

Valence bands of KHgC_4 and KHgC_8

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We present core-level and valence-band photoemission spectra of stage-1 and -2 potassium-mercury intercalated graphite, taken using a monochromatic x-ray source. Besides confirming earlier-measured core-level shifts we have new evidence, in the core-level line shapes and in the valence photoemission intensities, regarding the electronic nature of these compounds. The core-level data suggest greater occupancy of states with K $4s$ character than in the binary compound KC_8 , consistent with the higher c axis compressibility of these compounds. The valence-band data indicate higher occupancy of states with Hg $6s$ character in the stage-2 ternary compound than in the stage-1 compound. This suggests that the Hg $6s$ electrons may play an important role in the superconductivity of KHg -intercalated graphite, as the stage-2 compound has a higher T_c than the stage-1 compound.

I. INTRODUCTION

In previous x-ray photoelectron spectroscopy (XPS) studies¹⁻⁴ of graphite intercalation compounds (GIC's), the selectivity of the photoemission cross sections has helped reveal the orbital character of the occupied valence states, especially where angle-resolved spectroscopies⁵⁻⁷ and theory⁸⁻¹⁰ have also been applied. We have studied the XPS valence-band spectra of the ternary GIC's KHgC_4 and KHgC_8 . Knowledge of the electronic structure may explain why the stage-2 compound has been found to have a higher superconducting transition temperature T_c than the stage-1 compound,¹¹ despite having a lower total density of states at E_F as determined by specific heat measurements.¹²

In these ternary GIC's the potassium ions have the same in-plane structure as in the stage-1 binary compound KC_8 , so that zone folding has the same effect on the graphite bands in all three compounds. In KC_8 the XPS data imply that the occupied states near E_F are graphitic, with nearly all of the K $4s$ charge having been transferred into the C π bands.^{2,8,9} We expect a different situation in the ternary compounds with their high metal-to-carbon ratio and their strong K-Hg interaction. While in KC_8 the K and C layers alternate, in the ternaries each K layer is bounded by one C layer and one Hg layer, with stacking units of C-K-Hg-K for KHgC_4 and of C-K-Hg-K-C for KHgC_8 . The Hg positions have not been experimentally determined but are likely to be as given in Fig. 1, since this arrangement of intercalant atoms would be only a mild distortion of the structure of the intermetallic compound KHg_2 .¹³ In any case, the local environment of the Hg atoms is very probably the same in stages 1 and 2.

It is probably most appropriate to think of the K-Hg-K layers as a unit and to think of interlayer interactions as occurring between the graphite bands and the amalgam's

bands. Comparisons should be made to the properties of KHg_2 rather than to those of potassium or mercury or even KHg , which has a very different structure.

Earlier XPS work¹⁴ on KHgC_4 and KHgC_8 revealed

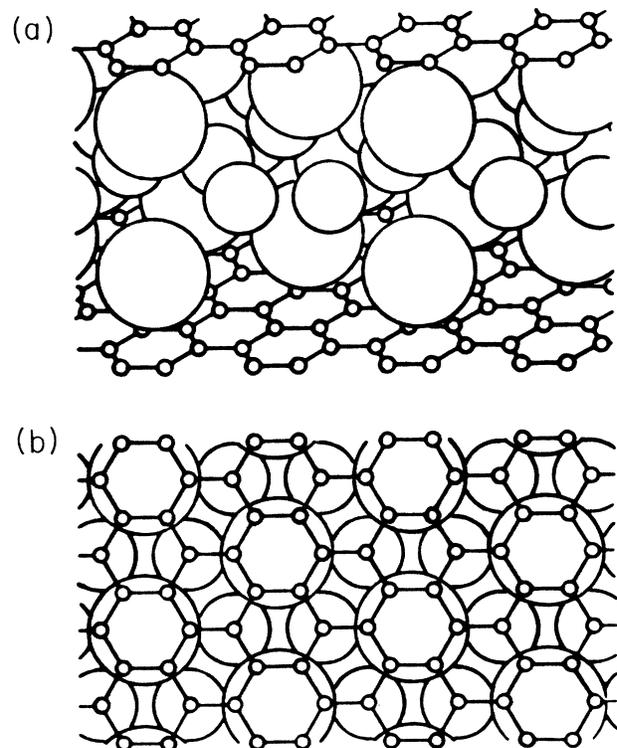


FIG. 1. (a) A "side view", perpendicular to the basal plane, and (b) a "top view" of the likely structure of KHg intercalated graphite. The atoms are not drawn to scale and are identified as, from largest to smallest, potassium, mercury, and carbon.

that the K $2p$ electrons appear at lower binding energy than they do in KC_8 . This immediately suggests that more electronic charge is retained by the potassium atoms in the ternary compounds than in the binary. Unfortunately, the usefulness of the data in Ref. 14 is limited by those authors' use of an unmonochromated x-ray source; line shape analysis was not attempted because of the poor resolution, and the valence-band photoemission was swamped by an unfortunate combination of intense, low-lying intercalate core levels and the satellite spectrum of the source. In this paper we present spectra of KHgC_4 and KHgC_8 taken using monochromatized x rays. The absence of satellites in the source radiation allows us to take reliable valence-band data, and our better resolution allows us to analyze the core electron line shapes.

II. EXPERIMENTAL

Samples (0.5–1.0 g) were prepared from highly-oriented pyrolytic graphite (HOPG) as previously¹⁴ and characterized by color, weight uptake, and x-ray diffraction. The Hg limits the penetration depth of the x rays to a small fraction of the total sample thickness. Since the photoemission data were taken on cleaved samples, the diffraction method is useful only as a gross check on the reaction conditions.

All samples were grown with no temperature gradient between the amalgam source and the HOPG, because for stage 1 this appears to minimize the amount of minority phase produced. This minority phase,^{15,16} of unknown composition, has a larger d spacing than the majority phase and a different in-plane superlattice. The stage-2 samples (KHgC_8) were made by reacting stoichiometric quantities of KC_8 and Hg, rather than by exposing HOPG to KHg_2 . The samples were briefly heated in a gradient prior to weighing, in order to distill any condensed amalgam. In all cases the weight uptakes were correct to better than 1%, the x-ray $00l$ scans revealed only the expected reflections to within 2% relative intensity, and the correct colors (rose-purple for KHgC_4 , blue for KHgC_8) were observed and persisted after multiple cleaves in UHV. The samples were epoxied to Ni-plated holders using Hysol S-20 conducting epoxy, and sealed in evacuated pyrex tubes for transport to the spectrometer.

The samples were transferred through a glove bag into a vacuum chamber, the tubes being opened in an inert atmosphere (Ar gas). After this transfer chamber was pumped down to a pressure in the 10^{-9} Torr range, the sample was transferred into the spectrometer chamber, where the sample holder was cooled by liquid nitrogen to a temperature lower than -100°C before cleaving, to prevent de-intercalation at the cleaved surface. All photoemission data were taken on cooled, freshly cleaved surfaces in ultra-high vacuum (base pressure $< 10^{-10}$ Torr), in an ESCALAB Mark II spectrometer, using monochromatic Al $K\alpha$ radiation (1486 eV). Core-level spectra were taken with a 20-eV pass energy, to ensure good resolution. The XPS cross sections for valence electrons are low, so these spectra were taken with a 40-eV pass energy in order to increase the intensity.

III. RESULTS

Figure 2 shows valence-band spectra from both of the ternary compounds, normalized to the Hg $5d$ peaks. Each is the sum of several spectra and required a total of approximately three hours to accumulate. During this time no sample deterioration was observed. One immediately notices that the relative intensity of the (unresolved) K $3p$ doublet is greater in the stage-1 spectrum, although the K/Hg ratio should be the same in the two compounds. This discrepancy results from the different nature of the cleaved surfaces. To understand this discrepancy, we begin by noting that because the interaction between carbon planes is the weakest of all the interlayer interactions, the stage-2 sample cleaves mainly between carbon layers, so that over most of the surface one finds the (very stable) sequence C-K-Hg-K-C-/C. In the stage-1 compound, however, every layer interacts strongly with its neighbors, so that there is no preferred cleaving layer. Because of its extremely high vapor pressure, any Hg that would be left in the top layer rapidly evaporates, even at liquid nitrogen temperatures. If one assumes that the stage-2 surface is as described above and that the surface of the stage-1 sample consists of regions with the initial sequence C-K-Hg-K-/C and of regions with the sequence K-C-K-Hg-/K, then given the finite escape depth of the photoelectrons, one can account rather well for the observed intensity ratios of the three elements in both compounds.

The π orbitals of graphite have no appreciable cross section for Al $K\alpha$ radiation,¹⁷ and thus XPS is essentially blind to any charge that might occupy those orbitals or, more generally, to any charge that might occupy states of

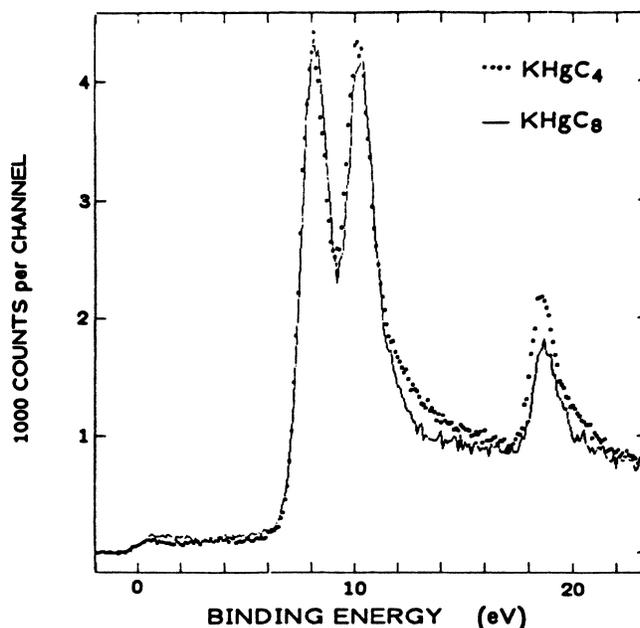


FIG. 2. Valence-band photoemission spectra of KHgC_4 and KHgC_8 (solid curve). The Hg $5d$ doublet appears at 8–10 eV and the K $3p$ doublet, which is not resolved, appears at 18–19 eV.

predominantly C π character. A comparison of intensities near the Fermi level tells us only about changes in valence bands derived from intercalate orbitals. In the spectrum for stage 2 the intensity is $\sim 40\%$ higher per Hg atom than in stage 1. This does not, of course, imply that the intercalate retains 40% more charge, which would contradict the common-sense expectation that the intercalate donates *more* charge to the graphite bands in the stage-2 compound. Rather, the intensity change must reflect a rehybridization of the valence states, one that favors orbitals with high photoemission cross section.

The Hg $6s$, Hg $6p$, and K $4s$ orbitals have cross-section ratios of 7:2:1. Obviously, as we are measuring simply the net photoemission yield, we cannot say exactly what contribution any of these orbitals makes to the occupied states in KHgC_4 or KHgC_8 , but clearly we are most sensitive to changes in Hg $6s$ occupancy and less so to changes in K $4s$ occupancy. Thus the observed change in intensity at E_F need not imply any change in charge transfer to the C π orbitals, but may simply reflect, e.g., an increase in occupancy of Hg $6s$ -derived states at the expense of Hg $6p$ or K $4s$. Thus a comparison of the XPS valence band spectra for KHgC_4 and KHgC_8 implies for the stage-2 compound an increase in the occupation of Hg $6s$ states, or of hybridized states that include Hg $6s$ character.

In Fig. 3 core-level spectra from KHgC_4 , KHgC_8 , and KC_8 are compared. The C $1s$ peaks (at lower binding energy) have approximately the same binding energy in each compound, whereas in KC_8 the K $2p$ doublets appear at

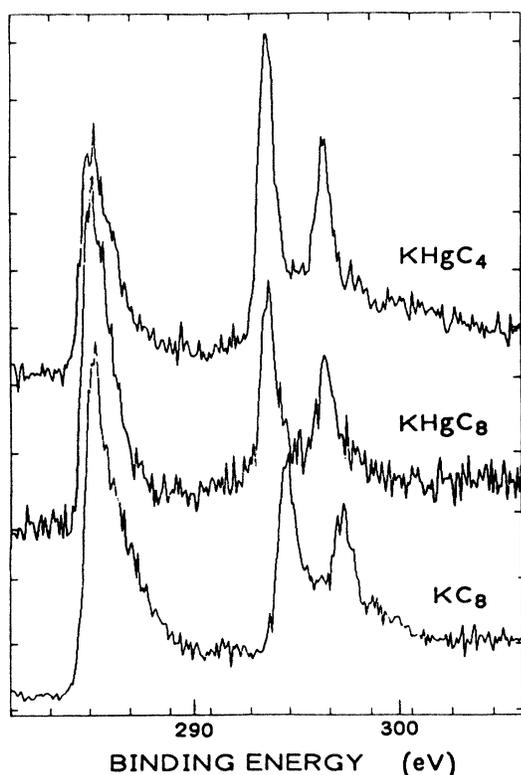


FIG. 3. Core-level spectra of KHg-intercalated graphite compared to that of KC_8 . The K $2p$ doublet appears at higher binding energy, and the C $1s$ peak at lower binding energy.

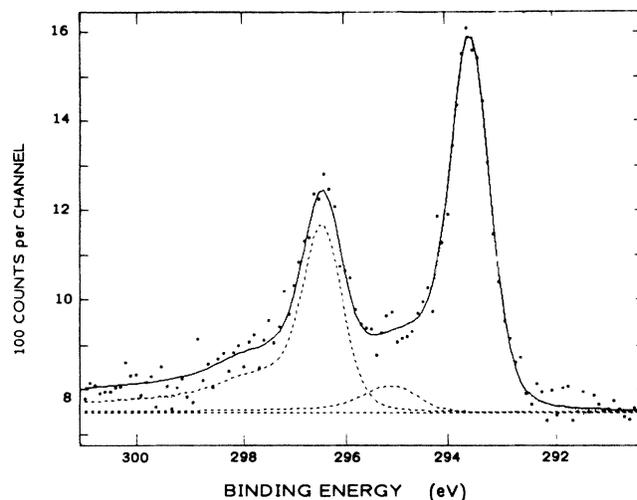


FIG. 4. Analysis of the K $2p$ spectrum of KHgC_4 . The solid curve is the fitted model function, and the dashed curves represent various components of the fitted function. Each member of the spin-orbit doublet consists of a main peak and a much weaker peak. For the $2p_{3/2}$ component (at lower binding energy) these are shown separately, while for the $2p_{1/2}$ the sum is plotted.

significantly higher energy. Each spectrum was acquired in approximately 42 minutes; in the data analysis discussed below, a better signal-to-noise ratio was achieved by summing several spectra, after confirming that the sample had not deteriorated during data taking.

Figure 4 illustrates our analysis of core-level spectra, showing in this case the K $2p$ doublet from KHgC_4 . The solid curve is the result of least-squares fitting of a model function to the data shown.¹⁸ The model function contains Doniach-Sunjić (DS) line shapes¹⁹ convolved with Gaussian functions. The DS function includes both the (lifetime) Lorentzian width and the asymmetry due to the metallic screening response to the core hole in the photoemission final state. The Gaussian function accounts for broadening due to phonons, for any small spread in binding energy due to inhomogeneity in the atomic environment, and for instrumental broadening. The additional weak doublet at higher binding energy indicates the presence of potassium not typical of the bulk sample, and is possibly due to surface potassium.

Despite the rather poor statistics, the fits determine the core electron binding energies to better than 0.1 eV. As seen in Table I, the binding energies are in good agreement with those obtained by Preil and Fischer.¹⁴ We also find that the fitted asymmetry parameter decreases for the

TABLE I. Binding energies (relative to E_F) of core electrons. The uncertainty in our measurements is typically 0.05 eV.

	K $2p$		C $1s$	
	This work	Ref. 14	This work	Ref. 14
KHgC_4	293.54	293.55	285.14	285.0
KHgC_8	293.57	293.45	285.11	284.9
KC_8	294.24	294.3	285.13	284.95

sequence KHgC₄, KHgC₈, and KC₈, from 0.22 to 0.16 to 0.14 net values.²⁰ As stated above, this parameter is a measure of the final-state response of conduction electrons to the core hole created by photoionization. This relaxation response proceeds via the creation of electron-hole pairs, that is, excitations from states just below the Fermi level to states just above it. Although the core hole can be screened by any nearby conduction electrons, screening by an atom's own valence electrons is most effective. Thus the measured asymmetry is most sensitive to the density at E_F of states of K 4s character.

The trends in both the asymmetry parameter and the binding energy shift suggest that the amount of K 4s charge at E_F increases in the sequence KC₈, KHgC₈, KHgC₄. Of course, equating an XPS core electron binding energy shift to the initial-state charge of the atom is in general too simplistic, as Madelung-type terms and final-state processes, at least, must be included in estimates of shifts. In BaC₆,⁴ for example, the measured Ba core electron binding energies can be understood only if one considers the intra-atomic redistribution of the charge remaining on the Ba atom and its effect on the final-state screening response. In comparing KHg-GIC to KC₈, however, the large K 2p binding energy shift and the structural similarities between the binary and the ternaries combine to give one some confidence in concluding that there is greater K 4s occupancy in the ternary GIC's. Comparisons between the two ternary compounds are more difficult. One does expect that the graphite bands accept more charge (per intercalate) in the stage-2 compound, and the valence-band data clearly indicate changes in the distribution of valence charge among intercalate-derived bands. Thus the rather weak evidence of the core-level data, for somewhat less K 4s charge in KHgC₈ than in KHgC₄, has the advantage of plausibility.

Another quantity sensitive to charge transfer between intercalate and graphite layers is the *c*-axis compressibility. For example, $\kappa = 2.1 \times 10^{-12}$ cm²/dyn for KC₈ as compared to 2.7×10^{-12} cm²/dyn for pure HOPG.²¹ KC₈ is stiffer than pure graphite due to its nearly ionic interlayer charge distribution (C⁻K⁺C⁻K⁺ ···). The less ionic nature of KHg-GIC is reflected in the compressibility of KHgC₄, which Kim *et al.* found to be 4.4×10^{-12} cm²/dyn,¹⁵ indicating that the intercalant layer has a high compressibility. We have now measured the KHgC₈ compressibility from pressure-dependent 001 reflections in neutron diffraction up to 12 kbar, and find $\kappa = 3.9 \times 10^{-12}$ cm²/dyn. If we invoke the composition law,²² we expect that

$$\kappa(\text{KHgC}_8) = (c_G \kappa_G + c_I \kappa_I) / (c_G + c_I),$$

where c_I and c_G are the layer spacing for KHgC₄ and pure graphite, respectively, and κ_I and κ_G are the respective compressibilities. This yields a value of $\kappa = 4.0 \times 10^{-12}$ cm²/dyn, in good agreement with our measured value. We note that the values of c used above are certainly correct to within a few percent for KHgC₈, but the adjacent carbon planes in KHgC₈ are charged and thus likely to have a lower compressibility than HOPG. However, given that $c_I \gg c_G$, the calculated value of $\kappa(\text{KHgC}_8)$ is rather insensitive to moderate changes in κ_G .

These results apparently conflict with work²³ that compares XPS binding energies and electron-energy-loss-spectroscopy (EELS) energies for what are presumed to be K 2p to K 4s transitions. The EELS results imply that the K 4s threshold lies at least 2 eV above E_F in all three materials. According to the EELS results, the K 4s minimum lies farthest above E_F for KHgC₄; this is exactly opposite to the trend suggested by our data.

In comparing the Hg 4f spectra for the two ternary compounds, we found nearly identical line shapes, except for a slightly lower asymmetry (0.23 compared to 0.26) in the stage-2 compound.

IV. SUMMARY

We have confirmed earlier measurements of core electron binding energies in KHgC₄ and KHgC₈. Our analysis of the K 2p spectra of KC₈, KHgC₈, and KHgC₄ reveals a trend of decreasing binding energy and increasing line shape asymmetry; both phenomena suggest increasing occupancy of K valence orbitals, or of hybridized valence states with significant K character. These observations are quite consistent with the reflectivity measurements,²⁴ which indicate, for each stage, the same amount of charge transfer to the C π bands *per carbon atom* in the binary and the ternary compounds. In the ternary compounds, with their higher K-to-C ratio, this leaves a substantial amount of K 4s charge to be distributed in intercalate orbitals. That the intercalate itself does not consist of ionic layers (i.e., K⁺Hg⁻K⁺) is confirmed by the relatively high *c*-axis compressibility of the ternary GIC's compared to KC₈.

Comparison of our valence-band spectra for the two compounds suggests that in the stage-2 compound, more of the intercalate charge occupies states with Hg 6s character. This in turn suggests that the Hg 6s charge plays an important role in the superconductivity of these compounds.

Subtle processes, such as rehybridization, manifest themselves in photoemission spectra via phenomena that cannot be reliably interpreted without additional independent information. Band structure calculations for both stages of KHg-intercalated graphite should predict the nature of the states near E_F , especially the hybridization involved in the intercalate bands. Such theoretical results would enable us to offer a more specific interpretation of our experimental phenomena. The calculations of Senbetuet *al.*²⁵ do show considerable hybridization, as well as substantial Hg 6s occupation near E_F , in KHgC₈. Unfortunately, they deal only with the stage-2 compound, and thus do not help us interpret the observed differences between the stage-1 and -2 valence-band spectra.

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