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## ELECTRONIC BAND STRUCTURE OF LITHIUM-GRAPHITE INTERCALATION COMPOUND C6Li

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The band structure of the first-stage lithiumgraphite intercalation compound C<sub>6</sub>Li is calculated non-empirically by introducing the pseudopotentials of constituent atoms and the Madelungtype potential due to the charge transfer. The amount of charge transfer from lithium to carbon layers is determined self-consistently to be 100 percent. The obtained Fermi surface is constructed entirely from the folded graphite  $\pi$  bands.

### I. Introduction

Band structure calculations have been reported for the firststage alkali-graphite intercalation compounds. Inoshita, Nakao and Kamimura calculated for the first time the detailed band structure of C8K by the semi-empirical tight binding scheme and found that there were two distinct types of Fermi surfaces, one of which was potassium-like and nearly isotropic, and the other of which was carbon-like and of cylindrical shape[1]. Then Ohno, Nakao and Kamimura developed a new method for calculating the band structure of the first-stage compounds by using the pseudopotentials and the Madelungtype potential due to charge transfer. They applied the method to CgK, confirmed the coexistence of the two distinct types of Fermi surfaces and found the charge transfer from potassium to carbon layers to be 60 percent non-empirically[2]. This Fermi surface structure is supported by a variety of experiments. On the other hand, Holzwarth, Rabii and Girifalco calculated the band structure of C6Li by assuming the complete charge transfer from lithium to carbon layers, and found that the Fermi surface was constructed entirely from the graphite  $\pi$  bands which were folded into the smaller Brillouin zone of C6Li[3]. It is interesting to investigate from the first principle whether a lithium-like Fermi surface exists or not, in other word the charge transfer is 100 percent or not.

In this paper we perform the band structure calculation for  $C_{6}$ Li by employing the previous method applied to  $C_{8}K[2]$  and determine the amount of charge transfer non-empirically.

# II. Formulation

We first describe briefly the method of band structure calculation developed by us[2]. The total crystal potential  $V(\mathbf{r}:f)$  is composed of a superposition of atomic pseudopotential  $v_{\alpha}(\mathbf{r})$  and the Madelungtype potential  $V_{M}(\mathbf{r}:f)$  deu to the charge transfer as follows:

$$V(\mathbf{r}:f) = \sum_{j\alpha} v_{\alpha} (\mathbf{r} - \mathbb{R}_j - \mathbb{R}_{\alpha}) + V_{M}(\mathbf{r}:f) ,$$

(1)

where  $\alpha$  means a carbon or lithium atom, f represents the amount of charge transfer (0  $\leq f \leq 1$ ) and  $\mathbb{R}_{\alpha}$  is a nonprimitive lattice vector specifying an  $\alpha$  atom in the unit cell at lattice site  $\mathbb{R}_j$ . The basis functions used for the band calculation at the point  $[\mathbf{k}, \mathbf{k}_Z]$  are

$$\phi_{\mathbb{k}k_{Z}L\mathbb{G}}(\rho,z) = f_{\mathbb{k}ZL}(z) \frac{1}{\sqrt{S}} \exp[i(\mathbb{k}+\mathbb{G})\cdot\rho] , \qquad (2)$$

where  $\rho = (x,y)$  and  $k = (k_x, k_y)$  are the two-dimensional coordinate and wave-number vectors along layers, respectively. In eq.(2) S is the area of a layer and G a two-dimensional reciprocal lattice vector. The z-dependent part of the basis function  $f_{k_{\rm ZL}}(z)$  is the L-th eigenfunction of the wave vector  $k_z$  for the one-dimensional Schrödinger equation

$$-\frac{1}{2}f''_{k_{zL}}(z) + \overline{V}(z:f) \cdot f_{k_{zL}}(z) = \varepsilon_{k_{zL}} \cdot f_{k_{zL}}(z) , \qquad (3)$$

where the average potential  $\overline{V}(z:f)$  is defined by

$$\overline{V}(z:f) = \frac{1}{S} \int V(\rho, z:f) d\rho$$
.

The atomic pseudopotential  $v_{\alpha}(r)$  is obtained in an analytic form by fitting to the model potential of Heine and Abarenkov for lithium and carbon atoms[4].

The Madelung-type potential  $V_M(r:f)$  is independent of x and y when we assume that the charges transferred from lithium to carbon layers and the remaining charges in the lithium layers are homogeneously distributed parallel to the layers. Then  $V_M$  is obtained by solving a one-dimensional Poisson equation with the charge distribution coming from the charge transfer.

#### III. Results and Discussions

We perform the band calculation for C6Li by employing 6 one-dimensional eigenfunctions and 37 two-dimensional plane waves in eq.(2). Self-consistency is achieved by equalizing the input charge distribution averaged over a plane parallel to the layer to the corresponding output one. We find the amount of charge transfer in C6Li to be 100 percent in accuracy of about 5 percent. Therefore it is shown that the assumption of complete charge transfer by Holzwarth et al. [3] is correct.

In Fig.(1) we present the calculated band structure of C6Li. The overall feature of this band structure is interpreted as a composite system of the lithium 2s band and the graphite band folded into the smaller Brillouin zone of C6Li. The lowest band of lithium 2s character has its minimum at  $\Gamma$  point ( $\Gamma_1^4$ ) about 0.05 au above the Fermi level EF and is completely unoccupied. All the occupied bands are essentially the folded graphite bands. To accommodate the charge transferred from lithium to carbon layers, the Fermi energy increases by about 0.08 au relative to graphite and the folded graphite upper  $\pi$  bands become partially filled. Therefore the conduction bands in C6Li are found to be of graphite- $\pi$ -band-character.

In the following we discuss some detailed characteristics in this band structure. First, the folded graphite bands of C<sub>6</sub>Li have considerably large dispersion along the c axis compared with the original graphite because the distance between the adjacent carbon layers is small and the stacking of these layers is not of A-B type as in graphite but of A-A type. Second, the lithium 2s state is mixed into the graphite bands to some extent, and this mixing effect produces band gaps among the graphite bands. As a result of this hy-



Fig.l The calculated band structure of C6Li along the symmetry lines K- $\Gamma$ -M-K, H-A-L-H and  $\Gamma$ -A

bridization, the wavefunctions of the graphite bands are not purely of carbon character but include lithium character to some extent. Therefore, rigorously speaking, the charge transfer from lithium to carbon layers is not 100 percent as we mentioned before, but is reduced by a few percent. Last, the Madelung-type potential shihts the lithium 2s band downwards relative to the graphite bands. As a result, the magnitude of the gap between the bottom of the lithium 2s band ( $\Gamma_1^+$ ) and the extremum of the graphite upper  $\pi$  band ( $\Gamma_6^-$ ) is reduced from 0.184 au in case of no charge transfer to 0.101 au in case of complete one. These values are in good agreement with the corresponding ones in [3], which are 0.185 au and 0.110 au, respectively.

The calculated density of states of C<sub>6</sub>Li near the Fermi level is presented in Fig.(2). The peaks near about -0.21 au and -0.03 au correspond to the saddle points in the lower and upper  $\pi$  bands at



Fig.2 Density of states of C6Li

the M point in the Brillouin zone for the two-dimensional graphite, respectively. These peaks have larger width than those in two-dimensional graphite because of the large caxis dispersion. Therefore the density of states at these peaks become smaller. The Fermi level of C<sub>6</sub>Li is located at -0.03275 au near the saddle point peak and the density of states N(E<sub>F</sub>) is 4.9 states/ This value is in C-atom/au. good agreement with the value of 5.8 ± 0.3 states/C-atom/au obtained from the specific heat measurements by Delhaes et al. [5].



Fig.3 The sketches of the Fermi surfaces for (a) lower conduction band and (b) upper conduction band

The sketch of the Fermi surface is shown in Fig.(3). These Fermi surfaces are similar to those obtained by Holzwarth et al.[3], which are constructed entirely from the folded graphite  $\pi$  bands. It is clearly seen from this figure that the Fermi surface for the lower conduction band is strongly warped by the considerable interaction between the A-A carbon layers, while that for the upper conduction band is nearly cylindrical. This warped Fermi surface reduces the anisotropy in the conductivity.

In conclusion, we have calculated the band structure of C6Li selfconsistently by using the atomic pseudopotentials and the Madelungtype potential due to the charge transfer, and found the amount of charge transfer from lithium to carbon layers to be 100 percent. The detail of the obtained band structure is somewhat different from that which was calculated by a KKR method on the assumption of the complete charge transfer[3]. However, the position of the lithium 2s band relative to the graphite  $\pi$  bands and the Fermi surface structure are in good agreement with those in [3]. This implies that our simple treatment of the effect of charge transfer is reasonable for the determination of the amount of charge transfer and the Fermi surface structure. In this way our method, which has the advantage of calculating the band structure with ease, can be applied widely to the first-stage graphite intercalation compounds.

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