example, SbCl₅-GIC which shows interesting kinetic phenomena associated with the ordering of the $\sqrt{7} \times \sqrt{7}$ in-plane superlattice [3].

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EXPERIMENTAL PROCEDURE

Natural single crystals of graphite were intercalated in the vapor of a 50/50 mixture of fuming and normal HNO_3 to give stage 4. Only pure stage samples were selected. After intercalation (~ 24 hours) the samples were removed from the reaction tube and transferred quickly to the cold finger of a closed cycle helium cryostat. To prevent vacuum desorption of the intercalant the shroud of the cryostat was not evacuated until the sample temperature fell below $T \approx 255\text{K}$, the "melting" point of the molecular layer [4]. The samples were found to be perfectly stable at these temperatures for periods of at least two weeks, as judged by the $hk0$ and $00l$ diffraction intensities. The X-ray data were obtained using a four-circle offset Huber diffractometer in conjunction with a 12 kW rotating anode ($\text{MoK}\alpha$) generator.

IN-PLANE STRUCTURE

The in-plane diffraction pattern of stage 4 HNO_3 -GIC at $T = 200\text{K}$ is shown in Fig. 1, represented as a contour map of the scattered intensity.

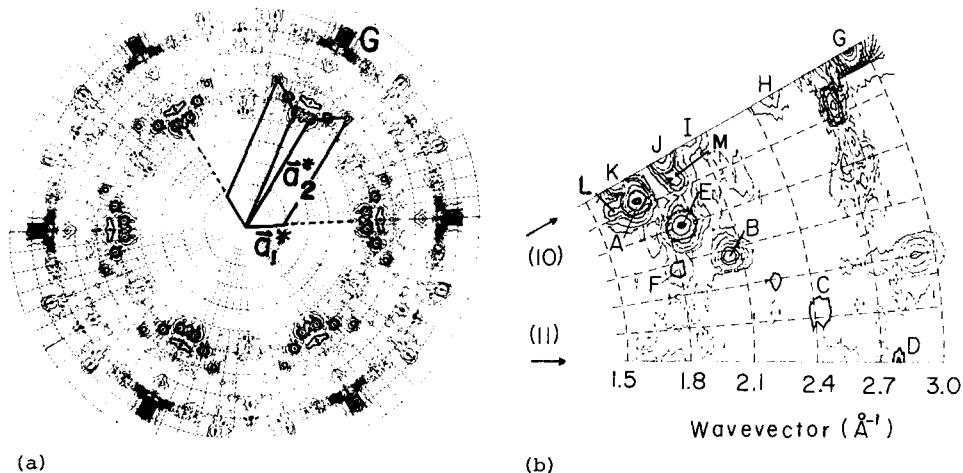


Fig. 1. (a) In-plane diffraction pattern of stage 4 HNO_3 -GIC at $T=200\text{K}$. (b) Detail of (a) showing peaks from graphite (G), oblique (A-D), and hexagonal (E,H,I,K) lattices discussed in the text.

Accompanying the six expected graphite (10) peaks are a large number of relatively sharp intercalant peaks arranged in a star-shaped pattern which immediately suggests that the symmetry of the GIC at $T = 200\text{K}$ is no longer hexagonal. Our interpretation of the complex ($hk0$) diffraction data shown in

Fig. 1 is based on a long period superlattice ordering of the intercalant. A portion of the proposed unit cell is shown in Fig. 2. Out-of-plane (c^*) scans through several intercalant peaks suggests that the intercalant layers are effectively uncorrelated in stage 4 and so a quasi-two-dimensional treatment should be sufficient.

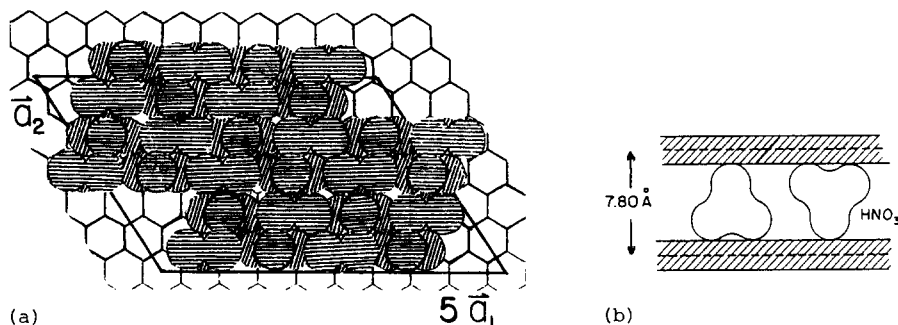


Fig. 2. (a) Oblique unit cell of $C_{4n}(HNO_3)$ based on the packing of NO_3^- ions suggested by Touzain [5]. (b) Viewed normal to c -axis.

Transformation of the reciprocal translation vectors shown in Fig. 1 to direct space gives $a_1 = 4.43\text{\AA}$, precisely parallel to graphite $\langle 100 \rangle$, and $a_2 = 14.94\text{\AA}$, rotated by an angle $\gamma = 4.5 \pm 0.2^\circ$ relative to $\langle 100 \rangle$. The former distance, 4.43\AA , is consistent with an alignment of nitrate ions suggested recently by Touzain [5] in which the NO_3^- plane is approximately normal to the layers and parallel to $\langle 100 \rangle$ [Fig. 2(b)]. Note that $5 \times 4.43\text{\AA} = 9 a_0$, where a_0 is the graphite in-plane unit cell dimension; thus a chain of 5 HNO_3 molecules is exactly in registry with graphite along $\langle 100 \rangle$. Also, the actual periodicity may be doubled, i.e., $18a_0$, because of the up-down alternation of molecules [Fig. 2(b)].

The a_2 lattice spacing yields no such obvious registry although we strongly suspect that some kind of registered arrangement must exist because the diffraction pattern, in particular the spacing of peaks, shows no temperature dependence from just below the order-disorder transition at $T \approx 255\text{K}$ down to $T = 10\text{K}$. Extending the a_2 translation vector out to a length of approximately $12 a_0$, at the 4.5° rotation angle indicated by the diffraction pattern, brings the structure into registry in this direction. The presence of closely spaced superlattice satellites [e.g., peaks F and L in Fig. 1(b)] also supports this picture. A closer inspection of the in-plane diffraction pattern [see Fig. 1(b)] reveals a series of peaks (labeled H, I, K, ...) exactly along the $\{100\}$ reciprocal graphite axes coinciding with those expected for a 7×7 commensurate hexagonal superlattice. We therefore conclude that the in-plane arrangement is actually a coexistence of *two registered structures*, one oblique and the

other hexagonal. Possible explanations may include the existence of other nitrate reaction products [6] and/or several equivalent molecular orientations in the host. Note that we see no evidence for a "residue" phase [7] in our samples.

MOLECULAR ORIENTATION

In order to better understand the in-plane structural arrangement in the ordered phase of HNO_3 -GIC a fit was made to the 00ℓ structure factor which is very sensitive to the orientation of the HNO_3 molecules. We assumed undistorted HNO_3 molecules [6] and confirmed Touzain's finding that a perpendicular arrangement [Fig. 2(b)] gives a better fit to the 00ℓ intensities than the parallel orientation originally suggested by Rüdorff [8]. However, allowing the perpendicular configuration to tip a little relative to the c-axis, a still better fit could be obtained (see Table I). The fit gave a tilt angle of $12 \pm 2^\circ$ and an average composition of $\text{C}_{4n} \cdot \text{HNO}_3$ (stage $n=3$) could also be derived from the structure factor fit.

The slightly off-vertical molecular tilt is consistent with recent γ -ray resonance scattering measurements [9] and with recent experiments showing HNO_3 vibrational modes polarized predominantly normal to the layers [6]. It was suggested some time ago that the forces acting between nitric acid molecules may pull the graphite blocks out of their A/A alignment [10]. This kind of mechanism, involving a tilt of the molecules, could provide a reason for the oblique in-plane structure that we observe.

Table I. Comparison of measured and calculated 00ℓ intensities for stage 3 HNO_3 -GIC. Corrections for Lorentz factor, polarization and Debye Waller effects ($\Delta u = 0.21\text{\AA}$) are included.

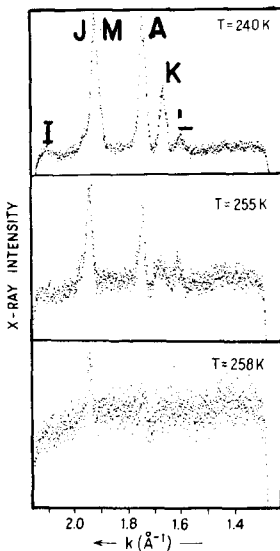
ℓ	I_{meas}	I_{calc}	ℓ	I_{meas}	I_{calc}
2	1.27	0.06	7	0.01	0.04
3	0.30	3.24	8	3.14	3.56
4	100	100	9	6.63	6.56
5	21.63	22.00	10	0.03	0.00
6	1.50	1.43			

ORDER-DISORDER TRANSITION

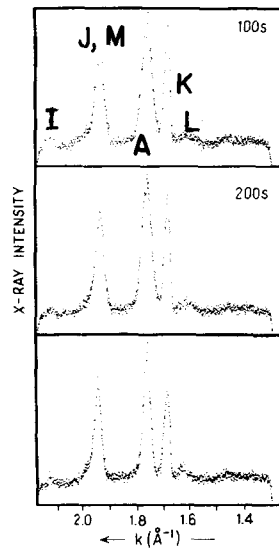
The order-disorder transition in HNO_3 occurs at $T \approx 250\text{K}$ and is known to be somewhat hysteretic [11]. A detailed sequence of diffractometer scans through several superlattice peaks close to the (10) reciprocal axis is shown in

Fig. 3(a) with the temperature slowly increasing through the transition. The coexistence of a diffuse peak ($k = 1.77\text{\AA}^{-1}$), from the "liquid" phase, and sharp peaks from the ordered phase can be seen at $T \approx 255\text{K}$ clearly identifying the transition as first-order, as expected since the symmetries of the upper and lower phases are not related. Note also, in Fig. 3(a) that the peaks associated with the hexagonal axes tend to fade out a few degrees higher than those from the oblique phase. The different stability of the two phases may be responsible for the observation of *two* closely spaced peaks (at 150K and 154K) in the calorimetry measurements of Dworkin et al. [12].

The data shown in Fig. 3(a) were taken using a position sensitive X-ray detector which allows the recording of many X-ray peaks simultaneously. The method therefore lends itself to probing *time-dependent* X-ray scattering such as one might observe near a phase transition. Fig. 3(b) shows the results of quenching through the transition of stage 4 HNO_3 -GIC at a rate of more than 20K s^{-1} . The peaks from the oblique phase evolve much more slowly than those from the hexagonal phase. In fact, on quenching to only 30K below the transition, the peak from the oblique phase remains broad for hundreds of seconds. The inverse width of this peak corresponds to a domain size of only $\sim 80\text{\AA}$ whereas the hexagonal-phase peaks achieve resolution width after a few



(a)



(b)

Fig. 3. (a) Series of in-plane diffraction scans on heating through the order-disorder transition. Peak labels correspond to those in Fig. 1(b). (b) Time resolved scans after quenching to 230K. The lowermost scan was taken after annealing for 5 min. at 245K.

seconds. This behavior implies that domains of the low symmetry phase are essentially pinned, even near T_C , whereas the hexagonal phase is free to undergo rapid evolution. This latter finding is consistent with recent quenching experiments in high stage $SbCl_5$ -GIC [3] and is related to the results of recent computer simulations [13] of domain growth in highly degenerate systems. These studies show that the *symmetry* of the domain walls is crucial in determining the nature of the evolution of the ordered structure.

Finally we comment on previously reported results on stage 2 HNO_3 -GIC [1] showing an incommensurate phase and an extra associated transition. The incommensurate phase seems to be absent in the stage 4 samples and is possibly stabilized by the stronger interlayer interactions at lower stage.

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