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Band model for the electronic structure of $KHgC_8$

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There is both theoretical and experimental evidence that the band structure of graphite intercalation compounds (GIC's) can be considered as a first approximation, as a superposition of graphitic and intercalant bands. Assuming such a rigid-band-type model is valid, we have obtained the band structure of second-stage potassium-mercury amalgam GIC, $KHgC_8$, by superposing K-Hg-K sandwich bands with the two-dimensional graphite bands. The graphite bands have been zone folded into the smaller Brillouin zone of $KHgC_8$. The self-consistent full potential linearized-augmented-plane-wave formalism for thin films has been used to calculate the sandwich band structure and density of states. The K $3p$ states lead to a dispersionless set of bands at -17.75 eV. Hybridization of K $4s$ states with Hg $6p$ states is very strong. From our band calculation we extract the partial density of states (DOS) due to the intercalant at the Fermi level of $KHgC_8$. Comparison with low-temperature specific-heat measurements suggests a very small contribution to the DOS at the Fermi level from carbon layers. We also compare the model predictions with optical experiments.

I. INTRODUCTION

There has been a great deal of interest in graphite intercalation compounds (GIC's) containing alkali-metal—mercury amalgam, particularly because of their unusual sandwich structure[1] and superconducting properties.[2,3] Experimentally the superconducting properties of these materials have been investigated more extensively[3,4] than other physical properties. Even though few in number, there are also reports of experimental data on Shubnikov—de Haas[5] and optical[6,7] measurements on potassium-mercury amalgam GIC. These data have been used to obtain some information on the electronic structure of potassium mercurographitides. So far the major effort and emphasis has been in the experimental investigation of properties. Thus, theoretical studies of the electronic structure of these compounds have lagged considerably behind experimental work. One major reason for this is that detailed and accurate *ab initio* calculations of the band structure are difficult and time consuming due to the large number of atoms in a unit cell.

The band structure of the binary compound KC_8 has been studied based on rigid-band model[8] as well as from first principles.[8,9] It is found that rigid-band approach explains the electronic structure reasonably well. This approach is essentially similar to the treatment of alloys in the dilute limit. Thus the Fermi energy of the pristine graphite crystal is raised or lowered depending on whether charge is transferred to or from the crystal by the intercalant. For the potassium mercurographitides, there is experimental evidence[10] that the charge transfer from KHg to carbon layers is much less than that in KC_8. There is also measurement of c-axis resistivity[11] of these compounds which indicates much weaker s-π hybridization compared to KC_8. Therefore, these experimental results suggest that a rigid-band model can represent, to a first approximation, the electronic structure of the ternary compounds and can provide a guide for a coherent interpretation of available experimental data.

The aim of the present work is to use a rigid-band-type model in an attempt to obtain for the first time the band structure of second-stage potassium mercurographitide ($KHgC_8$). This system is chosen because by analogy to pure graphite[12] we expect a five-layer (C-K-Hg-K-C) thin-film band calculation to give reasonable results for $KHgC_8$. As it turns out, even this five-layer calculation is still difficult and time consuming because there are twenty atoms per unit cell. So for simplicity we have used a two-step approach. We first calculate the band structure of an isolated K-Hg-K sandwich using the semirelativistic self-consistent full potential linearized-augmented-plane-wave (SC-FLAPW) method for thin films.[13] We next construct the band structure of $KHgC_8$ by simply superposing the sandwich bands with the zone-folded two-dimensional graphitic π bands. The Fermi energy of $KHgC_8$ is then determined by filling the empty π bands according to the rigid-band model. Finally, the predictions from this comparatively simple model are compared with existing low-temperature specific heat and optical measurements on $KHgC_8$.

The organization of the paper is as follows. In Sec. II the crystal structure and the model input parameters are introduced. Section III presents a brief description of the formalism for the band-structure calculation. The energy bands and density of states of the K-Hg-K sandwich, and the $KHgC_8$ bands are given in Sec. IV. Section V discusses the present results in terms of the available experiments on $KHgC_8$.

II. CRYSTAL STRUCTURE AND MODEL

The alkali-metal—mercury amalgam GIC's have a stoichiometry[1] of $MHgC_{4n}$ ($n=1,2$; M represents K,Rb). The intercalant layer consists of two layers of alkali metal contacting bounding carbon layers and a mercury layer sitting between the two alkali metal layers as shown in Fig. 1. The distance between the two bounding carbon layers is 10.16 Å for the potassium-mercury amalgams. There is some evidence[1] that the Hg layer may actually consist of two layers a distance d apart, where $d \lesssim 0.25$ Å. In the present calculation we assume we have a single layer of Hg atoms sandwiched between the potassium layers. For the second-stage compounds, the in-plane configuration of alkali atoms is $(2\times 2)\ R\,0°$, similar to that of KC_8.

A projected view of $KHgC_8$ structure is shown in Fig. 2. The planar arrangement of K atoms is hexagonal close packed, while the Hg atoms form a two-dimensional graphite like structure. The specific values of the interlayer distances between K and Hg and the carbon layer are unknown. For our model system we assume a K-Hg layer separation of 4.97 a.u. Then, since the bounding carbon layers are reported to be 10.16 Å apart, the spacing between a carbon layer and the nearest-neighbor K layer is 4.63 a.u.

The model system we will investigate has a thin-film geometry and is investigated by rigid-band approach. This consideration of a thin-film and a rigid-band—type model to describe the band structure of $KHgC_8$ is motivated by the following observations.

(i) The K-Hg interaction is much stronger than the K-carbon layer interaction. Thus, the intercalant K-Hg-K sandwich is a thin film whose electronic structure is weakly perturbed by the presence of bounding graphite layers.

(ii) Graphite π bands near the Fermi level are essentially weakly perturbed by the intercalant sandwich. This is partly due to the fact that π bands are weakly bonding or antibonding in nature.

(iii) Graphite layers on opposite sides of the K-Hg-K sandwich do not interact directly since their separation is large.

A justification for assumption (i) is the observation that a bulk KHg alloy with triclinic structure[14] exists in crystalline form. A further justification for assumptions (i) and (ii) comes from the experimental result of C-axis resistivity measurements[11] which suggest very weak s-π hybridization. In addition to this, since the interaction between adjacent graphite layers is weak, the consideration of thin-film geometry is a reasonable approximation.

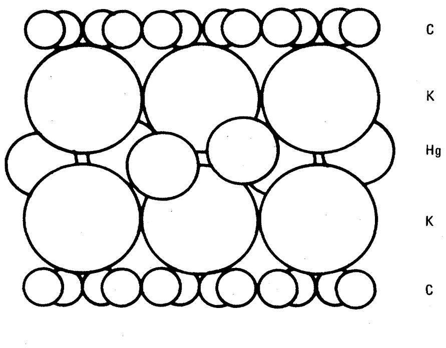

FIG. 1. Crystalline structure of $KHgC_8$.

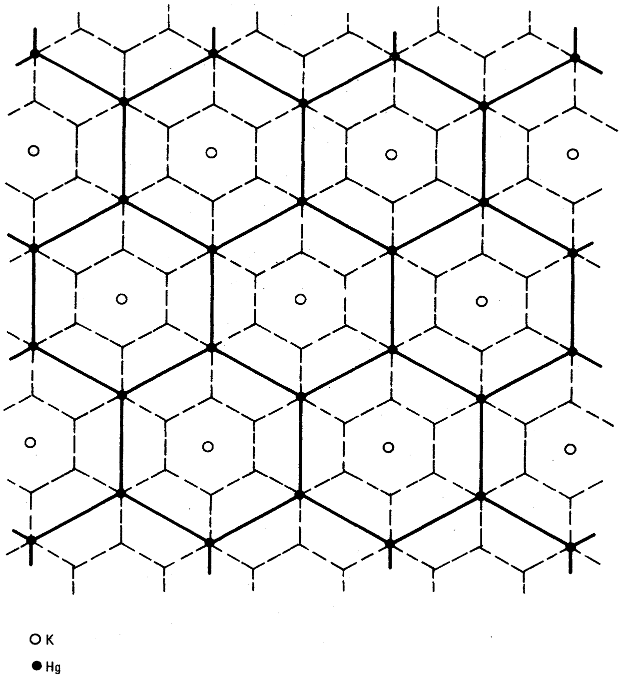

FIG. 2. Projected view of crystal structure of $KHgC_8$.

To characterize the thin-film geometry completely we have to specify the thickness and its two-dimensional structure. The two-dimensional lattice constant determined by the K-atom occupied lattice sites is 9.278 a.u. The K-Hg-K sandwich thickness is given by $D=15.272$ a.u., while the distance used in defining the z component Fourier expansion of the FLAPW basis[13] has a dimension of $D'=17.50$ a.u. For both K and Hg atoms we assume a muffin-tin radius of 2.684 a.u. Within a primitive cell defined by the above dimensions, we have a total of four atoms: two K and two Hg atoms. This essentially completes the definition of the model and some of the input parameters used in the calculation of the K-Hg-K sandwich band structure.

The three-layer K-Hg-K system has z-reflection symmetry. Therefore, it is possible to use basis functions that are symmetrized under this operation. This symmetrization of FLAPW's reduces the computation time substantially.

III. FORMALISM

A. LAPW band method

The film geometry of the K-Hg-K sandwich system dictates the choice of band-structure method. One of the accurate band methods for treating this type of geometry is based on the linearized-augmented-plane-wave (LAPW) scheme. The self-consistent LAPW method used in the present work has been described in the literature;[13] here we will only outline the basic approach. A set of variational basis functions of the form

$$\phi_{i,\mathbf{k}}(\mathbf{r})=\sum_{l,m}[A^{i}_{lm}(\mathbf{k})U_l(E_l,r)+B^{i}_{lm}(\mathbf{k})\dot{U}_l(E_l,r)]Y_{lm}(\hat{r}) \tag{1}$$

and specified by the wave vector **k** is used to expand the Bloch functions inside muffin-tin spheres around each atom. The constant energy parameters E_l control the shape of the radial functions and can be given different values for each l and each atom type. The radial function energy derivative $\dot{U}_l=\partial U_l/\partial E\,|_{E=E_l}$ are chosen to allow an efficient expansion of the eigenstates for energies close to E_l. During computation, the parameters E_l are normally chosen to lie near the center of the band of interest.

For the film geometry only two-dimensional periodicity holds. So in the interstitial regions outside the atomic muffin-tin spheres the basis function is defined as

$$\phi^{mn}_{\mathbf{k}}(\mathbf{r})=\Omega^{-1/2}e^{i\mathbf{K}_{mn}\cdot\mathbf{r}}\ , \tag{2}$$

where Ω is a normalizing factor and $\mathbf{K}_{mn}=\mathbf{k}+\mathbf{g}_m+g_n\hat{z}$. Here **k** is the two-dimensional (2D) Bloch vector, $\mathbf{g}_m$ is a 2D reciprocal-lattice vector, and g_n labels the Fourier components for the expansion in the nonperiodic z direction denoted by the unit vector $\hat{z}$.

For the film geometry, it is convenient to consider the exterior or vacuum regions outside the film to develop an efficient expansion of the basis functions for $|z|>D$, where D is the film thickness given in Sec. II. In this region, the basis is defined as a product of 2D plane wave and a z-dependent function and its energy derivative:

$$\phi^{mn}_{\text{vac},\mathbf{k}}(\mathbf{r})=[A^{\text{vac}}_{mn}(\mathbf{k})U_m(E_v,z)+B^{\text{vac}}_{mn}(\mathbf{k})\dot{U}_m(E_v,z)]e^{i\mathbf{K}_m\cdot\mathbf{r}} \tag{3}$$

in analogy with Eq. (1). Here the U_m are solutions of the one-dimensional Schrödinger's equation for the average of the full potential over the x-y plane, and $\mathbf{K}_m=\mathbf{k}+\mathbf{g}_m$. Depending upon the value of the vacuum energy parameter E_v, the basis function may have either damped or oscillatory behavior for large z.

The expansion coefficients A^i, B^i of Eq. (1) are determined by matching the LAPW's and their radial derivatives across the muffin-tin sphere boundaries. Similarly, the expansion coefficients in the exterior region are obtained by again matching the LAPW's at the vacuum-film boundary. This completes the definition of the basis set. Using this set and applying the variational principle, we obtain a secular equation to determine the eigenenergies and the corresponding eigenvectors for a discrete grid of **k** values. The wave functions of the form:

$$\Psi_n(\mathbf{k},\mathbf{r})=\sum_i C_{ni}(\mathbf{k})\phi_{i,\mathbf{k}}(\mathbf{r}) \tag{4}$$

are then occupied according to Fermi statistics to generate the charge density required for self-consistent iterations.

B. Self-consistent crystal potential

The self-consistent crystal potential and charge density were calculated using the special **k** points of Chadi and Cohen.[15] For the film calculation presented in this work the 3—**k**-point set: $\{(\frac{1}{3},\frac{1}{9}), (\frac{2}{3},\frac{2}{9}), \text{and } (1,\frac{1}{9})\}$ in the irreducible two-dimensional wedge was used in the set of self-consistent iterations. The potential calculations are performed in the warped muffin-tin approximation, i.e., no shape approximations are made in the interstitial and vacuum regions, but the potential in the atomic spheres is spherically averaged.

At the end of the self-consistent iterations a finer **k** grid was used to calculate the density of states. The finer grid helps to minimize interpolation errors in the linear triangular method[16] used for the DOS calculation. We have used fifteen **k** points in the irreducible triangle to determine the total and layer-projected DOS for the K-Hg-K sandwich.

IV. BAND STRUCTURE

A. K-Hg-K level structure and DOS

In Fig. 3 we present the band structure for the isolated K-Hg-K sandwich. The solid and dashed lines represent bands which are respectively symmetrical and antisymmetrical with respect to z reflection. Not shown in the figure are the set of dispersionless K $3p$ bands which are located at -17.75 eV. The ten low-lying bands are Hg $5d$—like. Of these, the bands that are antisymmetric with respect to z reflection involve purely Hg $5d$ orbitals while the rest, even though predominantly d-like, have some s character. The energy range of the $5d$ core states is 2.20 eV. The two bands lying entirely below the KHg Fermi energy E_F and above the $5d$ bands are predominantly $6s$-like. The lower $6s$-like band has significant d character, while the upper band has significant p character. The bands which

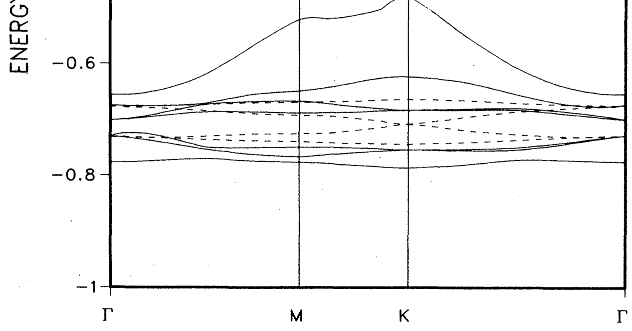

FIG. 3. Self-consistent FLAPW band structure of K-Hg-K sandwich. Solid (dashed) curves represent symmetric (antisymmetric) states with respect to z-reflection symmetry.

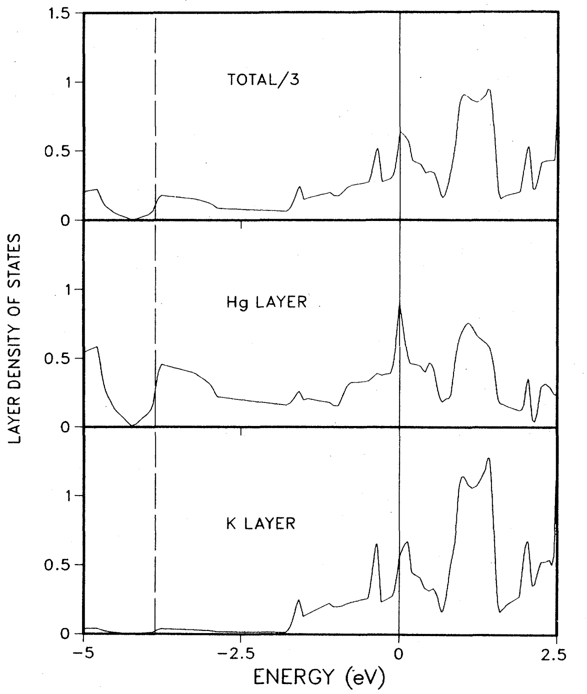

FIG. 4. Layer projected density of states in units of states per eV spin. The zero is at E_F (see Fig. 3), and the dashed line indicates the Fermi energy of $KHgC_8$.

lie partly below E_F have both Hg 6*p* and K 4*s* character in almost equal proportions. This considerable admixture of states is also evident in the partial density of states for the K-Hg-K sandwich.

In Fig. 4 we show the layer-projected DOS for the KHg film broadened by convolution with a Gaussian of width 0.2 eV. The zero of energy is taken at the Fermi energy $E_F = -2.41$ eV. As mentioned earlier, this DOS was obtained using 15 **k** points in the irreducible $\frac{1}{12}$ of the two-dimensional Brillouin zone. At the Fermi level, the contribution to the DOS from Hg layer is approximately equal to that from the two K layers.

B. $KHgC_8$ bands

The qualitative features of the $KHgC_8$ band structure for states near the Fermi level are obtained by application of a rigid-band-type model. Our basic assumption is that the electronic band structure of $KHgC_8$ is a superposition of two-dimensional graphitic bands and intercalant KHg bands. This means that there is no interaction between carbon layers, between carbon and Hg layers, and that the K potential is vanishingly small at the graphite planes. Since the interlayer spacing between the carbon layers and that between carbon and Hg layers is large enough, the assumption of negligible interactions in these cases is justified. The vanishing of the K potential is at this point an approximation assumed to simplify the problem.

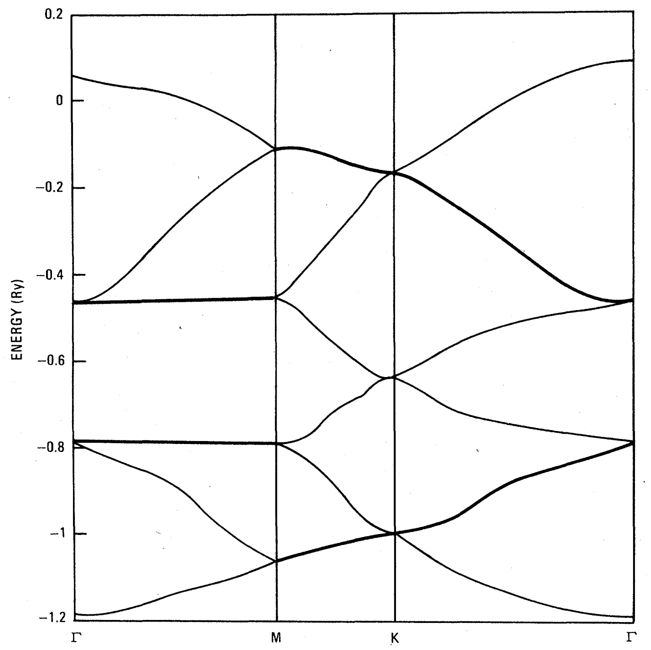

FIG. 5. Zone-folded π bands of two-dimensional graphite, adapted from the calculation of Painter and Ellis (Ref. 12). Degenerate bands are indicated with thickened line.

Figure 5 shows the π bands of two-dimensional graphite taken from the calculation of Painter and Ellis[12] zone-folded into the corresponding two-dimensional Brillouin zone of $KHgC_8$. This zone is one-fourth the area of that of graphite. In the folded π-band structure shown in Fig. 5, the *M* point of graphite has been mapped into the Γ point of $KHgC_8$. The *K*-point structure of graphitic bands is found at the *K* point in $KHgC_8$. On this band structure, the Fermi energy of graphite lies at approximately -8.85 eV.

The $KHgC_8$ band structure is obtained by a superposition of the π bands with KHg bands. Here it is assumed the zeros of Figs. 3 and 5 are the same. In particular, the Fermi level of $KHgC_8$ is determined by partially filling the unoccupied π bands of graphite below the KHg E_F. This gives a value of $(E_F)_0 = -6.27$ eV. A further examination of the superposed bands shows that the bands involving Hg 6*p* and K 4*s* states are completely empty, while the upper Hg 6*s*—like band is only partially occupied. This is shown clearly in the DOS plot of Fig. 4, where $(E_F)_0$ is indicated by the dashed line. We also note that at this Fermi level, the partial DOS due to the KHg intercalant is 0.16 states/(eV atom).

V. DISCUSSION AND CONCLUSION

There have been relatively few experimental results published that give relevant information on the band structure of $KHgC_8$. This might be primarily due to the lack of theoretical band calculations that can be used to interpret the experiments. The few available experiments are not sufficient to provide rigorous comparison between theoretical models and experiment. Keeping this in mind we now review some of the measurements and their interpretation in the light of the present rigid-band-type approach.

The DOS of $KHgC_8$ at the Fermi level has been determined by low-temperature specific heat measurements.[2] The value reported is 0.18 states/(eV atom). In the present calculation, we have only determined the intercalant, KHg DOS (see Fig. 4). This figure shows that at the $KHgC_8$ Fermi level, indicated by the dashed line, the K-Hg-K sandwich partial DOS is approximately 0.16 states/(eV atom). Thus, a comparison to the experimental result suggests a very small contribution to the DOS from the carbon layers.

Another property of $KHgC_8$ that has been measured is the optical reflectivity in the energy ranges 0.5—6.0 eV (Ref. 6) and 0.16—5.8 eV.[7] The results indicate that the threshold at which interband transitions occur is 1.2 eV. A theoretical calculation of the optical-absorption coefficient would involve evaluating matrix elements of the operator $\hat{\epsilon}\cdot\nabla e^{i\mathbf{k}\cdot\mathbf{r}}$, where $\mathbf{k}$ is the photon wave vector and $\hat{\epsilon}$ is its polarization. We have not evaluated these matrix elements. Instead we adopt the view that structures in the reflectivity spectrum can be correlated with direct transitions at high symmetry points in the Brillouin zone. Furthermore, if by following Ref. 6, we assume that the interband transitions involve only Hg levels, the present model predicts a transition of 0.9 eV at the M point. This is in agreement with the observed threshold value.

The results from our simple model are qualitatively consistent with the specific heat and reflectivity measurements. However, besides further experimental data, more improvement of the present model is needed to carry out rigorous comparison of theory and experiment. Since band calculations of $KHgC_8$ are unavailable currently, we have not been able to demonstrate the deviations from the predictions of the present model. An obvious shortcoming in the present approach is that the direct superposition of intercalant and graphitic bands neglects any interaction between the KHg bands and graphitic bands even though the Hg $5d$— and $6s$—like bands lie within the folded π bands. Thus, to obtain the detailed band structure of $KHgC_8$ we must consider the five-layer, C-K-Hg-K-C thin film. This will give relevant data for predicting the details of the Fermi surface, besides providing information on the possible deviations from the present model. But this five-layer study using SC-FLAPW scheme is both computationally difficult and time consuming, because the unit cell consists of 20 atoms. Furthermore, before even attempting this, more experimental measurement is needed to resolve the uncertainty in the position of the mercury atoms in $KHgC_8$. In the meantime, it is hoped that the present simple model will be useful as a first step for interpreting experimental results.

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