VOLUME 27, NUMBER 2

15 JANUARY 1983

In situ x-ray investigation of stage transformations in potassium-graphite intercalation compounds

M. E. Misenheimer and H. Zabel Department of Physics and Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801 (Received 30 August 1982)

We have studied stage transformations and growth kinetics of potassium-graphite intercalation compounds by x-ray (001) scans. The samples were prepared *in situ* in a high-temperature two-zone x-ray furnace. In the transition regions of stages $1 \leftrightarrow 2, 4 \leftrightarrow 5$, and $6 \leftrightarrow 7$, two distinct stages coexist and all Bragg reflections exhibit resolution-limited widths. This implies that the stage transformation is a direct process with no need of forming intermediate structures. The kinetics of the transformation indicate that the staging process is nucleation rather than diffusion controlled.

The ability to form stages is one of the most exciting and unique properties of graphite intercalation compounds. By staging, we understand the formation of an ordered array of alternating graphite and intercalant layers, where the stage number n designates the number of graphite layers between any two intercalant layers. The phenomenon of staging has been known for a long time,¹⁻³ however, only recently has it attracted considerable experimental as well as theoretical research activity.^{4-7,9-11,13-16} In general, intercalation is readily achieved, and the stage transformation $n \rightarrow n \pm 1$ takes place with ease. This is especially true for the heavy alkali-metal atoms. The range of order is usually quite long, extending well over 1000 Å in both directions, normal and parallel to the layers.^{7,8} Daumas and Herold⁹ (DH) have proposed a staging model which assumes domains of intercalant between any graphite planes. These domains are then stacked in columns to form ordered stages [see Fig. 1(a)]. Stage transformation merely requires a spreading out and rearrangement of the islands without the necessity of large spatial motion of the intercalant atoms. Although compelling in its principle concept, the DH model has not yet received direct experimental verification.

Here we report on an x-ray investigation of the immediate transition region of the stage transformation $n \leftrightarrow n+1$, which can be considered as a first-order phase transition. According to the DH model, during the transformation the intercalant islands may partially overlap, causing stacking disorder and/or large coherency stresses at the edges of the intercalant islands to occur [compare Fig. 1(b)]. Disorder and stresses, in turn, should give rise to diffuse scattering and broadening of Bragg reflections, respectively. In addition, the study of the time dependence of the stage transformations should yield information on the transition rate determining processes.

All x-ray results, reported on here, are confined to

the (001) reflections. These measurements were carried out on samples prepared *in situ* in a hightemperature x-ray furnace. Details of this furnace, which is based upon the standard "two-bulb" technique, ^{1-3,10} will be published in a future work. We used Mo $K\alpha$ radiation monochromated either by a graphite (002) or, for higher resolution, flat silicon (111) monochromator in the incident beam. Pristine highly oriented pyrolytic graphite (HOPG) of grade ZYB from Union Carbide and potassium metal with a stated purity of 99.8% from A. D. Mackay were used.

Figure 2 shows a sequence of (001) reflections taken during the transition from stage 1 to stage 2. The temperature of the potassium metal furnace was kept







1443

<u>27</u>





constant at 208 °C, while changing the graphite temperature. Starting with a stage-1 compound [Fig. 2(a)], we increased the graphite temperature from 272.8 to 276.8 °C so that it fell in the middle of the transition region. Within 5 h we found two sets of reflections, one corresponding to stage 1 and another corresponding to stage 2 [Fig. 2(b)]. The peaks are labeled by their *l* value, disregarding the actual stacking sequence of the graphite and alkali layers. After 8 h the stage-2 component had grown at the expense of the stage-1 part. After 50 h the stage transformation leveled off and the sample had become mostly stage 2, but with an appreciable amount of stage 1 still present [Fig. 2(c)]. Finally, 185 h later, we increased the graphite temperature to 278.6 °C and obtained an almost pure stage-2 compound [Fig. 2(d)]. With respect to the sample temperature, the transition region is not wider than 6 °C. By reversing the stage transformation from stage 2 to 1 we noticed a hysteresis of not more than 2°C. Notice that the widths and the structure factors of the stage-1 and stage-2 (001) reflections in the transition region are the same as in the pure stage compounds. Also, there is no observable diffuse scattering. Thus, in the transition region, two distinct stages coexist and the growth kinetics seem not to disturb the longrange order of the single compounds.

In Fig. 3 we plot the time dependence of the integrated intensity in the transition region, normalized to its value in the corresponding pure stage compound, for the stage-1 (002) and stage-2 (003) reflections. The intensities were measured by scanning across the (001) reflections in the h direction and then were corrected for background scattering. This procedure effectively cancels out intensity variations



FIG. 2. (a)-(d) Sequence of x-ray (001) scans taken during the transition from stages 1 to 2. (a) Pure stage 1. (b) Two sets of reflections indicating a coexistence of stages 1 and 2 during the transition. (c) Same as (b) but at a later time in the transition. (d) Stage-2 (001) reflections, after raising the temperature.

FIG. 3. Time dependence in the transition region between stages 1 and 2 of the integrated intensity normalized to its value in the pure stage compound for the stage-1 (002) and stage-2 (003) reflections.

IN SITU X-RAY INVESTIGATION OF STAGE ...

1445

due to different mosaic spreads in both stages and possible misalignment of the sample. After 30 h a first equilibrium was reached. Ten hours later a fluctuation of the temperature controller initiated a new stage transformation which again leveled off 20 h later. By this time the stage-1 intensity had fallen to 35% of its initial value and the stage-2 intensity had risen to 50% of its final value.

Similar experiments, but with higher angular resolution, were carried out during the stage transformations $4 \rightarrow 5$ and $6 \rightarrow 7$. Figure 4 shows an (001) scan for the former, during the transition. Again, we observed two sets of reflections corresponding to the pure stage compounds with no indication of stress or domain size broadening effects. The widths of all (001) Bragg reflections are resolution limited. Apparent broadening of some reflections occurs only if (001) reflections of different stages tend to overlap.

The stage transitions investigated here can be considered as reconstructive transformations, in which both diffusion of alkali atoms and interfacial reaction play an important role. Usually, one of the processes involved requires almost all of the free energy available for the transformation and therefore determines the rate of transition. In our case, the rate of the transformation may be either controlled by the nucleation rate of alkali domains and/or by the growth of stage $n \pm 1$ domains in an environment of stage n. With respect to domain growth, one has to distinguish between growth parallel and normal to the planes, which may have different time constants. In this experiment, we only probed the growth rate normal to the planes.

As mentioned before, we have not noticed any reflection broadening effects due to finite domain size normal to the planes or time-dependent widths of



FIG. 4. X-ray (001) scan during the transition from stages 4 to 5.

(001) reflections. We have only observed a time dependence in the integrated intensity of the (001)reflections, originating from coexisting stages. Since HOPG and the intercalated compounds are actually composed of numerous crystallites, the coexistence of two sets of (001) reflections present in the transition region indicates that part of the crystallites is stage n and part is stage n + 1. Due to this fact, we cannot completely rule out the possibility of domain growth, as sketched in Fig. 1(b), during the transition within a crystallite. We only "see" the statistical average of all the crystallites, of which only a few may be changing stage at any one time. However, the time scale of the stage change must be small. Otherwise, there would be an ensemble of crystallites, all with different grades of completion of the transition which, in turn, would cause a broadening of the (001) reflections. Since the height of the (001) reflections is a slow function of time, while the width apparently does not change, we conclude that the stage transformation is predominantly controlled by the nucleation rate of domains rather than by the diffusion dependent growth kinetics of the alkali islands.

The observation of pure stage compounds in the transition region yields additional information on the major stabilizing forces of pure stage ordering in graphite intercalation compounds. Safran and Hamann¹¹ have shown that elastic interactions allow the formation of equilibrium nonpure stages,¹² but that electrostatic interactions would drive these structures to pure stage ordering. If nonpure stages exist, then the stage transformation $1 \leftrightarrow 2$ should proceed through transitions to "successively lower" nonpure stages (i.e., from, say, four filled-one empty to three filled-one empty), which is analogous to the fact that the stage transformation $n \rightarrow n + m$ always proceeds via the sequence $n \rightarrow n + 1 \rightarrow n + 2 \rightarrow \ldots \rightarrow n + m$ $-1 \rightarrow n + m.^{13,14}$ Thus, depending on the rate of transformation, the (001) reflections should show one of two possibilites. First, one set of reflections would exist corresponding to a single nonpure stage. These peaks would have the same width as in a pure stage since long-range order is preserved; however, as the transition to lower nonpure stages occurs, the 2θ position of these reflections would shift from their stage-1 to their stage-2 values. In the other possibility, an ensemble of crystallites, all at various steps of the transition, would give rise to numerous sets of reflections corresponding to each of the intermediate nonpure stages, which would appear as a broadening of the pure stage reflections. Since neither possibility was seen, we conclude that nonpure stages do not exist, which implies that the dominant stabilizer of pure stage compounds is the electrostatic interaction. Safran¹⁵ has also calculated a phase diagram for stage transformations based on the DH model using a mean-field approach. If nonpure stages do not exist,

<u>27</u>

then this calculation predicts a two-phase separation in the transition region between all stages n and n+1. We believe the coexistence of stages 1 and 2 found in the transition region, and reported on above, arises from this two-phase separation.

Our results differ from those found in acceptor compounds. Metz and Hohlwein¹⁶ have seen a three-phase separation in the stage $1 \rightarrow 2$ transition region of FeCl₃ compounds, namely, stage 1, stage 2, and pure graphite. Further, stage 1 was the only true pure stage compound. Higher stages were a random mixture of stages. Since elastic interactions should be independent of the donor or acceptor nature of the intercalant species, these differences again indicate the importance of electrostatic interactions.

We wish to thank Dr. A. W. Moore for providing the HOPG material used in this experiment and S. A. Safran for fruitful discussions. We acknowledge support by the Department of Energy, Division of Materials Research, under Contract No. DE-AC02-76 ER01198. Equipment support has also been obtained from the Research Corporation and the University of Illinois Research Board, which we gratefully acknowledge. Part of the x-ray studies were carried out in the Center for Microanalysis of Materials, which is partially supported by the Department of Energy, Division of Materials Research.

- ¹K. Fredenhagen and G. Cadenbach, Z. Anorg. Allg. Chem. 158, 249 (1926).
- ²K. Fredenhagen and H. Suck, Z. Anorg. Allg. Chem. <u>178</u>, 353 (1929).
- ³A. Schleede and M. Wellmann, Z. Phys. Chem. Abt. B <u>18</u>, 1 (1932).
- ⁴D. E. Nixon and G. S. Parry, Br. J. Appl. Phys. <u>1D</u>, 291 (1968).
- ⁵Roy Clarke, N. Caswell, and S. A. Solin, Phys. Rev. Lett. <u>42</u>, 61 (1979).
- ⁶N. Caswell, Phys. Rev. B <u>22</u>, 6308 (1980).
- ⁷F. Rousseaux, A. Plancon, D. Tchoubar, D. Guerard, and P. Lagrange, in *Proceedings of the International Conference* on the Physics of Intercalation Compounds, Trieste, Italy,
- 1981, Springer Series of Solid-State Sciences, edited by L. Pietronero and E. Tosatti (Springer, Berlin, 1981), Vol. 38.

- ⁸M. E. Misenheimer and H. Zabel (unpublished).
- ⁹N. Daumas and A. Herold, C. R. Acad. Sci., Ser. C <u>268</u>, 273 (1969).
- ¹⁰A. Herold, Bull. Soc. Chim. Fr. 999 (1955).
- ¹¹S. A. Safran and D. R. Hamann, Phys. Rev. B <u>22</u>, 606 (1980).
- ¹²By nonpure stage we mean an ordered periodic structure of alternating graphite planes whose interlayer spaces are filled with intercalant, and graphite planes whose interlayer spaces are empty, for example, a sequence of four filled and one empty (see Ref. 11).
- ¹³C. C. Shieh, R. L. Schmidt, and J. E. Fischer, Phys. Rev. B <u>20</u>, 3351 (1979).
- ¹⁴A. Hamwi, P. Touzain, L. Bonnetain, A. Boeuf, A. Freund, and C. Riekel (unpublished).
- ¹⁵S. A. Safran, Phys. Rev. Lett. <u>44</u>, 937 (1980).
- ¹⁶W. Metz and D. Hohlwein, Carbon <u>13</u>, 87 (1975).