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Electronic structure of the hydrogen-potassium-graphite ternary intercalation compound C_8KH_x

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We present the results of the first band-structure calculation for the hydrogen-potassium-graphite ternary intercalation compound C_8KH_x. The Zunger-Freeman self-consistent numerical-basis-set linear combination of atomic orbitals method has been used within the Hohenberg-Kohn-Sham local-density-functional formalism. We find that hydrogen acts as an acceptor to graphite, while potassium acts as a donor. The charge transfer to the hydrogen atoms is imperfect and therefore the hydrogen 1*s* state forms a partially occupied metallic band. This hydrogen-1*s*-like band coexists with the graphite-π^*-like bands at the Fermi level.

Recently, much attention has been devoted to ternary graphite intercalation compounds. The hydrogen-potassium-graphite intercalation compound C_8KH_x is the most typical example of these compounds. The structure and electronic properties of C_8KH_x have been investigated by many experiments.[1–7] However, there are some controversial discussions about them. The central problem is the relative position in energy of the hydrogen state in C_8KH_x; whether the hydrogen 1*s* (H 1*s*) state lies below the Fermi level or forms a metallic band intersecting the Fermi level. Several experiments such as low-temperature specific heat,[1] Schubnikov–de Haas effect,[2] and optical reflectivity,[3] suggest the low-lying H 1*s* state. These results indicate that the hydrogen atom in C_8KH_x has a localized electronic state as a H^- ion, while other recent experimental results of proton NMR,[4,5] electrical conductivity, and thermoelectric power[6] are interpreted as showing the metallic character of the H 1*s* state. In addition, Saito *et al.*[7] very recently carried out ESR, ^{1}H NMR, and ^{13}C NMR experiments and found that the H 1*s* band intersects the Fermi level, showing a metallic character of hydrogen state. On the other hand, the band structure has not been theoretically established to date.

In this paper, we present the first calculated band structure of C_8KH_x and show that the hydrogen 1*s* state forms a metallic band in this compound. Further, we estimate the amount of the charge transfer among the individual atoms and show that the hydrogen atom acts as an acceptor, while the potassium atom acts as a donor.

C_8KH_x has a stage-2 structure where K–H–K sandwiched layers are formed in the intercalants. That is, the stacking order along the *c* axis is –C–C–K–H–K–C–C–. Adjacent carbon layers are separated by 3.35 Å and the distance between the potassium and hydrogen layers is 2.13 Å. The distance between the carbon and potassium layers is also 2.13 Å.[7] As for the in-plane atomic arrangement, the structure of carbon layer is a hexagonal net as in graphite. In a potassium layer, potassium atoms form a 2×2 superlattice. However, the structure of a hydrogen layer is not established to date. Some possible models were proposed. In this study, we use the simplest model; hydrogen atoms form a 2×2 superlattice. This structure leads to a hydrogen content, $x=0.5$. This model structure, based on the observed layer spacings and our assumption of H ordering introduced above, is shown in Fig. 1. In this model, the space group is D_2^6 ($C222$) and each primitive unit cell contains only 19 atoms: 16 carbon atoms, two potassium atoms, and one hydrogen atom. The carbon atoms are classified into four environmentally nonequivalent types by symmetry, and the two potassium atoms are equivalent. In the present calculation, we take account of the charge transfer among these individual atoms completely.

The electronic structure was determined in a Hohenberg-Kohn-Sham local-density-functional formalism using the Zunger-Freeman self-consistent numerical–basis-set linear combination of atomic orbitals method.[8] The Hedin and Lundqvist approximation[9] for the exchange-correlation potential was used. In this work, we take the 1*s*, 2*s*, and 2*p* orbitals of carbon, and

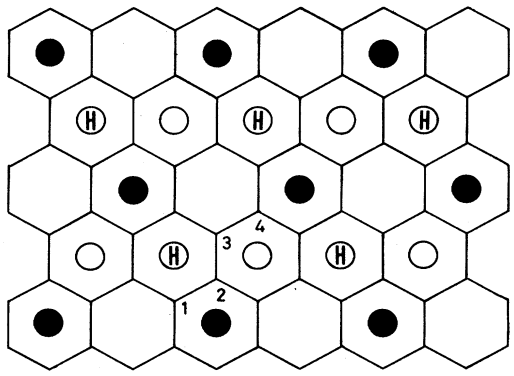


FIG. 1. Top view of the structural model of $C_8KH_{0.5}$. The hexagonal net represents the carbon layer. Hydrogen atoms are denoted by a circle with H, Ⓗ. Potassium atoms are denoted by closed circles, ● and open circles, ○. The stacking order along the *c* axis is $-C2\}-\{C1-K(\bullet)-H(Ⓗ)-K(\circ)-C2\}-\{C1-$. Here, { } represents a unit cell. Adjacent carbon layers (C1 and C2) are in the *A*-*A* stacking. The four environmentally nonequivalent carbon atoms are denoted by 1, 2, 3, and 4.

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1*s*, 2*s*, 2*p*, 3*s*, 3*p*, and 4*s* orbitals of potassium and 1*s* orbital of hydrogen as a numerical basis set. The details of the calculation are presented in a previous paper.[10]

The calculated band structure is shown in Fig. 2. The most remarkable feature is the appearance of a partially occupied conduction band around the Γ point in the Brillouin zone (BZ). It is proved, from the amplitude of the wave function, that this band originates mainly from the hydrogen 1*s* orbital. In addition, it is found that the two partially occupied conduction bands around the *K* point originate mainly from the carbon $2p_z$ orbitals. That is, the hydrogen-1*s*-like band coexists with the graphite-π^*-like bands at the Fermi level in C_8KH_x. The H-1*s*-like band has very little k_z dispersion. This is due to large separation (11.88 Å) between the nearest hydrogen layers. The bandwidth of this two-dimensional (2D) band is about 0.6 eV. Thus, the hydrogen in $C_8KH_{0.5}$ has a weakly metallic nature. Consequently, the hydrogen-1*s*-like 2D Fermi surface in the center of the BZ coexists with the graphitelike cylindrical Fermi surfaces in the corners of the BZ.

The overall band structure is similar to that obtained by superposing the 2D free-electron band of hydrogen on graphite bands folded into the smaller BZ of $C_8KH_{0.5}$. Thus, many of the C_8KH_x bands can be identified with the π and σ bands of 2D graphite. The unit cell in our model structure contains two graphite layers. Therefore, there are two degenerate folded 2D graphite bands if there is no interaction between the graphite layers and the potassium and hydrogen potentials are vanishingly small at the graphite layers. Due to the interaction, these two folded bands split off. It is found that the energy separations of the folded π bands are large (about 0.4 eV). This is consistent with a large overlap between the π orbitals of the adjacent graphite layers. On the contrary, the separations of the folded σ bands are small because of small overlap of σ orbitals.

In the present calculation, the atomic occupation numbers are treated essentially as iteration parameters in the self-consistent procedure to produce the best superposition potentials.[8,10] The obtained final occupation numbers are shown in Table I. The total population of each atom in the crystal is given in Table II. We define the amount of the charge redistribution of atoms as the difference between the above self-consistent population and the population of isolated (neutral) atoms.[10,11] These values are shown in Table II. Here, a plus sign represents the charge transfer from the atom and a minus sign represents the transfer to the atom.

These results indicate that the hydrogen atom acts as an acceptor, while the potassium atom acts as a donor. Further, the charge redistribution between the environmentally nonequivalent carbon atoms is produced; half of the carbon are donors, the other half acceptors. The averaged charge of these carbon atoms is about −0.04. Therefore, it is found that the graphite layers act as acceptors on the average. Though the K-4*s*-like bands lie above E_F, the amount of the charge redistribution of potassium atoms is not unity. This is due to the fact that the K 4*s* components are mixed slightly into the wave functions of many graphitelike states below E_F.

Figure 3 shows the calculated density of states for $C_8KH_{0.5}$ near E_F. It was calculated by using the eigenvalues at 960 **k** points in the $\frac{1}{24}$ irreducible BZ. The large peak near 0.2 eV below E_F is corresponding to the H 1*s* state. This large value is consistent with the small dispersion of the H 1*s* band. The structures near −12 eV and below −14 eV are corresponding to the graphite π and σ states, respectively.

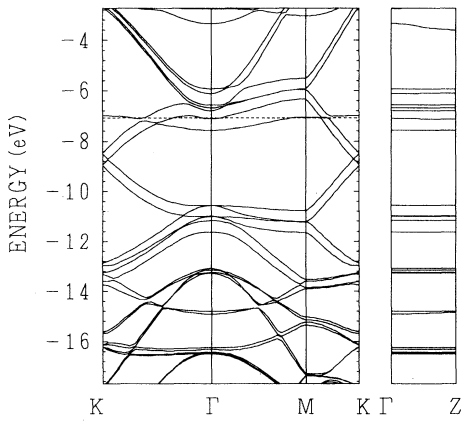


FIG. 2. Self-consistent band structure of $C_8KH_{0.5}$ along several high-symmetry directions in the Brillouin zone. Here, the dashed line represents the Fermi energy.

TABLE I. Occupation number.

Atom	Orbitals	Occupation number
Carbon 1	2*s*	1.22
	2*p*	2.95
Carbon 2	2*s*	1.22
	2*p*	2.96
Carbon 3	2*s*	1.20
	2*p*	2.78
Carbon 4	2*s*	0.85
	2*p*	2.96
Potassium	4*s*	0.54
Hydrogen	1*s*	1.37

TABLE II. Total population and amount of charge redistribution

Atom	Total population	Amount of charge redistribution
Carbon 1	6.17	−0.17
Carbon 2	6.18	−0.18
Carbon 3	5.98	+0.02
Carbon 4	5.81	+0.19
Potassium	18.54	+0.54
Hydrogen	1.37	−0.37

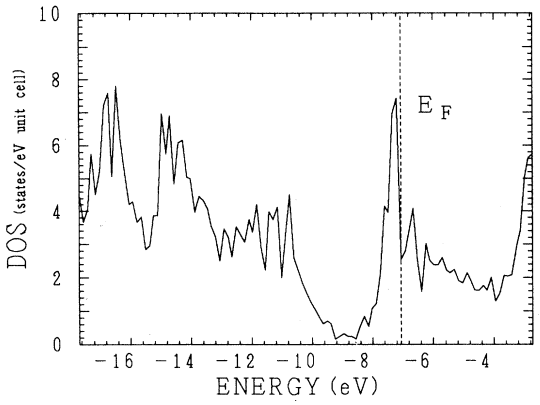


FIG. 3. Density of states of $C_8KH_{0.5}$ near the Fermi level.

Next, we will discuss several experiments in terms of our results. The following experiments suggested that the H 1*s* state forms a metallic band intersecting the Fermi level. Nomura *et al.*[4] carried out a ^{1}H NMR experiment and showed that the *s*-like band electron exists on hydrogen atoms. Enoki *et al.*[6] measured electrical conductivity and thermoelectric power. They showed that a large electron and a small hole Fermi surface coexist and that potassium acts as a donor to graphite, while hydrogen plays the role of an acceptor. Saito *et al.*[7] carried out ESR, ^{1}H NMR, and ^{13}C NMR and found that the hydrogen atom has a metallic character and the H 1*s* band intersects the Fermi level. Our results are consistent with these experiments.

The recent photoemission experiment[12] for $C_8KH_{0.8}$ indicates that there is a peak corresponding to the hydrogen state near 2.0 eV below E_F. In our density of states, this peak locates at about 0.2 eV below E_F. This discrepancy may be due to the different hydrogen content. The relative position of the H-1*s*-like band to the graphitelike band is very sensitive to the amount of the charge redistribution, and the charge redistribution is largely influenced by the hydrogen content. In this study, we use the simplest model structure; the hydrogen content is 0.5. In the above experiment, the content is 0.8. This different content will lead to the different relative position of the H-1*s*-like band.

In our model structure, one of the folded upper π bands intersects the Fermi level slightly at the Γ point. The position of the Fermi level is, however, very sensitive to the amount of the charge transfer. Therefore, it is expected that some folded upper π bands go down below the Fermi level around the Γ point and form metallic bands in the case of the different hydrogen content.

In conclusion, we have found that the H 1*s* state forms a 2D metallic band in $C_8KH_{0.5}$. We estimated the amount of the charge redistribution among the individual atoms and found that the hydrogen atom acts as an acceptor, while the potassium atom acts as a donor. The charge transfer to the hydrogen atom is imperfect. As a result, the H-1*s*-like 2D Fermi surface in the center of the BZ coexists with the graphitelike 2D Fermi surfaces in the corners of the BZ. The band structure of C_8KH_x with the different crystal structure and the stage-1 compound C_4KH_x will be given in the near future.

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