upper transverse-acoustic-phonon branch are also allowed to decay spontaneously.

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Evidence for Discommensurations in Graphite Intercalation Compounds

Roy Clarke, J. N. Gray, H. Homma, and M. J. Winokur

Department of Physics, The University of Michigan, Ann Arbor, Michigan 48109

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New x-ray diffuse scattering results are presented that show that the layer structure in stage-2 alkali-metal graphite intercalation compounds is almost commensurate with a $(\sqrt{7}\times\sqrt{7})R19.11°$ superlattice. Through model calculations, features of the in-plane diffraction patterns are associated with a hexagonal array of discommensurations oriented parallel to the real-space graphite [110] directions. The array appears to be disordered down to at least $T = 10$ K. Several previously unexplained results are understood through our model.

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The physics of systems with competing periodicities is currently a very active research area. Of particular interest is the transition, or sequence of transitions, from commensurate to incommensurate structures.[1] Studies of monolayers of adsorbed gases[2] and of charge density waves in layered chalcogenides[3] have proven especially interesting in that much direct information can be obtained by various diffraction techniques. However, in spite of several recent theoretical predictions[1,4] relating to the commensurate-incommensurate transition (CIT), experimental tests are very limited at this time.

In this paper we describe x-ray diffuse scattering experiments on a set of materials, related to adsorbates but not previously discussed in this context, in which monolayers of alkali metal (AM) ions are intercalated into the graphite structure.[5] We find that in some cases such materials are *weakly incommensurate* and, in single-crystal form, may provide important testing grounds for theories of the CIT. Our findings suggest a new structural interpretation of dilute AM graphite intercalation compounds (GIC's) which can explain several controversial and poorly understood aspects such as the origin of structural modulations and the interpretation of unusual diffraction effects.

The incommensurability of stages $n \geq 2$ of the Cs, Rb, and K GIC's has been recognized for

some time[6] ("stage n" denotes a stacking sequence in which neighboring intercalant layers are separated by n planes of carbon atoms). Several forms for the incommensurate layer structure have been suggested including a triangular lattice modulated by the hexagonal carbon potential[7] and a multiphase structure with incommensurate islands of intercalant.[8] In a further model,[9] the graphite matrix itself is modulated by the intercalant layer. Such models are motivated by the strong "modulation" satellites (labeled 4 in Fig. 1) grouped in rings[6] around each graphite reciprocal lattice point.

First, we consider the incommensurability. One measure of this is the magnitude of $\vec{k}_p$, the wave vector of the "primary" reflections from the intercalant layer (see Fig. 1). Just as important[10] is the angular direction, φ, of $\vec{k}_p$ relative to the graphite symmetry axes. In Fig. 2 we plot φ as a function of k_p for some single-crystal GIC's. Experimental details are given in Ref. 7. The linear behavior we observe, also apparent in a similar plot reported recently by Zabel,[9] is seen to extrapolate accurately through the calculated datum for a $(\sqrt{7}\times\sqrt{7})R19.11°$ superlattice. On this basis the Cs, Rb, and K GIC's are, respectively, 4.2%, 9.4%, and 12.1% incommensurate *relative to the* $\sqrt{7}\times\sqrt{7}$ *density*. Based on the evidence of Fig. 2 we propose that the intercalant layer structure of the higher-stage alkali metal GIC's could be described in terms of a domain structure [see Fig. 3, inset (a)] in which the locally commensurate order is modulated by domain walls or "discommensurations,[11]" a concept which has been extremely useful in physical descriptions of other weakly incommensurate systems. We have calculated the structure factors for such a model taking the simplest case of ordered narrow walls and neglecting relaxation effects. Specifically, we construct a hexagonal array of domains of $\sqrt{7}\times\sqrt{7}$ registry with the domain walls oriented parallel to the [110] real-space direction. Site occupation in the domain-wall region is restricted by a minimum separation of intercalants, taken[6] as $2a_0 = 4.94$ Å (where a_0 is a graphite lattice spacing). A diffraction pattern is then calculated using fast Fourier transform techniques [see Fig. 3, inset (b)].

The essential features of the observed diffraction patterns are well reproduced by our calculations including the unusual ringlike appearance and the weak satellites labeled 2 in Fig. 1. The latter occur between each pair of primary satellites (of wave vector $\vec{k}_p$) and arise in our model from the regular periodicity of the domain walls parallel to [110]. The [110] wall orientation that we observe in the GIC's is the same as that thought to occur in Kr monolayers on graphite.[12] Although the underlying $\sqrt{7}\times\sqrt{7}$ structure is oriented some 11° off the [110] direction, this wall orientation is consistent with Villain's suggestion[13] that at $T\neq 0$ "kinks" may form *within* do-

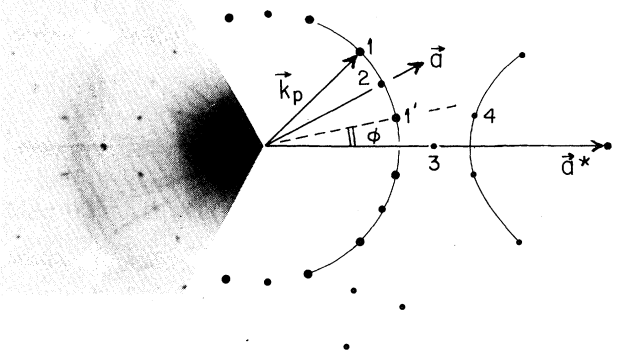

FIG. 1. In-plane x-ray diffraction pattern of a stage-2 Cs GIC crystal at $T = 45$ K. Reflections labeled 1 and 2 are interpreted as primary satellites of the discommensuration-modulated $\sqrt{7}\times\sqrt{7}$ structure. Those labeled 3 are half-order reflections from 2×2 regions discussed in text. The arc of spots labeled 4 is part of a ring of satellites around the (10) graphite reflection [see Fig. 3, inset (b)]. a^* is the primitive translation vector of the reciprocal lattice.

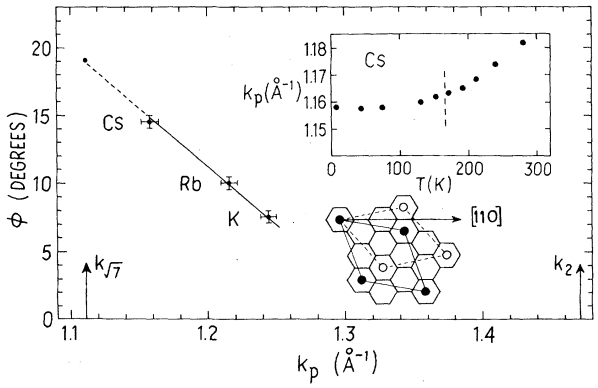

FIG. 2. Angular orientation of $\vec{k}_p$ relative to the a^*, (100), direction of graphite as a function of k_p for stage-2 single-crystal AM GIC's at $T = 100$ K. (Cs and Rb data, this work; datum for K taken from Ref. 9.) $k_{\sqrt{7}}$ and k_2 are the primary wave vectors of the closest registered phases. Upper inset: Temperature dependence of k_p for stage-2 Cs GIC. The dashed line denotes layer melting temperature. Lower inset: Two equivalent orientations of $\sqrt{7}\times\sqrt{7}$ superlattice.

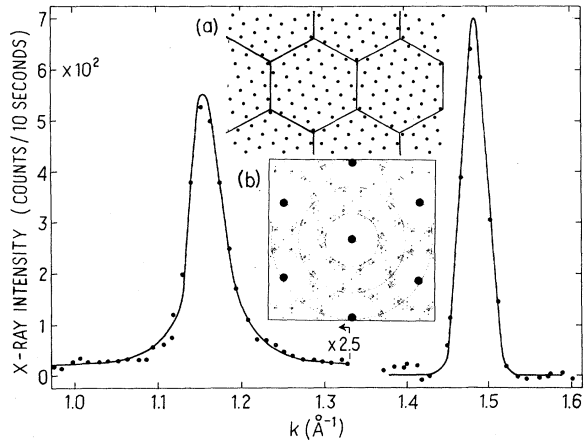

FIG. 3. Simultaneous in-plane diffractometer scans through incommensurate primary peak (on the left-hand side) and (on the right-hand side) registered peak labeled 3 in Fig. 1. The registered peak is fit by a Gaussian and the tails of the peak on the left-hand side are Lorentzian fits. Data taken on a pyrolytic sample of stage-2 Cs GIC at $T = 10$ K. Inset: (a) Intercalant arrangement for the domain model described in the text. (b) Fourier map of domain model (for $l \approx 40$ Å). The scale circles are drawn at 1-Å^{-1} intervals. Dots are graphite reciprocal-lattice points.

main walls to preserve a mean rotation angle of zero about some "easy" direction.

The observed variation of φ vs k_p shown in Fig. 2 is also quantitatively reproduced by our calculations up to incommensurabilities of at least 5%. Interestingly this behavior is obtained in our model simply by varying the domain size (and thus the incommensurability): Although there is a physical justification for the observation shown in Fig. 2 based on a *bulk* rotation[10] of the incommensurate "overlayer," the apparent rotation, φ, of the reciprocal lattice away from the commensurate value $\varphi = 19.11°$ seems to be a purely geometrical effect arising from the growing contribution of the domain-wall regions as the domain size is decreased. Other pieces of evidence supporting our model are as follows:

(i) The higher-order intercalant reflections cannot be indexed on the basis of a uniform incommensurate lattice. For example, in the Rb case, the wave vector $k_{(20)}$ of the satellite which becomes the (20) reflection of the $\sqrt{7} \times \sqrt{7}$ superlattice is some 3% smaller than $2k_{(10)}$. These small differences are also evident in our model calculations.

(ii) Shifting of satellite wave vectors with temperature T. As T is decreased, the reflections labeled 2 in Fig. 1 move radially outwards towards k_p. This effect can be understood in terms of a domain model taking into account the anomalous expansion of the Cs layer (see upper inset of Fig. 2). The incommensurate (I) phase becomes less dense at lower temperatures because of its coexistence, at fixed overall density, with a segregated 2×2 phase.[7] Thus, as the I phase density moves closer to the $\sqrt{7} \times \sqrt{7}$ density at lower temperatures, the domain size grows and consequently the satellite wave vectors shift towards the primary wave vector, k_p.

The reflections labeled 2 in Fig. 1 are very diffuse when they first appear at $T \approx 150$ K and gradually sharpen up at low temperatures. The detailed line shape is shown in Fig. 3. The Lorentzian tails of the peak on the left-hand side are more reminiscent of a fluid than a solid even at $T = 10$ K and may be associated with domain-wall disorder of a fluidlike[4] or chaotic phase[1] close to the CIT. The first experimental evidence for this was reported recently by Moncton *et al.*[12] Further work on single-crystal GIC's is suggested in order to test the prediction[4] that the line shape will remain broad to $T = 0$.

The model described above has important consequences for the description of the dilute GIC's:

(a) It can explain, without recourse to large-amplitude distortions of the graphite matrix,[9,14] the unusual strength of the "modulation" satellites; i.e., the rings in Fig. 3, inset (b). While we obtain satellite intensity ratios that are qualitatively in agreement with those observed, a detailed comparison would require inclusion of disordered layer-stacking corrections to our model.

(b) The model explains the multiplicity of twelve "primary" intercalant spots in terms of the two equivalent orientations for the $\sqrt{7} \times \sqrt{7}$ superlattice (see lower inset of Fig. 2). A related geometrical feature, that the higher-order diffractions appear[14] to lie on rings around each graphite reciprocal lattice point, is also explained by the near $\sqrt{7} \times \sqrt{7}$ registry.

(c) The model supports the recent extended x-ray–diffraction fine structure (EXAFS) findings of Caswell *et al.*[15] suggesting that a large fraction of the intercalant ions are registered in the stage-2 alkali-metal GIC's. Conversely, one may infer a narrow relaxation region or domain-wall width. This would also be consistent with the rather strong "substrate" interactions that are expected in these charge-transfer intercalation compounds.[5] The situation is distinct from the physisorption case of Kr on graphite[12] where a sinusoidal modulation is thought to be appropriate. A measurement of the harmonics of the domain-wall reflec-

tions (labeled 2 in Fig. 1) is planned which should resolve this question.

(d) *Commensurate* $\sqrt{7}\times\sqrt{7}$ ordering, as recently reported[16] in electron diffraction studies of stage-2 AM GIC's, is easily explained by our model if a slight desorption of the intercalant occurs. This may well be expected under heating by the electron beam. These results also suggest that the CIT could be studied in the Cs case by controlled desorption (without changing stage) together with the fine tuning provided by the anomalous expansion effect shown in the inset in Fig. 2.

(e) The domain structures considered here may be applicable to other GIC's. In particular, acceptor GIC's based on $SbCl_5$ show transitions[17] from commensurate $\sqrt{7}\times\sqrt{7}$ order to an incommensurate phase with a diffraction pattern reminiscent of that shown in Fig. 3, inset (b).

There are two further aspects of the stage-2 Cs GIC that offer exciting possibilities for future studies of the CIT. The first concerns a hitherto unexplained additional transition in the Cs samples at $T\approx 40$ K.[7] At least one new satellite reflection appears at the strongly first-order transition. It is tempting to speculate that this may be a transition to the "striped" phase predicted to occur closest in to the CIT.[1] Finally we point out that our experimental realization of an incommensurate phase with sublattice degeneracy $p=7$ offers access to possible ordering phenomena[18] that are precluded for the more widely studied $p=3$ systems.

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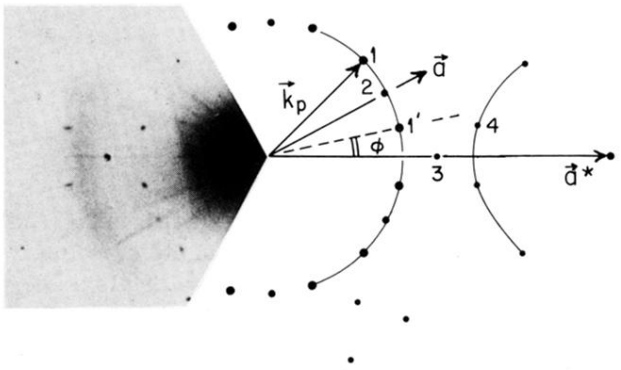

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