Fermi surface of the stage-1 potassium graphite intercalation compound

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(Received 31 May 1991)

de Haas–van Alphen (dHvA) experiments with angular-dependence measurements for the stage-1 potassium graphite intercalation compound C_8K have been done. Two dHvA frequencies, 3126 and 4250 T, were measured with the magnetic field parallel to the c axis. The angular dependence of the dHvA frequencies for directions within $\pm 18°$ of the c axis showed that there are both three-dimensional and two-dimensional parts of the Fermi surface in C_8K. When the c axis is parallel to the magnetic field, the three-dimensional Fermi surface has a cross-sectional area corresponding to the dHvA frequency of 3126 T and the two-dimensional cylinder gives rise to the frequency of 4250 T. The charge transfer per potassium atom measured directly from the dHvA effect is 0.97. This implies that the potassium is ionized completely. In addition, the corresponding effective masses $0.86m_0$ and $0.92m_0$ were obtained for C_8K from the temperature dependence of the dHvA amplitude.

I. INTRODUCTION

The stage-1 graphite intercalation compound (GIC) C_8K is considered to be a prototype for the understanding of the electronic properties of the large family of GIC synthetic metals. However, the electronic structure of this stage-1 compound has been controversial both theoretically and experimentally for more than a decade.

A band-structure for C_8K was calculated and proposed by Inoshita, Nakao, and Kamimura[1] in 1977, followed by the first principles, self-consistent calculation of Ohno, Nakao, and Kamimura (ONK).[2] In the ONK model, the potassium s band in C_8K is partially filled and the charge transfer from the potassium atoms to the graphite layers is incomplete with a charge transfer per potassium atom (f) of 0.6. The potassium 4s band (lower conduction band) crosses the Fermi level, forming a nearly spherical, three-dimensional (3D) Fermi surface in the center of the Brillouin zone (BZ). It coexists with a two-dimensional (2D) cylindrical Fermi surface (FS) at the corners of the zone. A higher conduction band from the potassium 4s band only crosses the Fermi level when the wave vector k is close to $k_z/2$ along the z direction, forming a small 3D Fermi surface at the top center of the BZ. Many experiments[3–12] have been reported to test the model. Some of them[3–9,12] have supported the band structure. Moreover, the experimental results of angle-resolved ultraviolet photoelectron spectroscopy by Takahashi *et al.*[13,14] give a value of $f=0.6$ for the charge transfer in C_8K, which is the same as that predicted by the ONK model.

However, in 1982, DiVincenzo and Rabii[15] (DR) found, using a non-self-consistent, Korringa-Kohn-Rostoker (KKR) method, that the K 4s-band minimum in C_8K is located 1.8 eV above the Fermi level, the charge transfer is complete ($f=1$), and the 3D FS does not exist. Then, using results of both high-energy electron transmission and x-ray photoelectron spectroscopy experiments, Ritsko and Bruckner[10] supported the band structure of DR.

In 1984, a calculation using the density-functional approximation for the band structure of C_8K was presented by Tatar and Rabii (TR).[16] Their calculations were made self-consistent by using the norm-conserving pseudopotentials. This model showed complete charge transfer from the alkali atoms and the s levels 1.5 and 3.4 eV well above the Fermi level. The FS consisted of large 2D trigonal prisms centered along the corners of the BZ and a small 3D elongated pocket at the center of the zone which was related to the graphite π band and not to the alkali metal. This TR model agrees with ONK's model with respect to the existence of a 3D FS in the center of the BZ, but the character of the 3D FS is very different; it has potassium character in the ONK model and graphite character in the TR model. Preil and Fischer[11] measured the x-ray photoelectron spectra of the valence bands of C_8K and found that the K 4s character at the Fermi level is very low [less than 0.04 electron/K atom (Ref. 17)]. This experimental result strongly favors that the FS of C_8K has a graphite character and therefore supports both the TR and DR models.

In 1986, Koma *et al.*[12] and Kamimura[18] gave an interpretation of the K 4s–like band in the ONK model by calculating the charge density distribution of the lowest occupied K 4s–like conduction-band states at $k=0$. They found the charge density is very different from the K 4s charge density and has the features of an interlayer state.[19] Therefore they explained that the lowest occupied K-like conduction band is a kind of interlayer state with graphite character at the center of the BZ (instead of a K 4s–like band), and the K 4s band is shifted to an energy that is higher than the interlayer band by more than 7 eV at $k=0$.[12] According to this interpretation, the alkali atom also yields a unit charge transfer, and the 3D FS at the BZ center should be related mainly to the interlayer band. Now, both the revised ONK (RONK) and the TR models agree on the full ionization of the alkali atoms and on the graphite origin of the central Fermi pocket.[20] However, the character of the central 3D FS is

still different in the two models in the sense that it is from an interlayer band extending along the K layers in the RONK model and it has carbon character extending along the graphite layer in the TR model.[12]

In 1987, Mizuno, Hiramoto, and Nakao[21] (MHN) performed another type of band-structure calculation for C_8K by using the self-consistent numerical basis set linear combination of atomic orbitals (LCAO) method within the local-density-functional scheme. They found that there exists a 3D FS (convex cylinder) in the center of the BZ which originates from the graphite bands and that this is due to the charge unbalance between environmentally nonequivalent carbon atoms in a graphite layer produced by the potassium atoms. From the final atomic configuration obtained by the self-consistent calculation, the amount of the charge transfer from a K atom to eight C atoms is 0.6 per K atom.[14] However, the K4*s* bands located at 2.9 eV above the Fermi level in the MHV model should result in a unit charge transfer. The experimental results from the angle-resolved ultraviolet photoelectron spectroscopy by Takahashi *et al.*[13] support the MHN band structure except that nondispersive conduction bands were observed instead of the 3D conduction band around the center of the BZ.

In summarizing all the band-structure calculations mentioned above, three questions arise from their discrepancies. Firstly, is there a 3D FS in the center of the BZ for C_8K? Secondly, is the charge transfer per K atom complete or incomplete? Thirdly, what is the character of the 3D FS, i.e., is it from a K 4*s*-like band, a graphite π band, or an interlayer band? In order to clearly resolve these questions and clarify these models, more definitive experiments are needed although many previous experiments[17] have been interpreted to support one or another of these models.

A very definitive experiment for providing unambiguous answers to the first two questions uses the de Haas–van Alphen (dHvA) effect. The frequency of the dHvA oscillations directly measures the FS cross section, the angular dependence of the dHvA frequency gives insight into the actual shape (3D or 2D) of the FS, and the dHvA frequencies are related to the charge transfer. In addition, the temperature dependence of the dHvA amplitude directly determines the electron effective mass which is related to the energy bands. However, dHvA experiments in C_8K are very difficult because of the high effective mass of the electrons,[22] imperfections in the samples,[5] and other effects. In 1980, Higuchi, Suematsu, and Tanuma[5] reported a single dHvA frequency, 2870 T, in C_8K for $\mathbf{H}\|c$ and in 1988 Wang, Ummat, and Datars[22] observed a strong dHvA frequency, 3070 T, in C_8K for $\mathbf{H}\|c$. The reason for the discrepancy between the two reported frequencies was not clear since they were probably from the small piece of Fermi surface. Also, the angular dependence of the dHvA frequencies is needed to determine whether the frequency is from a 2D FS or a 3D FS.

This paper presents the results of the investigation by the dHvA effect of the FS, charge transfer in C_8K, and angular dependence. The details of the sample preparation, x-ray characterization, and dHvA method are given in Sec. II and the experimental results are presented and analyzed in Sec. III. In Sec. IV, the experimental data are compared with the theoretical models and the charge transfer is derived. Finally, in Sec. V, the results are summarized and the conclusions are presented.

II. EXPERIMENT

All C_8K samples were prepared from highly oriented pyrolitic graphite (HOPG). The slabs of the HOPG were cut into pieces with a cross section of about 2.5×3.5 mm^2 and a thickness of about 0.7 mm. Thicker samples were not suitable because the dHvA effect could not be observed with them after they were intercalated. The outer layers were moved by peeling and then the pieces were washed in acetone in an ultrasonic cleaner. The cleaned HOPG was put into a Pyrex tube and dried under vacuum at an elevated temperature. After a few hours, it was transferred into a dry box filled with dry nitrogen where metal potassium was added into the tube.

C_8K samples were prepared by the vapor reaction[23] of the potassium in the vacuum sealed Pyrex tube. The potassium metal at one end of the tube was heated to about 263 °C and the HOPG at the other end was held at a temperature of about 297 °C. The period of the reaction was about eight days. Because of the instability of the alkali metal samples in the presence of air and moisture, after the reaction, the Pyrex tube with samples was broken in a dry box and samples were sealed in a brass-based sample holder for x-ray diffraction measurements and in a low-temperature sample holder for dHvA measurements.

Stage-1 C_8K is golden yellow in color. In order to make sure our golden-yellow samples were pure stage-1 from the surface through to the middle, x-ray examinations were carried out. By using a powder diffractometer and Cu $K\alpha$ radiation, the *c*-axis repeat distance I_c of the C_8K compound was measured to be $I_c=5.348$ Å. This value is the same as 5.35 Å reported by Nixon and Parry,[24,25] and consistent with 5.41 Å found by Rudoff and Schulze[26] for stage-1 C_8K.

The sensitivity of the dHvA detecting system is another key part for measuring high dHvA frequencies. A set of special detecting coils with high sensitivity was made to pick up the weak dHvA signal in C_8K. The sample was put inside the coils. The set of coils was placed inside a 5.5-T superconducting solenoid. The samples were cooled down slowly from room temperature to 77 K in about four days and dHvA experiments were performed between 1.3 and 4.2 K.

For measuring the angular dependence, a toothed wheel was glued to the end of the sample holder to allow the rotation of the sample with a small screw at the end of a rod that extended to the top of the Dewar. By rotating the sample holder, the angle between the magnetic-field direction and the *c*-axis of the sample was changed. Each quarter turn of rotation of the rod changed the sample position by 3°.

III. RESULTS AND ANALYSIS

The dHvA signal was detected at temperatures below 2.4 K and magnetic fields above 3.2 T. Figure 1 shows a

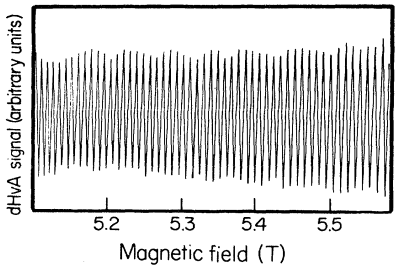

FIG. 1. de Haas–van Alphen oscillations of the stage-1 potassium graphite intercalated compound.

typical trace of the dHvA oscillations in C_8K. It was obtained at $T=2.2$ K in the magnetic-field range 5.1–5.6 T with the c axis of the sample parallel to the direction of the magnetic field ($\mathbf{H}\|c$).

Figure 2 shows the Fourier transform spectrum of data taken from 4.9 to 5.1 T at $T=1.4$ K with $\mathbf{H}\|c$. One can see that there are two frequencies in this spectrum. The stronger one is 3126 T and the second one is 4250 T. The two frequencies are reproducible from sample to sample. Totally, five C_8K samples were measured. The value of the first frequency is between 3070 and 3126 T, depending on the range of the magnetic field chosen to take the data. The second frequency only appears at temperatures below 1.7 K.

The cyclotron masses corresponding to the two frequencies were determined from the temperature dependence of the dHvA amplitudes between 1.3 and 2.2 K with $\mathbf{H}\|c$. Figure 3 shows a plot of $\ln(A/T)$ versus T. The effective masses were determined from the proportionality of the amplitude A:

$$A \propto T/\sinh(bm_cT/Bm_0)\ , \tag{1}$$

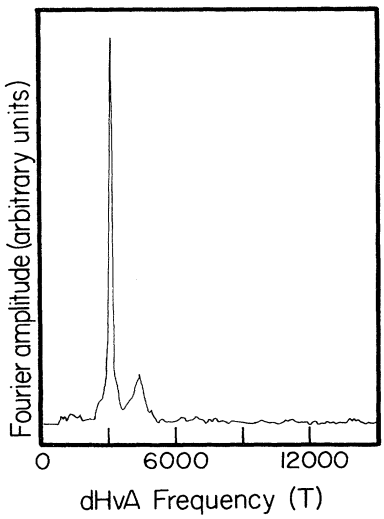

FIG. 2. Fourier transform of the dHvA signal of stage-1 potassium graphite.

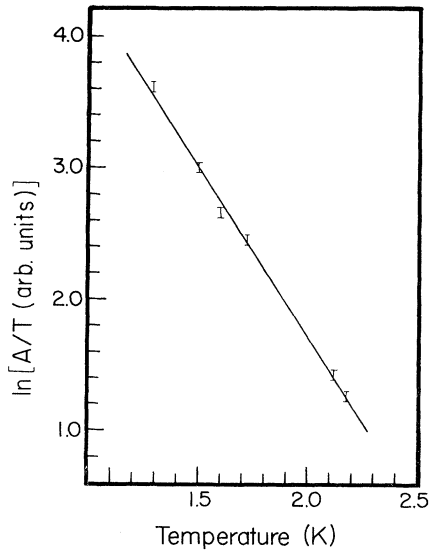

FIG. 3. Temperature dependence of A/T, where A is the amplitude of the 3126-T oscillation. The data are fitted to $A \propto T/\sinh(bm_cT/Bm_0)$ (solid line).

where A is the dHvA amplitude at temperature T and magnetic field B, m_c and m_0 are the cyclotron mass and free-electron mass, respectively, and $b=14.69$ TK^{-1}. The results are $m_1=0.86m_0$ and $m_2=0.92m_0$.

In order to investigate the actual shape of the FS for this compound, the angular dependence of the dHvA frequency was measured from $\theta=0°$ to $-21°$ for one side and $\theta=0°$ to 90° for the other side of the c axis. Here θ is the angle between the direction of the magnetic field and the c axis of the sample. The data were measured at 3° intervals. Figure 4 shows the experimental results and the theoretical predictions for the first frequency as a function of the angle θ. The solid curve represents the prediction for a 2D straight cylinder of the FS given by

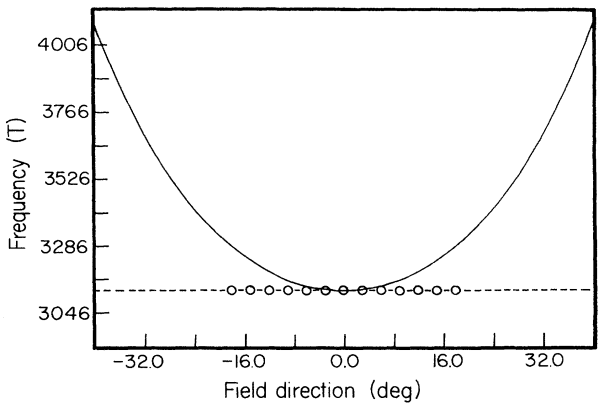

FIG. 4. The first dHvA frequency as a function of magnetic-field direction from the c axis of stage-1 K graphite. The solid line is a cylindrical fit and the dashed line is a spherical fit.

$f_\theta = f_0/\cos\theta$ where f is the dHvA frequency. The dashed line parallel to the axis for the field direction represents the prediction for a 3D spherical FS given by $f_\theta = f_0$. The circles are the experimental data. One can see, from Fig. 4, that the first dHvA frequency follows a 3D spherical behavior very well for angles up to 18° for both sides of the c axis. Therefore, the existence of the 3D FS in C_8K is proven experimentally.

The amplitudes of the dHvA frequency decreased dramatically with increasing θ, as shown in Fig. 5, and the dHvA signal disappeared after $\theta = 21°$. This limited the angular-dependence measurements of the frequency to the region $\theta < 21°$.

The decrease of the dHvA amplitude with angle occurs in many other GIC's but with different rates and different maximum angles at which the dHvA signal disappears. The maximum angle is stage dependent: it increases with stage index. For instance, it is greater than 70° for pure graphite,[5] 57° and 61° for stage-3 SbF_5 (Ref. 27) and $SbCl_5$ (Ref. 28), respectively, 30° for stage-2 $BiCl_3$,[29] and only 21° for stage-1 C_8K. Therefore it is reasonable to expect that, in addition to the increasing of the cross-section area with angle, the electron-intercalant scattering also limits the electron orbits with increasing θ, especially for the 3D FS in C_8K which has no change in cross-sectional area with angle.

The second dHvA frequency, 4250 T, is considered to be from the major 2D FS in C_8K because a 2D behavior is expected for one Fermi surface piece as in other GIC's. This frequency is very weak even at $\theta = 0°$ due to the high value of the cyclotron mass. It disappears when the angle is changed from $\theta = 0°$ to $\theta = 3°$.

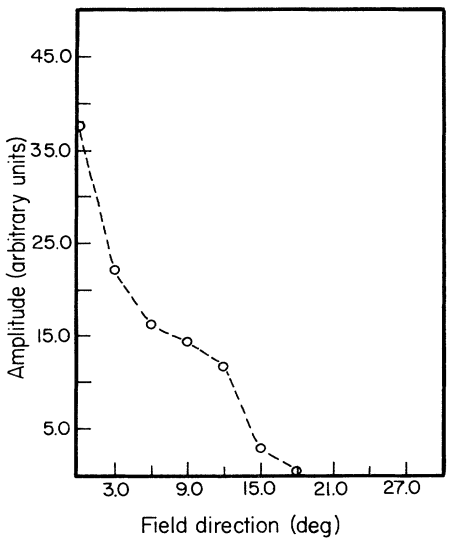

FIG. 5. The dHvA amplitude as a function of the angle between the magnetic field and c axis of the sample. The dashed line is drawn as a guide to the eye.

IV. DISCUSSION

A. The FS for C_8K

In principle, it seems that the experimental proof for the existence of both 3D and 2D FS pieces in C_8K supports all models which predict both a 3D and 2D FS for C_8K. However, different models have different discrepancies from the experimental results.

1. ONK and RONK models

The ONK and RONK models predict a rather spherical 3D FS centered at the center of the BZ for the lower band and at the top center of the BZ for the upper band, in addition to the triangular prismatic 2D FS sections which have nearly equal sizes in the upper and lower bands. The 3D FS and the 2D FS are separated by a small amount. This prediction for the FS in C_8K is in agreement with the experimental results qualitatively except for the following two aspects.

Firstly, two additional small extremal cross-section areas are predicted at the hexagonal BZ planes for the upper and lower bands. Therefore there should be four dHvA frequencies appearing in C_8K, according to the model. However, only two dHvA frequencies were observed. One may say that the two experimental frequencies could be from the two smaller areas and the two larger areas were missed due to the difficulties of the experiment. However, the answer is clear when the high values of the experimental frequencies and the fixed size of the BZ are considered. Moreover, the smaller areas should be observed more easily than the larger areas, but they did not show up. It seems that the two smaller FS areas in C_8K do not exist.

Secondly, in the theory, the calculated dHvA frequency from the 2D triangular FS is 3030 T.[5] Compared with the experimental value of 4250 T, the difference cannot be ignored.

Although differences between the experiment and the theory do exist, the main results are consistent. In fact, the band structure of the ONK model can be changed by adjusting parameters to fit the experimental data. Therefore the experiment actually gives qualitative support for the band calculations of the ONK and RONK model.

2. MHN model

MHN's model also predicts both 3D FS and 2D FS parts for C_8K with the energy bands similar to that of the ONK model. But the shape of the 3D FS from both the lower and upper conduction bands is a convex cylinder in the center of the BZ instead of a rather spherical FS as predicted by ONK or quite spherical FS as observed in the experiment. So, in this theory, not only the number of dHvA frequencies but also the shape of the 3D FS are contrary to the experimental results. However, the correct prediction for the existence of both the 3D FS and 2D FS indicates that this theory is partly supported by this experiment.

3. DR and TR models

In the DR model, the Fermi surface of C_8K contains only cylindrical parts with at most a very small isolated pocket at the center of the BZ. There is no 3D Fermi surface appearing in C_8K. The dHvA frequencies corresponding to the cross-section of the 2D cylindrical parts for both upper and lower bands are 4700 and 3700 T, respectively. These calculated values are close to the 2D dHvA frequency, 4250 T, observed from the experiment. Therefore, although this theory failed to predict the existence of the 3D FS, the calculation for the 2D FS is in good agreement with the experimental results.

In the TR model, there also exist both 3D and 2D FS pieces. However, the cross section of the 3D FS is smaller than that of the 2D FS, and, in particular, shrinks to zero at the top face of the BZ. According to this model, there should be just two dHvA frequencies in C_8K, and the frequency from the 3D FS should be smaller than the one from the 2D FS. This prediction is in agreement with the experimental results and is supported by the experiment.

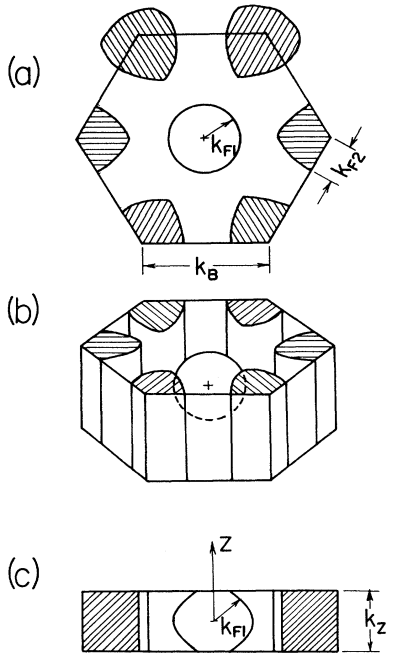

FIG. 6. (a) The horizontal cross section of the Fermi surfaces of C_8K at $k_z=0$. (b) A sketch of the Fermi surfaces of C_8K for $I_c=5.35$ Å. (c) The perpendicular cross section of the Fermi surfaces of C_8K for $I_c'=10.7$ Å.

B. Charge transfer in C_8K

The charge transfer is obtained from the dHvA data in the following way. The number of carriers per unit cell is equal to $2V_F/V_B$, where V_F is the total volume of reciprocal space enclosed by the FS and V_B is the volume of the BZ. The factor of 2 comes from the spin degeneracy.

The total charge per carbon atom, x, is equal to the ratio of $2V_F/V_B$ divided by n, the number of carbon atoms in the unit cell of the compound, that is,

$$x=2V_F/(V_B n) . \tag{2}$$

The volume V_F is related directly to the external Fermi surface area A_F, which is perpendicular to the k_z direction and

$$A_F=(\hbar/2\pi e)F , \tag{3}$$

where F is the dHvA frequency. Thus the dHvA effect measures the charge transfer directly.

The crystal structure of C_8K has as $P(2\times2)R0^0$ in-plane superlattice.[26] The planar unit cell for the C_8K compound is four times larger in area than the graphite unit cell, so that the corresponding planar unit cell for the compound in reciprocal space is one-fourth as large as that for graphite, and the length of the BZ edge is one-half of that in graphite, i.e., $k_B=0.85$ Å^{-1}, as shown in Fig. 6(a).

According to Eq. (3) and the observed dHvA frequencies $F_1=3126$ T and $F_2=4250$ T, the Fermi radii with the approximation of a circular cross section are $k_{F1}=0.31$ Å^{-1} and $k_{F2}==0.36$ Å^{-1}. One can see from Fig. 6(a) that in the k_x-k_y plane at $k_z=0$, $2k_{F2}$ is less than k_B along the line from corner to corner, and $k_{F1}+k_{F2}$ is less than k_B along the line from the corner to the center of the BZ. Thus the 3D FS is well separated from the 2D FS and the charge transfer can be calculated easily.

The volume of the BZ of the C_8K is given by

$$V_B=4\pi^2/(a^2 I_c\sqrt{3}) , \tag{4}$$

where $a=2.46$ Å is the length of the primitive lattice translation vector in graphite, and I_c is the c-axis component of the unit cell, or c-axis repeat distance for C_8K. Because the I_c can be chosen in different ways, the charge transfer should be calculated for each case.

For the unit cell which contains one potassium atom and eight carbon atoms, as chosen by TR, I_c is equal to 5.35 Å. It is the distance between the adjacent carbon layers.

Therefore $k_z=2\pi/I_c$ is 1.1744 Å^{-1}. The 3D FS is totally inside the BZ, because $2k_{F1}=0.62$ Å^{-1} is less than k_z. When the approximation of a perfect spherical 3D FS as shown in Fig. 6(b) is applied, the total volume enclosed by the FS is

$$V_F=4\pi k_{F1}^3/3+4(A_{F2}\pi/I_c) . \tag{5}$$

Combining Eqs. (2)–(5), the charge per carbon atom in the unit cell with eight carbon atoms is 0.122. Thus the charge per potassium atom is 0.97.

For a unit cell which contains two potassium atoms and 16 carbon atoms, as chosen by ONK, the I_c' is twice the distance between the adjacent carbon layers, that is, 10.70 Å. In this case, $2k_{F1}$ is larger than

$k_z'=0.5872$ Å^{-1}. So, the top and bottom of the 3D FS are cut by the BZ planes, as shown in Fig. 6(c). Therefore the volume of the 3D FS is

$$V_{F1}=2\int_0^{k_{z/2}'}\pi(k_{F1}^2-Z^2)dZ \tag{6}$$

and the volume of the 2D FS is

$$V_{F2}=2(A_{F2}4\pi/I_c') . \tag{7}$$

The factor of 2 comes from the fact that the energy band of the 2D FS is doubly degenerated for this unit cell.[1]

For the total volume $V_F=V_{F1}+V_{F2}$, the charge per carbon atom with this unit cell is 0.121 and the charge per potassium atom is 0.97.

Comparing the values of the charge transfer from the two kinds of unit cells, one can see that there is no difference between them and the charge transfer is almost unity. This result for the charge transfer is consistent with many other experiments. The recent measurement for the near-edge photoabsorption spectra by Loupias *et al.*[30] gives the charge transfer to be 0.85. From the same experiments done in 1988, Loupias, Chomilier, and Tarbes[31] conclude that the charge transfer in C_8K is nearly total. Other experiments, electron-energy-loss spectra,[10] x-ray photoelectron spectroscopy,[11] and soft-x-ray emission spectroscopy (SXES) carbon K emission band measurements[32] also imply[33] a complete charge transfer for C_8K.

The nearly complete charge transfer in C_8K means that this is the full ionization of the potassium atoms and an almost empty potassium band exists. Therefore the theory which has the 3D FS from the K 4*s* band is not acceptable by the present experiment. The models which predict incomplete charge transfer are also not consistent with the experimental results. Both the revised ONK and TR descriptions agree with the unit charge transfer and on the graphite origin of the 3D FS. They are supported by the dHvA experimental work. But, the difference between the two models, that is, whether the character of the 3D FS is the interlayer bands or graphite π band, cannot be clarified by the dHvA effect.

V. CONCLUSIONS

The dHvA experiments for C_8K show two dHvA frequencies, 3126 and 4250 T, with the magnetic field parallel to the *c* axis. The effective masses corresponding to the two frequencies obtained from the temperature dependence of the dHvA amplitude are $0.86m_0$ and $0.92m_0$, respectively. The angular dependence of the dHvA frequency shows that there exist both 3D FS and 2D FS sections in C_8K. The 3D FS, which has the cross-sectional area corresponding to 3126 T, is spherical for the field within $\pm 18°$ of the *c* axis. The Fermi structures constructed from the experimental data are reasonable with respect to the size of the BZ. The charge transfer per potassium atom is measured directly by the dHvA frequencies. It is 0.97 for the different unit cells chosen by the different models. This value of the charge transfer is consistent with many other experimental results. The almost complete charge transfer implies that the K 4*s* band is almost empty and the 3D FS does not arise from the K 4*s* band. By comparing the experimental results with the predictions of each theoretical model, the TR model is completely supported by the experiment. The revised ONK model is basically supported and could be supported strongly by the dHvA experiment if the size of the 3D FS could be adjusted to fit the experimental data.

ACKNOWLEDGMENTS

We wish to thank Dr. A. W. Moore for the HOPG graphite and T. Olech for technical assistance. The research was supported by the Natural Sciences and Engineering Research Council of Canada.

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