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Charge distribution in potassium graphite

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The *c*-axis charge distribution in higher-stage potassium graphite has been obtained from an analysis of carbon 1*s* core-electron binding-energy spectra. The highly localized distribution of transferred charge in the bounding layer effectively screens the positive intercalant ions. The interior layers are thus graphitelike and contain small but measurable amounts of transferred charge.

The recent renewal of interest in graphite intercalation compounds (GIC's) has largely focused on the structure of the intercalate layers.¹ The distribution of electronic charge within the GIC has received less attention,²⁻⁷ with no quantitative results yet obtained. Such data are obviously necessary to the eventual understanding of staging, especially since recent theoretical work suggests that staging results from the electrostatic interaction of charged graphite layers.⁸

The C 1*s* binding energy measured in x-ray photoelectron spectroscopy (XPS) depends on the charge associated with an individual carbon atom. Unfortunately, not knowing the detailed electronic properties of these systems, we cannot from first principles relate the XPS binding energy to the charge. Although we expect donated charge to decrease the C 1*s* binding energy relative to the vacuum level E_{vac} , we do not know the π^* -1*s* Coulomb integral needed to calculate this decrease accurately. Moreover, since XPS measures energy relative to the Fermi energy E_F , the core-level shifts relative to E_{vac} cannot be inferred without knowledge of the work function. Despite these limitations, the C 1*s* XPS data for higher-stage potassium GIC's, presented in this Communication, offer direct information about the charge distribution.

The samples used were made by the standard two-zone technique and characterized by x-ray diffraction. They were introduced into the spectrometer through an inert atmosphere and cleaved in a 10^{-8} Pa vacu-

um. The data shown were all taken during the first hour after cleaving, during which time the surfaces were quite stable. Compositions determined from the XPS intensities agreed with the nominal compositions of the well-staged KC_{12n} compounds. E_F was determined by evaporating silver onto each sample at the conclusion of data acquisition and directly locating the Fermi cutoff by XPS.

Data for three compounds, and for highly oriented pyrolytic graphite (HOPG), are shown in Fig. 1. Both binding energy and linewidth change systematically with stage number, the widths agreeing generally with those reported by Bach.⁹ The binding energy increases from stage 5 to stage 2, where the charge per C atom is expected to be largest. This trend shows that the motion of the Fermi level through the valence bands is more important than the net electrostatic shifts of the core levels due to the Madelung potential and the charge donated to the π^* orbitals. This is because the density of states¹⁰ at E_F is so small that a transfer of $\frac{1}{24}e$ per C atom will cause the Fermi level to shift 1.3 eV toward E_{vac} . With the single-ion Coulomb shift largely canceled by the Madelung potential, the rough agreement between this estimated Fermi-level motion and the observed binding-energy shift (~ 1 eV greater than that for HOPG) for stage 2 is explained.

The widest line occurs for stage 2, where all the C atoms are in bounding (*b*) layers, those layers adjacent to the intercalate. This broad line cannot result

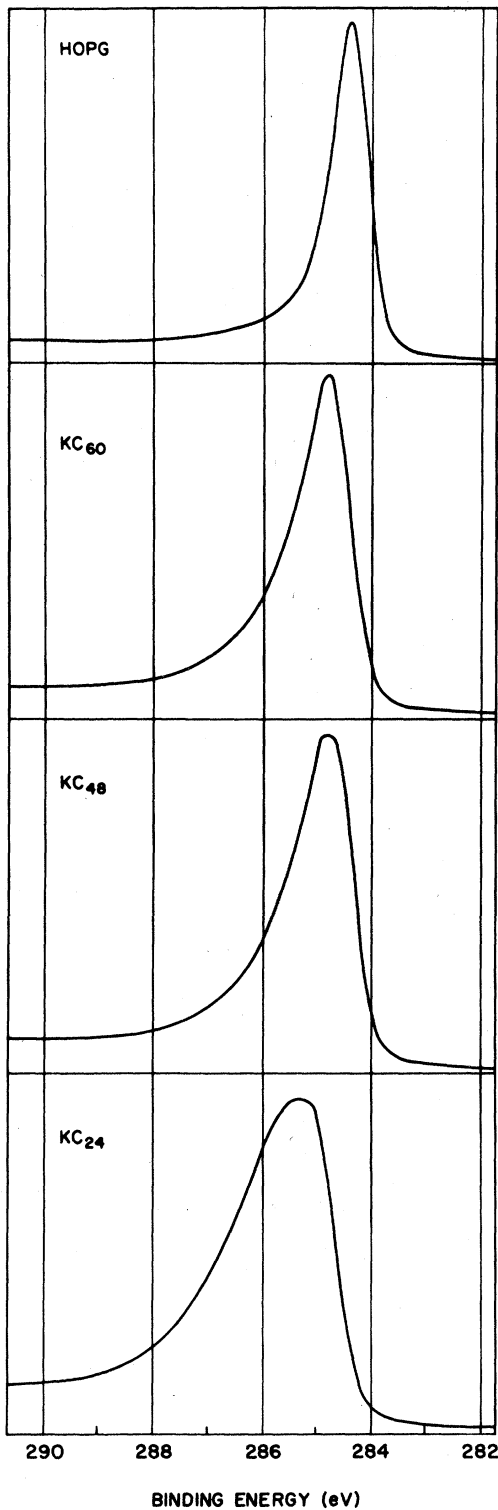


FIG. 1. Carbon 1s x-ray photoemission spectra for highly oriented pyrolytic graphite (HOPG) and for the three higher-stage potassium GIC's studied.

from the many-body screening response, and therefore indicates inequivalences among C atoms which can only be due to each atom's particular environment of K^+ neighbors. We elsewhere show that the shape and the width of this line imply that most of the charge donated to the b layer remains in the π^* orbitals of the C atoms nearest to an intercalate ion.¹¹ Thus, calculations which treat the b layer as a sheet of uniform charge ignore a significant spatial inhomogeneity of all GIC's except those of the form MC_6 , in which all the C atoms are equivalent.

In the stage-4 and -5 data the line narrows and approaches the shape of HOPG. This opposes the elementary notion that the coexistence of bounding (b) and interior (i) layers, which are electronically distinct, should lead to a broader spectrum in compounds of stage $n > 2$. The narrowing clearly signifies that i layers are broadened much less than the b layers and have small shifts relative to each other, so that the C 1s width is due mainly to the contribution of the b layers. This further implies the i layers are well screened from the intercalate ion by the (localized) charge in the b layer, and that their band structure is little changed from that of graphite. The main effect of intercalation on the i layers, then, is to shift E_F relative to the bands, allowing some electronic charge into the i layers, as indicated in Fig. 2.

This point of view can be used to analyze the data for the higher stages. We assume that the b layer remains similar to that in stage 2 while the i layers remain graphitelike. The proportions among these layers serve as constraints on the areas of the components of the C 1s spectrum. The HOPG C 1s line shape is appropriate to the i layers despite the additional charge in the π^* orbitals because the line shape is determined by excitonic screening in the final state.¹² The use of the stage-2 line shape for the b layers is more problematical: (1) The intercalate

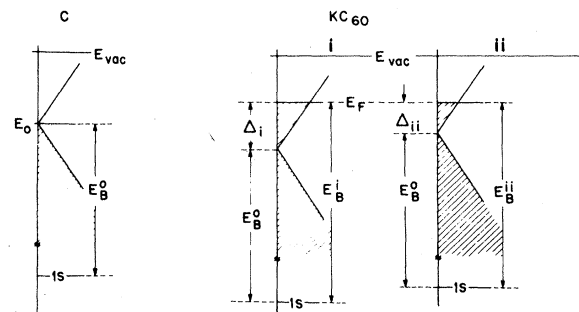


FIG. 2. Schematic density-of-states plots for graphite and for the interior layers of stage-5 potassium-intercalated graphite. The C 1s binding energy (E_B^0) is indicated for pure graphite, as well as for the interior layer farthest from the intercalate (ii), and for the interior layers that are also adjacent to bonding layers (i). The binding-energy shifts (Δ_x) for these layers are also indicated. The figure is not drawn to scale.

layer structure in stage 2 may differ from that in higher stages,¹³ and (2) a *b* layer in contact with another *b* layer is not identical to one in contact with an *i* layer. Because of these difficulties, we allow the width of the *b*-layer component to vary in the analysis of the higher-stage data.

The results of least-squares fits incorporating these concepts are shown in Fig. 3. The quality of the fits tends to confirm the validity of the model. The essential numerical results, given in Table I, are the shifts in the binding energies associated with the *i* and the *b* layers relative to HOPG. As stated above, the dominant effect of charge transfer is the Fermi-level motion. If we make the approximation of assuming that the 1s core level does not move relative to the other bands, then the shift for the *i* layers directly measures the Fermi-level motion. The *i*-layer charge can then be obtained by integrating the density of states of graphite. These values (Table I) confirm earlier order-of-magnitude estimates of the *i*-layer charge.³ Owing to its different shape, only an average shift, at best, can be defined for the *b*-layer component. Furthermore, the graphite band structure is unlikely to apply to this layer, which lacks the high in-plane symmetry of the *i* layers. Nevertheless, the average shift gives at least a rough estimate of the *b*-layer charge. Safran and Hamann,⁸ assuming an electrostatic basis for staging, have calculated the charge transfer and the potential for each layer in higher-stage GIC's; their results for unit charge transfer are shown in Table I. Although a detailed comparison with our data is precluded by their treatment of the *b* layer as a uniformly charged sheet, there is good qualitative agreement. The typically

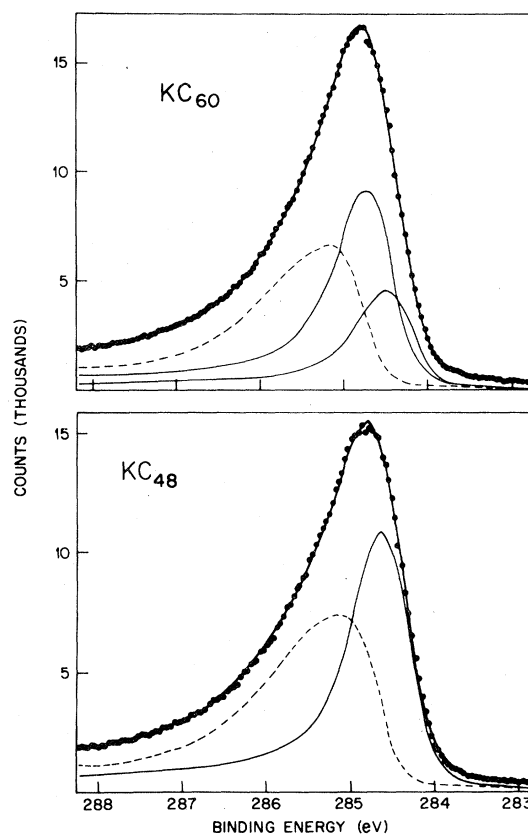


FIG. 3. Results of fitting the stage-5 and the stage-4 spectra using the stage-2 and the HOPG data. The dashed curve is the (compressed) stage-2 spectrum, representing the bounding layers, while the thin-solid curves result from simply shifting the HOPG spectrum, and represent the interior layers.

TABLE I. *c*-axis charge distribution in KC_{12n} .

Compound	Layer ^a	Binding energy shift (expt.) ^b	Layer potential (theor.) ^c	Charge transfer ^d	
				Expt. ^e	Theor. ^c
KC ₂₄	<i>b</i>	~1.0		0.325	0.5
KC ₄₈	<i>b</i>	~0.85		0.235	0.402
	<i>i</i>	0.23		0.029	0.098
	<i>b-i</i>	0.62	0.628		
KC ₆₀	<i>b</i>	~0.87		0.242	0.395
	<i>i</i>	0.35		0.054	0.082
	<i>ii</i>	0.16		0.017	0.047
	<i>b-i</i>	0.52	0.672		
	<i>b-ii</i>	0.71	0.822		

^a*b*, bounding layer; *i*, interior; and *ii*, second interior layer.

^bIn eV, relative to HOPG.

^cIn eV from Ref. 2, assuming unit charge transfer and a dielectric constant $\epsilon = 3$. Layer potentials are calculated relative to the *b* layer.

^dIn units of electrons per layer per intercalant atom.

^eAssuming a rigid two-dimensional band structure, as in Fig. 2; obtained by integrating the graphite density of states.

lower experimental values of the layer potentials may suggest a charge transfer of less than one unit per K ion, in accord with an earlier observation of an alkali-like conduction band near the Fermi energy in alkali GIC's, which limits the charge transfer.¹⁴

The electrostatic model of staging is thus in accord with our XPS data. Other conclusions are as follows; (1) That graphitic interior layers, well screened from the intercalate ions' potential, carry a small but finite amount of charge; and (2) that in the bounding layer

the distribution of charge, and consequently of core-electron binding energies, is strongly modulated by the ionic potential.

ACKNOWLEDGMENT

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¹For a comprehensive review of efforts in this field, see *Intercalated Layered Compounds*, edited by F. Levy (Reidel, 1979).

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