

Low-temperature structural transition in KC_{24}

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Results of single-crystal x-ray diffractometer studies of stage-2 KC_{24} are presented. The data show conclusively that the transition at $T_l \approx 95$ K is of first order and involves a fragmentation into multiple high-order commensurate phases. The transition is discussed in terms of the discommensuration-domain model previously applied to other alkali intercalates.

Significant advances have been made recently in understanding the structural aspects of low-stage alkali graphite intercalation compounds (GIC's).¹ The dominant feature in these systems is the formation of a discommensuration-domain structure with narrow domain walls.² This type of modulated structure is the result of competing interactions, in this case the interplay of alkali-alkali interatomic forces and alkali-carbon "substrate" interactions.³ Such a competition of forces introduces many subtleties which result in the creation of an extremely rich and diverse structural phase diagram. One interesting result, supported by recent neutron⁴ and x-ray studies,⁵ is that there exists disorder among intercalate atoms near the domain wall and that the intercalant retains substantial mobility well below the three-dimensional ordering transition.

Although the discommensuration-domain model appears to be appropriate for all the heavy alkali GIC's (K, Rb, Cs), stage-2 potassium samples have an additional transition somewhat below the ordering transition at $T_u \approx 125$ K. The structural transformation in question, which occurs at $T_l \approx 95$ K, has been seen by a number of research groups but has so far defied interpretation within this model. The first published account was by Parry and Nixon,⁶ who reported a stacking transition from $A\alpha A\beta A\gamma A$ to $A\alpha A\beta A\gamma A\alpha' A\beta' A\gamma' A$. Hastings, Ellenson, and Fischer⁷ have also discussed the 95-K transition and stated that it appeared to be first order with changes in the c -axis stacking perhaps related to a multiphase structure. More recently, Rousseaux *et al.*⁸ have made detailed in-plane studies of single-crystal samples using flat film techniques (which are sensitive only to a projection of the in-plane structure) and have described the transition in terms of a symmetry breaking by the potassium atoms. The authors claim that this results in the formation of a complex oblique structure, as yet undetermined.

In this paper we report on single-crystal x-ray diffractometer studies of stage-2 potassium GIC's. Our results show conclusively that the 95-K transition is first order in nature, in agreement with Hastings *et al.*,⁷ and that changes in the in-plane structure accompany c -axis stacking transformations. More specifically, we find that it is possible to interpret the experimental data in terms of a discommensuration-domain structure which transforms to a number of *high-order commensurate phases* at low temperature, i.e., the 95-K transition is the result of a lock in to commensurate structure at low temperatures. A generalization of this result to all alkali GIC's has important

implications (e.g., for band structure calculations). The result also requires modification of the current theoretical model for alkali GIC's in which the magnitude of the alkali wave vector and its orientation are supposedly related by a continuous, universal, curve.^{9,10}

Complete details of our experiment are reported elsewhere,¹¹ but the following gives a brief overview. All data were acquired by a computer-controlled four-circle diffractometer using a 12-kW rotating molybdenum anode x-ray source. The longitudinal resolution was 0.03 \AA^{-1} FWHM appropriate to graphite monochromatization. The single-crystal sample of stage-2 potassium GIC was encapsulated in a thin glass bulb and then mounted in a closed-cycle He cryostat. By design, the glass-encapsulated samples are never exposed to oxidizing environments and the x-ray data are completely free from parasitic diffuse glass scattering. One slight defect is that the stage-2 potassium contained traces of stage 1 as an impurity. Hence all diffraction scans show weak additional peaks at $2a_0 \times 2a_0$ carbon superlattice positions, where a_0 is the in-plane graphite vector. These peaks exhibited no change of any kind throughout the entire course of data collection. In addition there were no detectable changes in the intensity of $(00l)$ scans. Thus the low-temperature transitions are *not* accompanied by changes in staging.

The basic changes in the in-plane structure are seen by comparing an $(hk0)$ map of stage-2 potassium at 100 K, with that at 70 K, as shown in Fig. 1. The most notable features are the similarities of the 100-K diffraction pattern with those of other stage $n \geq 2$ alkali GIC's and the appearance of many new diffraction peaks at temperatures below $T \approx 95$ K as also noted by Rousseaux *et al.*⁸

In order to identify the nature of this transition we have performed high-resolution diffractometer scans of the encircled region in Fig. 1 while cycling thermally through the transition. There is marked thermal hysteresis with onset at 95.0 K on cooling (with a rapid change between 95 and 94.7 K). The transition occurs at $T \geq 96$ K on heating (see Fig. 1, inset). In addition, all diffraction peaks show negligible shifts in wave vector. On cooling, peaks associated with the high-temperature structure lose intensity rapidly (for example peak A at 95 K) while new low temperature peaks (B,C,D) grow smoothly. These results imply that there is a spontaneous, first-order transition in the intercalant structure, a finding that is compatible with either the symmetry breaking model⁸ or with the lock-in interpretation proposed here.

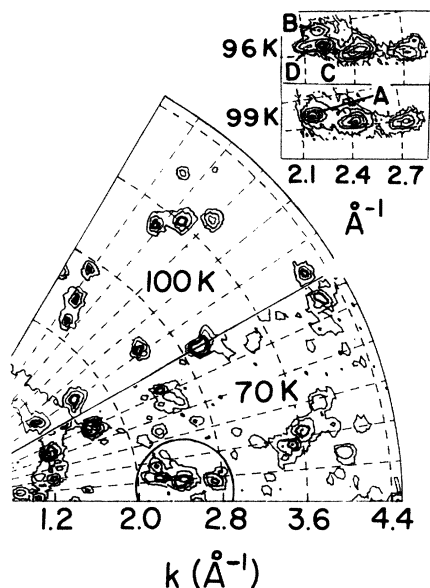


FIG. 1. $(hk0)$ x-ray diffraction contour maps of KC_{24} single crystals for the phases above and below T_l . The circled region is shown expanded in the inset at two different temperatures on heating through the transition.

It is important to note that our $(hk0)$ data are not identical with those obtained from the in-plane diffraction photographs. There are substantial and systematic wave-vector differences for many of the low-temperature-phase peaks which we are able to resolve because of the diffractometer's intrinsic power to distinguish diffraction from each (hkl) layer; in particular, the $(hk0)$ layer alone. Scans parallel to the c^* axis through various $(hk0)$ peaks at $T < 95$ K are shown in Fig. 2. In this figure one readily observes the unusual line shape characterized by sharp shoulders and broad flat tops common to many of the potassium reflections. This leads to the conclusion that the c^* profiles, which contain information about the three-dimensional stacking order, are not composed of single broad peaks but rather a superposition of several closely spaced sharp peaks. The implication is that for $T < T_l$ the alkali stacking structure has a large period; we have yet to identify its exact form.

The low-temperature transition at $T_l \approx 95$ K is best characterized as a polymorphic one in which the single domain-structure existing at temperatures above T_l (see inset Fig. 3) fragments into at least four microphases below T_l . Moreover, the structure of each of these microphases can be defined uniquely as a high-order commensurate structure. A similar conclusion has been inferred recently from Shubnikov-de Haas studies in other alkali GIC's by Mitani and Morita.¹² The data in Fig. 2 suggest that the stacking structure may be different for each of the microphases.

Figure 3 depicts the universal equilibrium curve which Yamada and Naiki¹⁰ have justified in terms of a thermodynamic treatment of the discommensuration-domain model. Superimposed are circles (from Ref. 12) whose centers define an alkali wave vector and rotation angle and

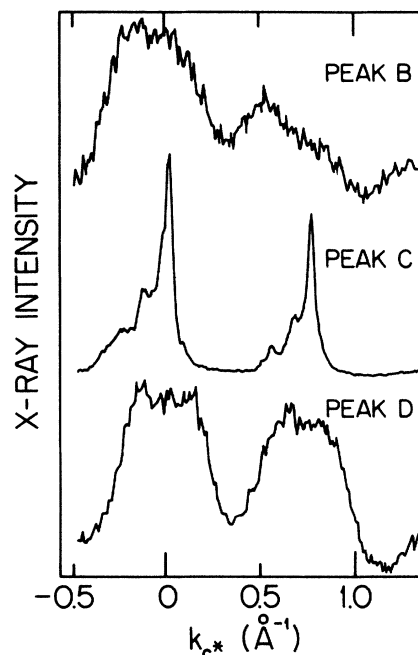


FIG. 2. c^* scans through peaks labeled B, C, and D in the inset of Fig. 1 ($T = 70$ K).

whose diameters are inversely proportional to the number of atoms per unit cell. The circles refer to the possible commensurate in-plane arrangements of potassium atoms with periodicity less than $12a_0$.

In view of the thermodynamic basis of the curve shown in Fig. 3, domain I, with $z (\equiv k_p/k_G) = 0.423$ and $\phi = 8.08$

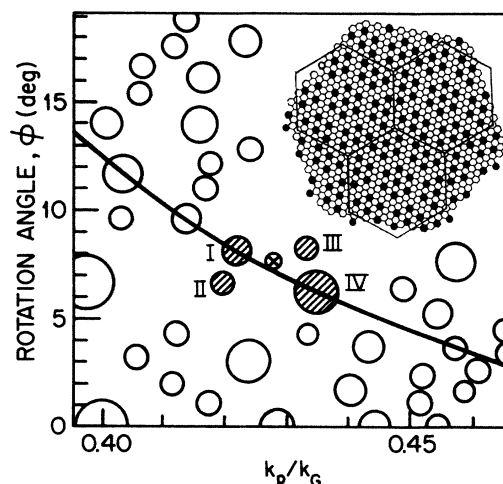


FIG. 3. Universal equilibrium curve calculated by Yamada *et al.* (Ref. 10). k_p is the principal wave vector of the intercalant determined by the average intercalant density, and k_G is the graphite in-plane wave vector. Superimposed are circles representing possible commensurate structures with periodicity less than $12a_0$ in the vicinity of KC_{24} . The phase for $T_l \leq T \leq T_u$ is indicated by \otimes and the corresponding intercalant structure ($\sqrt{201} \times \sqrt{201}$) is shown inset. I-IV indicate the commensurate phases appearing at $T < T_l$.

degrees (see Fig. 4), seems to be the most likely candidate for stage-2 potassium at temperatures above 95 K. Experimentally, this expectation is not realized: all reported stage-2 potassium data,^{4,8,9} including ours, indicate $\phi \leq 8^\circ$. Also, the Fourier transform of domain I does not agree at all with the $(hk0)$ diffraction pattern of Fig. 1.¹¹ If one allows the domain size to increase slightly, there exists a $\sqrt{201}a_0 \times \sqrt{201}a_0$ domain (shown in Fig. 3) with $z = 0.428$ and $\phi = 7.57^\circ$ located just off the curve, whose diffraction wave vectors give excellent agreement with existing data.^{4,7-9,11}

This model structure now provides a thermodynamic rationale for the 95-K transition. Referring back to the inset of Fig. 3, it can be seen that an ordered structure of this form would require nearest-neighbor distances of $\sqrt{3}a_0$ across domain walls. This is virtually impossible to achieve at ambient pressures given the potassium ionic radius. Careful inspection shows that no simple motion of atoms at the domain wall will alleviate the formation of $\sqrt{3}a_0$ neighbors. Therefore, it is concluded that this domain is fundamentally unstable. If high-order commensurate structures that are slightly off the orientational epitaxy curve are favored, this allows a straightforward identification of the constituents of the low-temperature ($T < 95$ K) phase. We propose that this phase is a mixture of the nearest four commensurate structures (designated by I, II, III, and IV in Fig. 3) that surround the unstable high-temperature phase. In Fig. 4 we show the corresponding real-space structures; Fourier transforming each structure and superimposing the calculated peak positions gives a diffraction profile in excellent agreement with that of Fig. 1 ($T = 70$ K).¹¹ In addition, the intensities calculated from the Fourier transform agree qualitatively with the measured x-ray intensities. The fit could be improved by relaxing the restriction of 100% registry and by introducing c -axis correlations,⁵ although this has not yet been attempted for the potassium GIC's.

Thus, the stage-2 potassium transition can be understood in the following context. As the potassium cools from the disordered phase above $T_u = 125$ K, it orders into the nearest stable and accessible in-plane domain structure appropriate to the intercalant density. In this case, the available domain lies near, but off, the universal alkali curve. For $T_l \leq T \leq T_u$ the disorder at domain walls is sufficient to stabilize the domain structure. However, as the temperature is further lowered, the domain ordering is increasingly frustrated due to the necessity of $\sqrt{3} \times \sqrt{3}$ correlations across the domain wall. Thus, at T_l the domain structure fragments into a metastable configuration which maintains overall alkali in-plane density. Hence, on average, there is no driving force for a staging transition. As can be seen in Fig. 3, four adjacent structures are available and the stage-2 potassium sample forms a mixture of all four. It is interesting to note that this

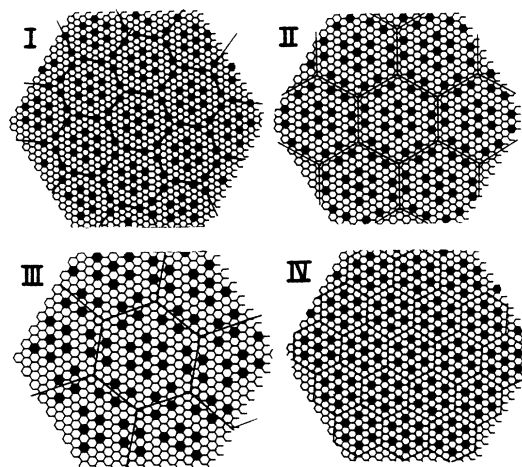


FIG. 4. High-order commensurate intercalant structures coexisting at $T < T_l$: I: $\sqrt{73} \times \sqrt{73}$; II: $\sqrt{108} \times \sqrt{108}$; III: $\sqrt{112} \times \sqrt{112}$; IV: $\sqrt{37} \times \sqrt{37}$. These structures are all characterized by groupings of atoms with 2×2 registry separated by light "domain walls."

behavior is the converse of that observed in the high-stage K-GIC's.¹³ In that case, local changes in the K/C ratio resulting from in-plane ordering are accommodated by restaging transitions.

While it is unlikely that the multiphase structure represents the true thermodynamic ground state of the system, the kinetics of ordering are sufficiently slow at these temperatures that the observed configuration appears to be very stable, and consequently only slight changes in the diffraction pattern are detectable as the temperature is further lowered. There may be additional influences due to potassium stacking.

In conclusion, we have shown that it is possible to reproduce all of the major features of the experimental data by using a model in which high-order commensurate arrangements are the desired low-temperature structure. As a result, this transition is consistent with the discommensuration-domain framework that has been previously established for other alkali GIC's. Thus it appears necessary to modify the currently accepted picture that the low-temperature structures of alkali GIC's reside on the continuous equilibrium curve of Mori *et al.*⁹ A more appropriate model would include discrete regions of stability on and near the curve, corresponding to high-order commensurate structure.

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