In-plane charge distribution in potassium-intercalated graphite

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Carbon-core-electron binding energies, measured with the use of x-ray photoelectron spectroscopy, give direct information on the distribution of the transferred electronic charge in graphite intercalation compounds. Both the stage-one and stage-two compounds, KC_8 and KC_{24}, with all carbon atoms in bounding layers, should be well suited to the study of the in-plane charge distribution; however, cleaved samples of KC_8 proved to be extremely unstable at room temperature in ultrahigh vacuum. For the stage-two compound, the C 1s spectra reveal an electronic charge distribution which is very strongly localized on those carbon atoms which are nearest the intercalant ions.

INTRODUCTION

Although considerable effort[1] has been devoted to understanding the structure[2-4] and the electronic properties[5] of alkali-metal—graphite intercalation compounds (GIC's), little is known about the distribution of the transferred electronic charge among the carbon atoms in a single layer. This in-plane charge distribution, especially in those layers adjacent to the intercalant layer (the bounding layers), is essential to an understanding of the intercalation mechanism. The stage-one and stage-two GIC's are logical choices for the study of the in-plane charge distributions, since in these compounds all carbon layers are equivalent and all are bounding layers. Moreover, x-ray photoelectron spectroscopy (XPS) is a suitable technique for such a study, as the carbon—core-electron binding energy is quite sensitive to any change in the electronic charge density. In a previous XPS study[6] of the stage-two compound LiC_{18}, we observed a spread of C 1s binding energies which we attributed to the variety of carbon-atom environments in the bounding layer. The heavy-alkali-metal GIC's differ significantly from the lithium compounds, not least in the lower intercalant density for stage two, and in the greater separation between carbon layers bounding each intercalant layer. We have elsewhere presented the results of an XPS study of the higher-stage potassium compounds, in which the charge transfer to the interior layers was mea-

sured.[7] In this paper we present the C 1s spectra for KC_8 and KC_{24}, with the conclusions which can be drawn about the charge distribution in the bounding layer.

The surface sensitivity of XPS and its implications for these data must be considered. The mean free path of the photoelectrons detected in XPS is small enough that a substantial minority of the strength in the C 1s spectrum is due to carbon atoms in the surface layer. The stage-two surface layer presumably results from cleaving between two carbon layers, where the interlayer interaction is weak. Thus only charge-neutral "sandwiches" of carbon-intercalant-carbon are removed, and we assume that the carbon atoms in the surface layer are little affected by cleaving. In the stage-one compound, there are no adjacent carbon layers, so that we expect equal occurrences, at least initially, of carbon layers or intercalant layers on the cleaved surface. Although the surface layer contribution to the C 1s spectrum is then expected to be smaller than in the stage-two spectrum, there may be greater differences in the environments of bulk carbon atoms and of surface carbon atoms.

The stage-two samples were prepared from Union Carbide highly oriented pyrolytic graphite (HOPG) by the usual two-zone technique and checked by 00*l* x-ray reflections to verify proper staging. The samples were mounted on holders and inserted into the preparation chamber of the HP5950A spectrometer system under an inert at-

mosphere. Measurements were made on fresh surfaces prepared by cleaving the samples in a vacuum of $\sim 5 \times 10^{-10}$ torr. The data presented here were obtained in the first hour after cleaving, during which time the sample did not degrade detectably. After 24 h the K to C yield ratio had increased, as shown in Fig. 1; we tentatively attribute this to the buildup of oxidized potassium at the sample surface. The zero of the binding energy scale was determined for each cleaved sample by measuring the Fermi edge for a thick layer of Ag deposited on the surface after all other data had been taken.

Stage-one samples were prepared by allowing the intercalation process to saturate, but were otherwise handled in the same way as the stage-two samples. However, these deteriorated rapidly after cleaving, with significant changes evident in the C $1s$ spectrum after less than 15 min. The evolution of the C $1s$ spectrum was completely reproducible, both with different samples and with successive cleavings of the same sample. The K to C ratio decreased with time, indicating a rapid loss of potassium through the cleaved surface. The C $1s$ spectra obtained at ten minute intervals immediately after cleaving the sample, and spectra obtained many hours later, show a broad peak at higher binding energies which grows rapidly for several hours, and then rather slowly for at least several days thereafter. The shape of this degraded peak was determined from the data for a highly deteriorated sample. The solid curve in the KC_8 spectrum in Fig. 2 approximates the inferred spectrum for "pure" KC_8, obtained by subtracting the
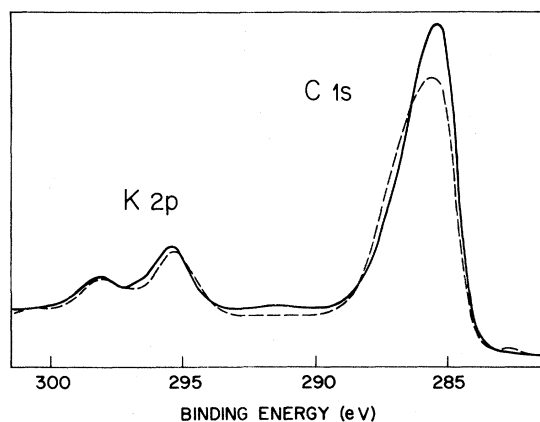

FIG. 1. Smoothed stage-two spectra taken three hours (solid curve) and one day (dashed curve) after cleaving, illustrating the increase in the K to C ratio.
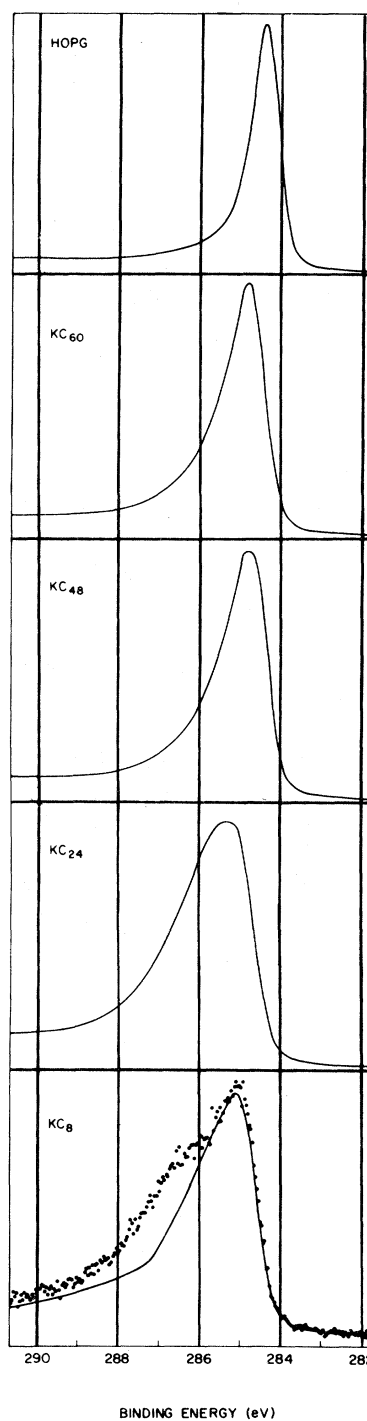

FIG. 2. Carbon $1s$ photoemission spectra for graphite and for the four potassium GIC's studied. The data points in the KC_8 spectrum are the raw data acquired within 15 min of cleaving; the curve approximates the spectrum determined by subtracting the fitted deterioration component.

degraded component from a spectrum taken during the first 15 min after cleaving. A high equilibrium vapor pressure for potassium at room temperature and the greater in-plane density of the intercalant layers in the stage-one compounds make KC_8 less stable than the higher-stage compounds. The observed deterioration is inevitable for a cleaved surface under UHV conditions at room temperature, so that better XPS data for KC_8 can be obtained only if the sample is kept at a low temperature both during and after cleaving.

DATA

Shown in Fig. 2 are the C $1s$ spectra for several stages of potassium GIC's and for pure HOPG. The principal observation is that increasing intercalant concentration broadens the C $1s$ peak and displaces it toward higher binding energy. The horizontal scale is binding energy relative to the Fermi energy; the vertical scales are chosen to make the peak heights the same.

The dependence of width on stage was established qualitatively by Bach[8] in an earlier XPS study of KC_n, using nonmonochromatized Al$K\alpha$ radiation. Allowing for the higher resolution of our spectrometer system, the peak widths for the higher stage compounds agree generally with those reported by Bach, as shown in Fig. 3. Bach, however, observed a shoulder on the $1s$ peak for KC_8 which he ascribed to a component at 1.3 eV greater binding energy than the main peak. The degraded component we have observed for KC_8 is centered
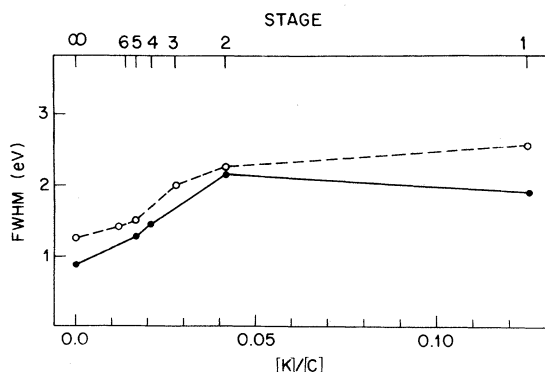

FIG. 3. Full width at half maximum (FWHM) of the C $1s$ peak, as a function of K concentration, as reported by Bach (open circle) (Ref. 8) and as determined in the present work (closed circle). The stage-one width reported here refers to the spectrum after the correction for deterioration has been made.

at nearly 2 eV greater binding energy than the main peak. As we shall discuss later, the main peak can itself be decomposed into two components, with the weaker component at 1 eV higher binding energy. It is therefore likely that the shoulder observed by Bach was due in part to deterioration of the KC_8.
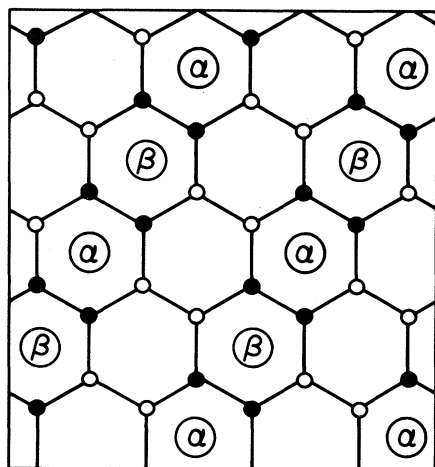
DISCUSSION

In the earlier work on the higher-stage compounds, we demonstrated that the binding energy for the interior layers increased as the amount of charge transferred to them increased, despite the expected decrease due to Coulomb repulsion. This increase is easily understood when it is recalled that the XPS binding energy is measured relative to the Fermi level. Given the low density of states near the Fermi energy in graphite, the addition of electronic charge to the valence π orbitals causes a motion of the Fermi level through the band structure, and relative to the core level, contributing an increase to the observed binding energy which more than offsets the decrease contributed by the Coulomb repulsion. Thus the increase, relative to pure graphite, of the C $1s$ binding energy for the stage-one and stage-two compounds is explained. While the largely two-dimensional band structure makes it possible to consider the filling of levels in particular layers and to expect a higher C $1s$ binding energy in carbon layers with more transferred charge, such arguments cannot be applied to the carbon atoms within a single layer. Thus the spread of binding energies in the all-bounding-layer compounds discussed in this work must result from the varying interactions of the $1s$ electrons with the K^+ ions and with the varying amounts of charge in the initially empty π orbitals, and cannot be explained with the simple density-of-states arguments[7] which were applied to the higher-stage compounds.
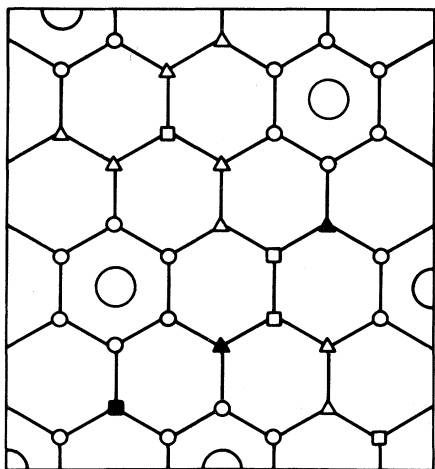
Stage one

The variety of intercalant-ion environments for the carbon atoms in the bounding layer of a low-stage GIC leads to a C $1s$ spectrum consisting of more than one component. In the exceptional case of the stage-one compound LiC_6 all carbon atoms have identical environments and the C $1s$ photoemission peak is observed to be quite narrow.[9] As

illustrated in Fig. 4(a), the lower in-plane density of the intercalant in KC_8 guarantees at least two distinct environments, with either one or two potassium nearest neighbors for each carbon atom. For the $\alpha\beta\gamma\delta$ stacking known to occur in the ordered stage-one compound, there are equal numbers of these two kinds of carbon atoms; only where a stacking fault produces $\alpha\alpha$ stacking can there be a carbon atom with no K^+ nearest neigh-

bor. Because of the loss of in-plane symmetry, the band structure of graphite cannot be applied to this compound. Thus the components of the C 1s spectrum of KC_8 will have a line shape different from that for pure graphite. This expectation is not altered by the observation that the simple commensurate periodic structure of the intercalant layer in KC_8 apparently allows use of a folded (rigid) band model[10] based on the graphite band structure.

Given the rapid deterioration of the surface of the stage-one sample in vacuum at room temperature, reliable, high-statistics data cannot be obtained with our present apparatus. The following comments on the present data are therefore tentative at best.

Figure 5 shows the data of Fig. 2 with a fit which uses three components, one of which is the degraded component described above. The other two components, constrained for this fit to have identical shapes, might be expected to represent the true KC_8 spectrum. However, their ratio changes with time, as the peak at higher binding energy gains in relative intensity. Based on the distribution of carbon environments discussed above, the principal peak, at lower binding energy, must be due to carbon atoms both with one and with two K^+ nearest neighbors. This would mean that the binding energies of these two distinct types of carbon atoms are too similar to allow resolution of the two components. If this identification is correct, then the width of the principal peak provides only an upper bound on the width of the C 1s peak for a single type of carbon environment. If
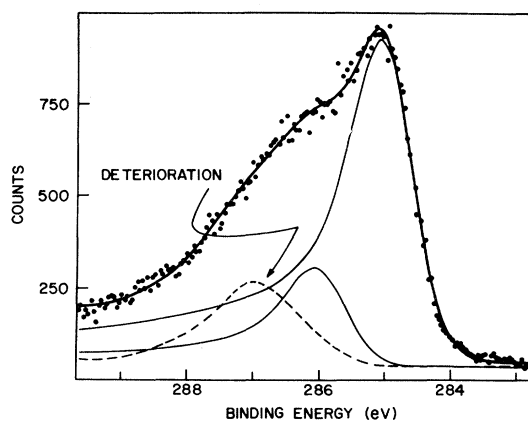

(a)

(b)

FIG. 4. Illustration of possible potassium neighbor environments of the carbon atoms in the bounding layers; the potassium ion positions are projected onto the graphite plane. Carbon atoms with two nearest neighbors (closed circles), with one nearest neighbor (open circle), with one (open triangle), two (closed triangle), or three (closed square) next-nearest neighbors, or with no nearest or next-nearest neighbors (open square) are indicated for (a) KC_8 with $\alpha\beta$ stacking of the two adjacent K layers and (b) for KC_{12n}, with a registered K layer.

FIG. 5. Least-squares fit to the C 1s spectrum of KC_8, using data acquired within 15 min of cleaving. The component labeled "deterioration" has a shape and position determined from data acquired several days after cleaving.

the smaller peak is due to carbon atoms with no K^+ nearest neighbors, but with some K^+ next-nearest neighbors, then its growth from 30% to 57% of the main peak intensity may reflect the growth of regions of lower intercalant density, which result from the removal (or the oxidation) of some of the potassium. This component may, e.g., correspond to the surface layer immediately after cleaving, as those carbon atoms would "see" a low intercalant density. The broad degraded peak might at the same time be attributed to the carbon atoms in regions totally depleted of intercalant.

Stage two

In the stage-two compound as in the stage-one compound, the binding energy of a C atom in a bounding layer depends both on its location relative to the intercalant ions and on the distribution of transferred electronic charge. Thus, conclusions about the charge distribution in KC_{24} cannot be drawn from the XPS data without assumptions about the structure of the intercalant layer. There is as yet no consensus on what that structure is at room temperature. In particular, there is the question of whether or not, at room temperature, the potassium layer is in registry with the graphite lattice, that is, whether or not the K ions occupy the sites of sixfold symmetry above the graphite hexagon center, as in KC_8 (Ref. 11). This would result in several distinct kinds of carbon atoms, as illustrated in Fig. 4(b), each kind contributing a discrete component to the C $1s$ photoemission spectrum. One can construct registered, simple periodic coverages consistent with stoichiometry[12] by, for example, removing one-third of the K ions from the KC_8 intercalant layer structure. However, these structures would have unmistakable x-ray diffraction structure which is not observed in experiments.[3,4,13,14] However, this does not rule out other kinds of registered structures, such as the relaxed close-packed structure discussed below. It should be noted that, whether or not the K atoms are registered, the diffraction experiments show that the intercalant layer does not have a commensurate, simple periodic structure. One consequence of this is that a folded band model cannot be applied to KC_{24}, as is possible for KC_8. At the other extreme from the assumption of registry, the intercalant layer may be supposed to have a structure which is not modified by the graphite lattice, and in which all potassium ion locations are allowed.

The C $1s$ spectrum will then reflect a continuous distribution of environments of the carbon atoms.

For the analysis of our XPS data, we first consider the case of an incommensurate, unregistered intercalant layer, even though such a structure is in conflict with the electron diffraction data[15] and with the EXAFS data.[11] Assuming unit charge transfer from each K atom and a uniform distribution of transferred charge, and including the instrumental resolution function, we have calculated the C $1s$ spectrum expected for KC_{24} and have found that the calculated peak is significantly narrower than that observed. A slight localization of charge on the C atoms nearest the intercalant ions would tend to narrow the calculated peak, as would a charge transfer of less than one unit. Thus if this unregistered structure is assumed for the intercalant layer, the C $1s$ spectrum suggests that the distribution of transferred charge must be strongly localized. Because the spectrum of binding energies cannot uniquely determine the charge distribution, and the variation in the π-orbital charge of carbon atoms near an intercalant ion is difficult to calculate, we do not proceed further with the data analysis under the assumption of an unregistered structure for the intercalant layer.

Assuming now a registered structure for the intercalant layer, the C $1s$ spectrum should consist of five components arising from the five distinct environments illustrated in Fig. 4(b). Moreover, perfect KC_{24} stoichiometry requires half of the carbon atoms to have exactly one K^+ nearest neighbor, and half to have none. Discrete, narrow components are not evident in the KC_{24} spectrum in Fig. 3. It is nevertheless possible that this spectrum consists of five discrete components, particularly if each component is broader than the graphite $1s$ peak. Such broadening relative to the graphite lineshape could certainly result from the different band structure which is appropriate to the carbon atoms in a bounding layer. In addition, displacements of the potassium ions from the sixfold sites, whether due to thermal motion or other causes, will also result in broadening of the components of the C $1s$ spectrum. It is also possible that potassium ions more distant than next-nearest neighbors contribute to the widths of the components. Thus the XPS data do not contradict the experimental evidence for registry of the potassium ions, and we therefore investigate the implications of these data assuming a registered intercalant layer.

For this approach to the data analysis we have

made least-squares fits of five components to the measured spectrum. If the individual components can be identified with particular neighbor environments, then their relative binding energies yield at least qualitative information on the charge distribution. In calculating each component, the Doniach-Sunjic expression[16] was combined by convolution with phonon (Gaussian) and lifetime (Lorentzian) broadening. The graphite lifetime width was used, so that the fit varied the four parameters for the binding energy, the intensity, the asymmetry, and the phonon broadening. Figure 6 shows the result of one five-component fit in which four components were constrained to have identical shapes while the asymmetry and the phonon width of the fifth, in this case the largest component, at low binding energy, were allowed to vary independently. This was done in recognition of the possibility that much more electronic charge is transferred to the carbon atoms with K^+ nearest neighbors, resulting in quite different screening responses to the core holes created in XPS. It should be noted that the widths of the fitted components, while smaller than the upper bound established by analysis of the KC_8 data, are comparable with the spacing between components, as expected for a fit of discrete peaks to a continuous function. This bears out our earlier observation that the data do not require the assumption of a registered structure for the intercalant layer.

Local minima in the summed deviations can be found for more than one combination of parameters. For example, if the magnitudes of the components are normalized to a total of 24, the fitted magnitude of the low-energy component ranges from 10.3 to 12.5, depending on the starting values of the parameters. There are similar variations of approximately one unit in the components at higher binding energy. Although this analysis is therefore not very precise, all fits have the following in common: (1) approximately half the intensity (12 units) appearing in a component at low binding energy, (2) a component with a magnitude of approximately 7 units at ~ 0.7 eV greater binding energy, and (3) most of the remaining strength centered at binding energies 1.5 to 2.5 eV higher than the large component. Thus the trend of the components is determined, if a registered structure is assumed for the intercalant layer. For the fit shown in Fig. 6, for example, the magnitudes of the components, in order of increasing binding energy, are { 11.9, 0.6, 7.4, 3.1, 0.9 }.

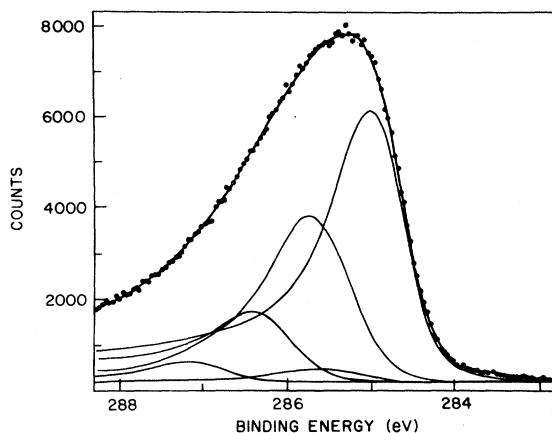We associate the component at lowest binding

FIG. 6. Five-component least-squares fit to the C 1s spectrum of the stage-two compound. The four peaks at higher binding energy were constrained to be identical in shape, although this has no significant effect on the components' intensities or positions.

energy with the 50% of carbon atoms which have K^+ nearest neighbors. Although a 1s electron on such a carbon atom is nearest the positive ion and thus experiences the attractive potential most strongly, its binding energy is the lowest; this is understood to be due to the repulsive interaction between the 1s electron and the excess transferred charge in the π orbital of the same atom. In addition to this highly repulsive interaction is the interaction with the screening charge on the other nearest-neighbor carbon atoms, which reduces the effect of the K^+ attraction. This argument implies a strong localization of charge on those carbon atoms with potassium nearest neighbors.

It is difficult to identify each of the remaining components with one of the four other types of carbon atoms illustrated in Fig. 4(b) because the distribution of environments depends on the structure of the intercalant layer, that is, on how the sites are occupied by K ions. For example, for the random lattice gas considered elsewhere,[14,17] approximately $\frac{4}{24}$ of the C atoms have three K next-nearest neighbors and $\frac{7}{24}$ of them have no K neighbors. For this structure our data analysis would imply that the C atoms with no K neighbors have lower binding energy than those with next-nearest neighbors, which in turn would mean that the stronger attractive interaction of the latter C atoms with the K ions is not compensated by a repulsive interaction with an excess of valence charge. However, the random lattice gas is known experimentally to be an inappropriate description of the intercalant layer. A more plausible re-

gistered structure can be produced if an unregistered, incommensurate, close-packed lattice of K ions is relaxed so that the K ions occupy the nearest sixfold sites. The proportion of C atoms with one K nearest neighbor of course remains at $\frac{12}{24}$, but there is a shift of strength from the fraction with three next-nearest neighbors, and from those with no neighbors to C atoms with one next-nearest K neighbor. The details of the distribution of C environments depend on the initial orientation of the incommensurate lattice with the graphite lattice, but there are typically approximately $\frac{6}{24}$ C atoms with exactly one K next-nearest neighbor, and approximately $\frac{3}{24}$ with no neighbors. Our data analysis would then imply that the C atoms with no K neighbors have a higher binding energy than those with one next-nearest neighbor, again indicative of an excess of valence charge on those C atoms that are nearer the K ions.

CONCLUSION

In conclusion, the rapid deterioration of the stage-one potassium GIC upon cleaving in ultrahigh vacuum makes an XPS study of KC_8 impractical at room temperature; however, the stage-two samples were more than adequately stable. Our stage-two data imply that the charge transferred to a C atom in a bounding layer is a sensitive function of its environment, being strongly localized on those C atoms which are nearest to K ions. This conclusion is independent of whether or not the intercalant ions are assumed to be in registry with the graphite lattice. Unfortunately, these data do not allow us to test that assumption, nor otherwise to determine the structure of the intercalant layer. However, this work does make it clear that any attempt to model the electronic structure of these compounds must take into account this highly nonuniform in-plane charge distribution.

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