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Electronic Structure of Potassium-Graphite Intercalation Compound: C_8K*

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The electronic band structure of the first-stage potassium-graphite intercalation compound C_8K was calculated by a semi-empirical tight-binding scheme. The calculated Fermi surfaces can be classified into two distinct types. One is potassium-like and nearly isotropic; the other is carbon-like and of cylindrical shape. In addition, the cylindrical portions show nesting property, which is likely to induce charge-density-wave instability. The isotropic portions of the Fermi surfaces are responsible for the large reduction of anisotropy in conductivity of C_8K relative to graphite. The calculated density of states has a peak around the Fermi level and is in good agreement with the observed density of states derived from the specific heat measurements.

§1. Introduction

It is well known that many layered substances can easily absorb a variety of atoms and molecules between layers to form intercalation compounds.[1,2] Although the effects of intercalation upon the electronic properties of the host substances have been attracting widespread attention recently, all of the theoretical work up to now has been based on simple rigid band models.

In view of the fact that no study has been made of the real band structures of such intercalation compounds,** we report in this paper the results for the band structure of the potassium-graphite intercalation compound C_8K as obtained by the tight-binding method and extended-Hückel approximation. Our choice of C_8K out of numerous graphite intercalation compounds was motivated by its relatively simple crystal structure[1] as well as by its superconducting property discovered in 1965.[3]

In what follows we describe in §2 the crystal structure of C_8K and how we construct our Brillouin zone, in §3 the methods of calculation, and in §4 the results and discussion.

The most notable features of our findings are: (1) The coexistence of isotropic three-dimensional carriers and extremely two-dimensional carriers; (2) The occurrence of nesting Fermi surfaces which may possibly give rise to charge-density-waves. The authors believe that these features are typical of intercalation compounds and hope that this work will form the basis for the understanding of the electronic properties of intercalation compounds in general.

§2. Crystal Structure and Brillouin Zone

The first-stage potassium-graphite C_8K consists of alternating layers of carbon and potassium,[1] whose layer stacking sequence is $C\alpha C\beta C\gamma C\delta C\alpha C\beta C\gamma C\delta$—where C denotes a carbon layer and α, β, etc. stand for potassium layers as shown in Fig. 1(a). In each metal sheet, potassium atoms form a two-dimensional triangular lattice with a side of $a=4.91$ Å (Fig. 1(b)), and the stack of these metal sheets is staggered. The in-plane structure of a carbon layer remains the same as in the original graphite, that is a hexagonal net with a side of 1.42 Å, while the distance between adjacent carbon layers increases from 3.37 to 5.41 Å upon intercalation, reducing the overlap between carbon π orbitals in adjacent layers by order of 10^{-2}. C_8K belongs to the space group D_2^7; the point group D_2 consists of four symmetry operations—E, C_2^x, C_2^y, C_2^z—, where E is the identity, and C_2^x, C_2^y, and C_2^z denote two-fold rotations about mutually perpendicular axes x, y, and z respectively. The x and y axes

* A preliminary report of this work appeared in Bull. Amer. Phys. Soc. **22** (1977) 420.

** Although there have been no published reports on this matter, the first study was made on the band structure of C_8K by R. Swanson (Ph.D. Thesis, Stanford University, 1969).

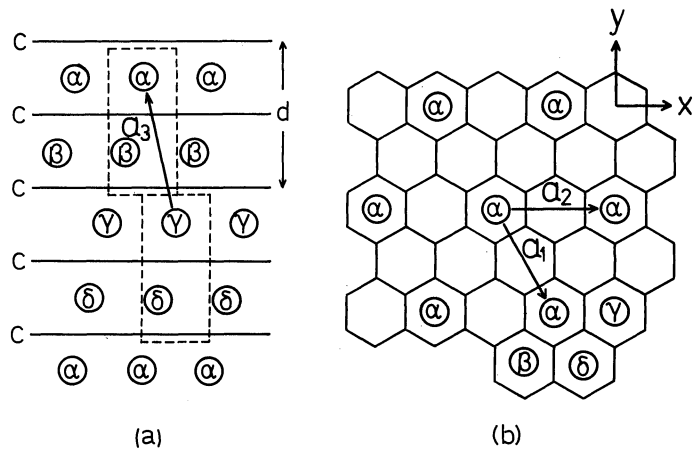

Fig. 1. The crystal structure of C_8K as seen from the side (a) and as seen from above (b). Here α, β, γ and δ denote potassium atoms in non-equivalent staggered layers. The in-plane structure of these metal sheets is the same. A unit cell, indicated by broken lines, involves two potassium and two carbon layers respectively.

are shown in Fig. 1(b) and the z axis is perpendicular to the layer plane.

A unit cell is made of 18 atoms—$(C_8K)\times 2$—and contains two sheets of carbon and potassium respectively as seen in Fig. 1(a). A set of primitive translation vectors is

$$\boldsymbol{a}_1=\left(\frac{a}{2}, \frac{-\sqrt{3}a}{2}, 0\right),$$
$$\boldsymbol{a}_2=(a, 0, 0),$$
$$\boldsymbol{a}_3=\left(-\frac{a}{2}, 0, d\right), \qquad (1)$$

where $d=10.84$ Å is twice the distance between carbon layers. The corresponding reciprocal lattice vectors are

$$\boldsymbol{b}_1=\left(0, -\frac{2}{\sqrt{3}a}, 0\right),$$
$$\boldsymbol{b}_2=\left(\frac{1}{a}, \frac{1}{\sqrt{3}a}, \frac{1}{2d}\right),$$
$$\boldsymbol{b}_3=\left(0, 0, \frac{1}{d}\right). \qquad (2)$$

The Brillouin zone defined by these reciprocal lattice vectors (Fig. 2) has a somewhat complicated shape reflecting the D_2^7 symmetry of the lattice. Instead of using this out-of-the-ordinary Brillouin zone, let us convert it into the familiar hexagonal prism without changing its volume. The procedure for this zone reconstruction is illustrated in Fig. 3.

It must be noted that this new Brillouin zone does not reflect the proper symmetry of C_8K in that some of its 'symmetry points' are spurious. For instance, the original Brillouin zone has only two M's, whereas the new zone has six M's; that is, four out of the six are spurious and do not have any special symmetry. Let us denote these spurious symmetry points as $\tilde{\mathrm{M}}$. (Fig. 4) Similarly, since the K's in the new zone are not present in the original

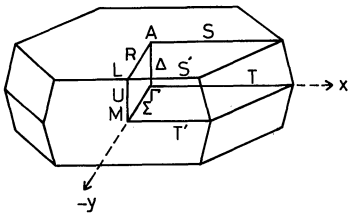

Fig. 2. The first Brillouin zone of C_8K as constructed from eq. (2) by the standard method.

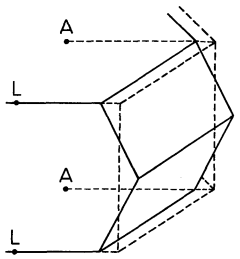

Fig. 3. The relationship between the original Brillouin zone (solid lines) and the modified zone (broken lines) which is the familiar hexagonal prism. (The inclination of the slanting sides of the original zone is exaggerated.)

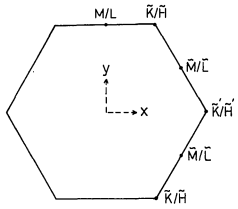

Fig. 4. The notation used for the modified hexagonal Brillouin zone. The notation ~ indicates spurious symmetry points.

zone, they are denoted as $\tilde{K}$ and $\tilde{K}'$. (The prime, in this case, denotes the inequivalent symmetry points which are not related to each other by any of the symmetry operations in the reciprocal space, namely the point group D_2 and the translation group generated by the recipoical lattice vectors.)

§3. Method of Calculation

Our calculations were performed by the tight-binding method with carbon $2p_z$ and potassium $4s$ orbitals as the basis. Since our purpose in the present paper is to derive the electronic structure of C_8K around E_F, we have neglected carbon σ orbitals, which are energetically quite far away from E_F.

The matrix elements of the one-electron Hamiltonian H for this basis set were evaluated with the extended-Hückel approximation[4]

$$H_{\alpha\beta}=\begin{cases} I_\alpha & \text{if } \alpha=\beta, \quad (3.a) \\ \dfrac{1.75}{2}(I_\alpha+I_\beta)S_{\alpha\beta} & \text{if } \alpha\neq\beta, \quad (3.b) \end{cases}$$

where I_α is the ionization potential of the α atomic orbital, and $S_{\alpha\beta}$ is the overlap integral between atomic orbitals α and β. $S_{\alpha\beta}$'s were calculated by representing the orbitals as Slater orbitals[5] with Clementi's exponents.[6] We have included seven $S_{\alpha\beta}$'s thus obtained (and corresponding $H_{\alpha\beta}$'s) in our calculations. For the ionization potentials, we used the Hartree-Fock values obtained by Herman and Skillman.[7] We found that the π bands of graphite obtained by these approximations agree well with the detailed calculation by Painter and Ellis.[8]

Further we modified eq. (3.a) so as to include the substantial charge transfer between carbon and potassium as follows:

$$H_{\alpha\alpha}=\begin{cases} I_\alpha & \text{if } \alpha=\text{carbon}, \\ I_\alpha-\varepsilon & \text{if } \alpha=\text{potassium}, \end{cases} \quad (3.a')$$

where ε, a disposable parameter, represents the change of the energy difference between carbon and potassium caused by the crystal field and Madelung potential. Since the energy shift is a relative quantity, we have fixed the carbon level and shifted the potassium level only. The energy shift ε is determined with the aid of experimental information.

The energy dispersion is obtained by solving the following secular equation

$$|\langle\psi_i|\mathrm{H}|\psi_j\rangle-E\langle\psi_i|\psi_j\rangle|=0. \quad (4)$$

Here $\psi_i(\boldsymbol{k}, \boldsymbol{r})(i=1\sim18)$ are the Bloch sums corresponding to the eighteen atomic orbitals considered here within the unit cell. If we label these orbitals so that $i=1$ to 16 correspond to carbon and $i=17$ and 18 to potassium, then the Bloch sums are

$$\psi_i(\boldsymbol{k}, \boldsymbol{r})=\begin{cases} \dfrac{1}{\sqrt{N}}\sum_{\boldsymbol{l}} \exp[2\pi i\boldsymbol{k}\cdot(\boldsymbol{r}_i+\boldsymbol{l})]\phi_{2p_z}(\boldsymbol{r}-\boldsymbol{r}_i-\boldsymbol{l}), & i=1\sim16, \\ \dfrac{1}{\sqrt{N}}\sum_{\boldsymbol{l}} \exp[2\pi i\boldsymbol{k}\cdot(\boldsymbol{r}_i+\boldsymbol{l})]\phi_{4s}(\boldsymbol{r}-\boldsymbol{r}_i-\boldsymbol{l}), & i=17, 18, \end{cases} \quad (5)$$

where ϕ_{2p_z} and ϕ_{4s} denote carbon $2p_z$ and potassium $4s$ orbitals respectively. The sum is taken over N lattice points in the crystal and $\boldsymbol{r}_i$ is a non-primitive vector specifying an inequivalent atom i in the cell.

§4. Results and Discussion

We determined the energy shift parameter ε so that the calculated Knight shift agrees with the experimental value. Unfortunately, there has been no available NMR data on C_8K. So we used the value for C_8Cs[9] instead. (A recent specific heat measurement[10] for C_8K and C_8Cs gives nearly the same electronic specific heat γ for the two compounds. This suggests the close similarity of the electronic structures of C_8K and C_8Cs near E_F and, therefore, of the Knight shifts.) On this basis, we chose 2.1 eV as the value for ε.

We show in Fig. 5 the calculated energy

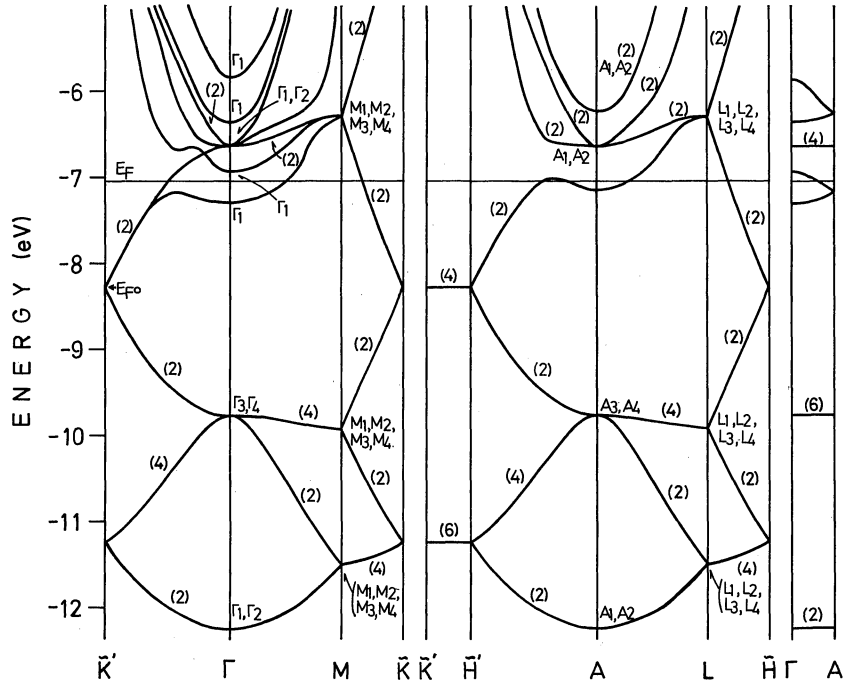

Fig. 5. The calculated energy dispersion for C_8K. The numbers in parentheses stand for the degrees of pseudodegeneracy. Here E_{F0} denotes the Fermi energy of graphite.

dispersion of C_8K. C_8K is found to be a metal with two conduction bands which are nearly degenerate in the peripheral regions of the Brillouin zone.* Both of the two conduction bands have the same qualitative feature. Namely, they are quite potassium-like and isotropic in the central regions of the Brillouin zone, i.e. in the vicinity of Γ and A; whereas, in the peripheral regions of the zone, they are extremely two-dimensional (2D), reflecting the characteristic of graphite. This two-dimensionality arises from the fact that the carbon-carbon layer spacing in C_8K is considerably enlarged by the insertion of potassium atoms. This point is further illustrated in Fig. 6 and Fig. 7 by showing the Fermi surfaces. The isotropic portions of the lower band Fermi surfaces are connected with the 2D portions as seen in Fig. 7(a).

The existence of the isotropic, potassium-like carriers is responsible for the large c-axis conductivity of C_8K.[11] Also, the small Hall coefficient obtained by Guérard *et al.*[12] can be explained by the hole-like closed orbits seen in Fig. 6(a), which tend to cancel the contribution of the electron-like orbits.

It must also be noted that the 2D portions of the Fermi surfaces show nesting property, which is likely to give rise to charge-density-waves (CDW). (The Fermi surfaces shown in Fig. 7 bear a resemblance to the Fermi surfaces of 2H–TaS_2, a typical substance where CDW was observed.[13]) This nesting property is more pronounced for the lower conduction band than for the upper band.

The electronic density of states $D(E)$ calculated on the basis of the above band structure is shown in Fig. 8. It has a peak around E_F besides a peak corresponding to the logarithmic singularity of 2D graphite. This $D(E_F)$ enhancement is mainly due to the staggered stacking of the metal sheets.** Recently Mizutani *et al.*[10] measured the specific heat of

* The space group D_2^7 gives no degeneracy. For the origin of the pseudo-degeneracy seen in Fig. 5, refer to the Appendix.

** As is seen in Fig. 5, the $D(E_F)$ enhancement results from the mixing of the carbon and potassium bands. This mixing would not take place, at least in the Γ-K-M plane, if these metal sheets were exactly on top of each other, because the carbon bands and the potassium bands, in the Γ-K-M plane, would have different parities as to the mirror reflection in the basal plane. Therefore, the staggered stacking is very important in enhancing $D(E_F)$.

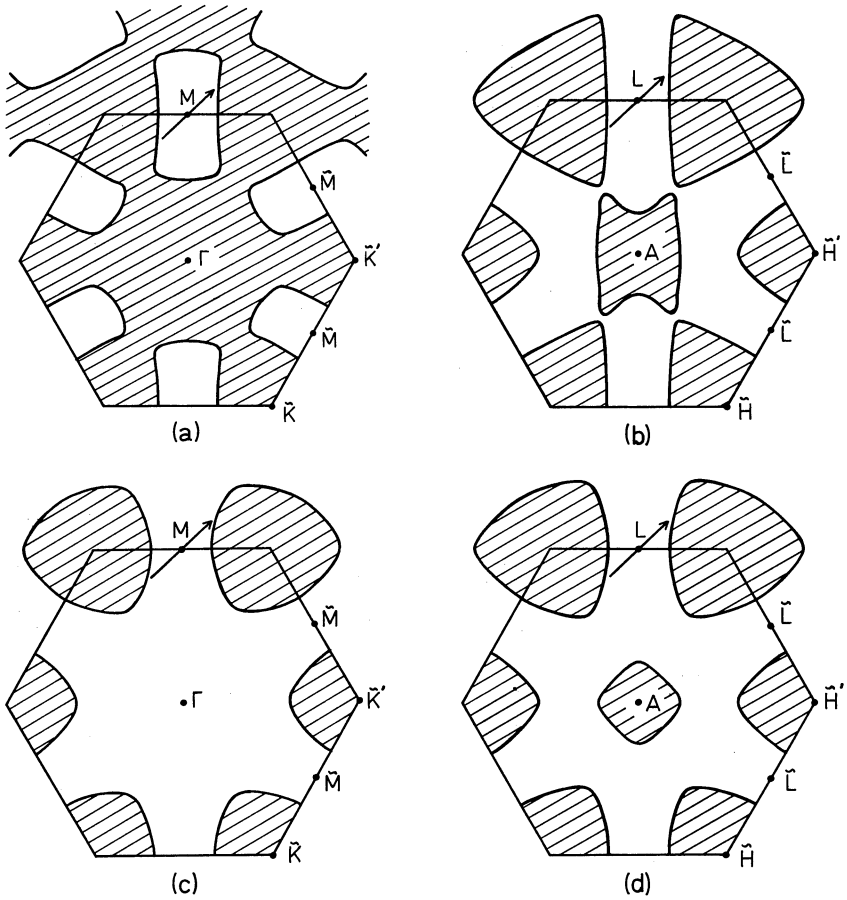

Fig. 6. The horizontal cross sections of the Fermi surfaces of C_8K. (a) Lower conduction band, Γ-K-M section; (b) lower conduction band, A-H-L section; (c) upper conduction band, Γ-K-M section; (d) upper conduction band, A-H-L section. The shaded regions are filled with electrons. The arrow denotes a possible nesting wave vector.

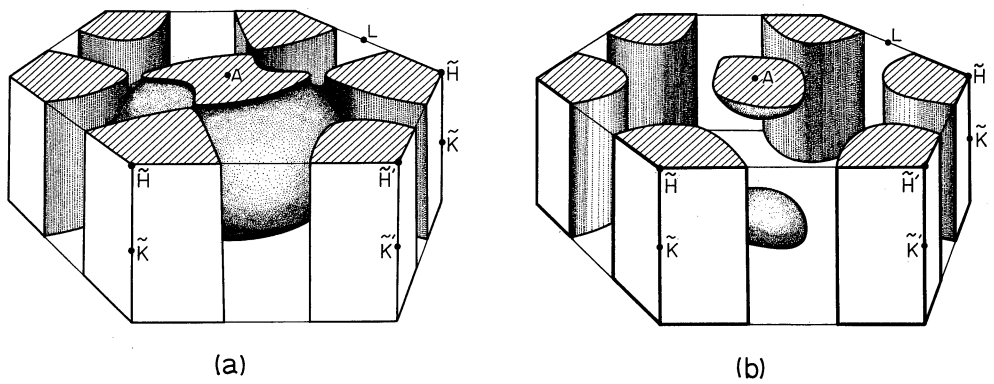

Fig. 7. The sketches of the Fermi surfaces for (a) lower conduction band and (b) upper conduction band.

C_8K and obtained an experimental value of $D(E_F)$. If we regard the ratio of the experimental $D(E_F)$ to the theoretical $D(E_F)$ as $1+\lambda$, where λ is the electron-phonon coupling constant, then we obtain $\lambda=0.21$. According to the McMillan formula[14] for strong-coupling superconductors, the Coulomb repulsion strength μ^* is related to T_c, λ, and the Debye temperature

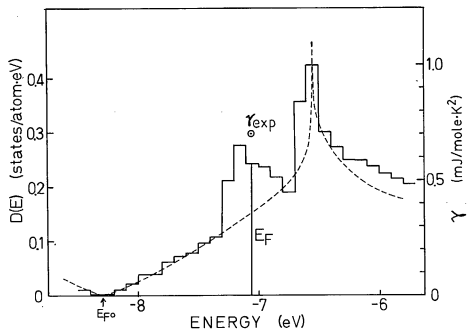

Fig. 8. The calculated density of states histogram for C_8K and the density of states based on the rigid band model of 2D graphite (broken curve). The experimental electronic specific heat γ (ref. 10) is indicated by the circle.

θ_D as follows:

$$\mu^*=\frac{1}{1+0.62\lambda}\cdot\left\{\lambda-\frac{1.04}{\ln(\theta_D/1.45T_c)}\cdot(1+\lambda)\right\}. \quad (6)$$

If we substitute $\theta_D=234.8$ K,[10] $T_c=0.55$ K[3] and $\lambda=0.21$ in eq. (6), then $\mu^*=-0.01$. We speculate that this unreasonable value of μ^* results from the following: (1) The phonon spectra of C_8K are quite different from those of Nb on which eq. (6) is based. Especially C_8K must have low frequency optical modes due to the intra-layer vibrations of potassium, which are totally absent in ordinally metals. Equation (6) should be modified, more or less, if we are to apply it to C_8K; (2) If CDW is really induced in C_8K, considerable portions of the graphite-like, 2D regions of the electronic spectra have gaps around E_F and do not contribute to superconductivity. Then, the effective carriers are chiefly on the potassium-like Fermi surfaces and their density is small compared with ordinary metals, and, therefore, μ^* is small. It may be that the low-frequency phonon modes of C_8K compensate for the smallness of the effective carrier density. Whether this is really the case or not is left for future investigations.

The results derived here suggest that there are a wide variety of intercalation compounds in which 2D as well as 3D carriers coexist. We believe that it is fruitful to study intercalation compounds from this viewpoint.

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Numerical computations were performed with the aid of HITAC 8800/8700 in the Computer Center of the University of Tokyo.

Appendix: Derivation of the Rigid Band Dispersion

For a better understanding of our results, let us compare the energy dispersion obtained in §4 with the rigid band dispersion derived from the familiar band structure of graphite.

Let us neglect the layer-layer interactions and consider the hypothetical '2-dimensional' C_8K crystal, i.e. a crystal which consists of a single carbon layer and a single potassium layer. Here the only role played by the potassium atoms is to make the diameter of the unit cell twice as large as the diameter of the graphite unit cell (Fig. 9). Thus the Brillouin zone for C_8K, in turn, is half as large in diameter as the graphite zone. (Here we denote the symmetry points of the C_8K zone as M, K and the corresponding points in the case of graphite as M^0, K^0.) The rigid band dispersion is obtained by folding the 2-D graphite bands (Fig. 10) back into this smaller Brillouin zone of C_8K.

The band-folding is performed along the same line as Harrison's argument of constructing reduced-zone Fermi surfaces.[15] First we divide the graphite zone into four regions which are denoted as A, B, C, D in Fig. 11. Since region A coincides with the C_8K zone, the dispersion along K-Γ-M in Fig. 10 remains

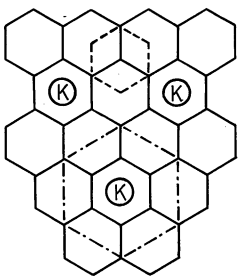

Fig. 9. The unit cells for 2D graphite (broken lines) and 2D C_8K (dashed lines).

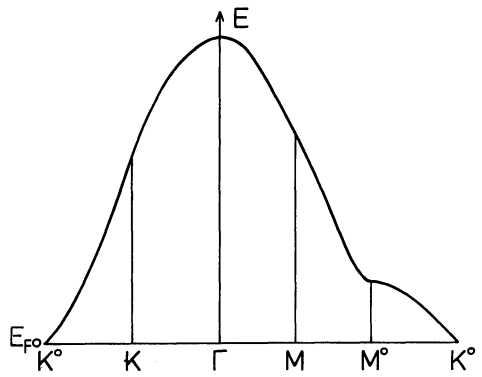

Fig. 10. The energy dispersion of the upper π band of 2D graphite.

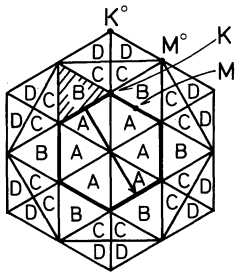

Fig. 11. The Brillouin zone for 2D graphite divided into four regions indicated as A, B, C and D. Region A is the Brillouin zone of 2D C_8K. The zone-folding is performed by transferring each triangle outside region A into region A by a proper reciprocal lattice vector of 2D C_8K. As an example, the translation vector for the shaded triangle is shown.

unchanged. Next we reduce the six regular triangles in region B into the C_8K zone. This is done by translating each triangle by a proper reciprocal lattice vector. We illustrate this procedure in Fig. 11. By doing this, $\overline{M^0K}$ is transferred to $\overline{\Gamma K}$, $\overline{M^0M}$ to $\overline{\Gamma M}$, thus producing a new band indicated by B in Fig. 12. Similarly the twelve right-angled triangles in region C(D) are reduced to form another band indicated by C(D) in Fig. 12.

The final result shown in Fig. 12 tells us that this band-folding brings about degeneracy. And when we double the height of the C_8K unit cell, so that it contains two carbon and two potassium layers respectively, as we did in the text, then this degeneracy is again doubled. Now we can understand the origin of the pseudo-degeneracies we saw in Fig. 3. (The inclusion of the carbon layer-layer and carbon-potassium interactions have lifted these

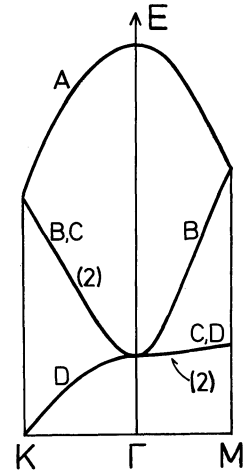

Fig. 12. The energy dispersion of the upper π band of 2D graphite after being folded back. A, B, C and D denote the regions in which the dispersion was initially located. The numbers in parentheses represent the degree of degeneracy.

degeneracies, however slight.)

We note that the qualitative features of the band structure derived in §4 are reproduced by simply superimposing free electron bands of potassium on the rigid band dispersion derived above.

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