Band structure and charge transfer of the stage-2 potassium graphite intercalation compound

G. Wang, W. R. Datars, and P. K. Ummat
Department of Physics and Astronomy, McMaster University, Hamilton, Ontario, Canada L8S 4M1
(Received 19 July 1991)

The de Haas–van Alphen (dHvA) effect of the stage-2 potassium graphite intercalation compound ($C_{24}K$) has been measured. Two dominant dHvA frequencies, 286 T and 2570 T, were observed. These frequencies were analyzed in terms of the two-dimensional rigid-band model of Blinowski *et al.* The charge transfer derived from the band model, $f_k = 0.87$, is in good agreement with the experimental result.

I. INTRODUCTION

Graphite intercalation compounds (GIC's) are classified into donor and acceptor types, depending on whether the graphite layers in the GIC acquire positive or negative charge. The electronic properties and Fermi surface parameters of both donor and acceptor graphite intercalation compounds can be determined by experimental techniques that involve the oscillatory Shubnikov–de Haas (SdH) effect of the magnetoconductivity and the de Haas–van Alphen (dHvA) effect of the magnetic susceptibility. In these experiments, donor GIC's cause many more experimental difficulties than acceptor GIC's because they usually have larger Fermi surface (FS) pieces, heavier cyclotron masses, and sample instability.

The stage-2 potassium compound ($C_{24}K$) is a donor GIC. The first SdH measurement of $C_{24}K$ was done by Dresselhaus *et al.*[1] There was a dominant SdH oscillation with a frequency of approximately 150 T and several other oscillations with frequencies up to 450 T. No higher frequencies were reported and their theoretical model for the electronic structure of GIC was not fit to the data.

Since the charge transfer in $C_{24}K$ has been estimated to be nearly complete from experiments of the specific heat[2,3] and Knight shift of the ^{13}C nuclear-magnetic-resonance (NMR) line,[3,4] one expects that larger pieces of the FS should exist in $C_{24}K$. The absence of a high-frequency orbit in the SdH measurements may be due to the experimental difficulties with the donor GIC's and to the fact that low-frequency orbits are detected more easily in the SdH effect. The purpose of this work was to measure all the dHvA frequencies of the stage-2 compound with a set of sensitive detecting coils and well-staged $C_{24}K$ samples.

The theoretical band model proposed by Blinowski *et al.*[5] (BR) is used to analyze the dHvA experimental data. This model keeps the lowest-order terms in the K-point expansion of the energy bands and leads to a circular Fermi surface cross section at each of the six corners of the two-dimensional (2D) hexagonal Brillouin zone. Although this model was proposed originally for acceptor GIC's, it describes the conduction bands also. In fact, it has been used to explain successfully the reflectance data in $C_{24}K$ below the threshold for interband absorption involving the K ($4s$) states, although it is not suitable for stage-1 C_8K. The charge transfer to the carbon band is about one electron per K atom.[6–8] It also explains the optical density for $C_{24}K$ reasonably well below the inter-π-band absorption threshold.[8] Therefore, this model is expected to provide a good description of the band structure of $C_{24}K$.

Another theoretical calculation for the band structure of $C_{24}K$ by Yang and Eklund[9] (YE) is based on the phenomenological, two-dimensional, tight-binding model of Saito and Kamimura.[10] The calculated dHvA frequencies from this band structure are 1399 and 1820 T. These theoretical values will be compared with the experimental results in this paper.

II. EXPERIMENT

The samples of the stage-2 potassium-graphite intercalation compound were prepared by the vapor reaction of potassium in Pyrex glass ampoules by the conventional two-zone method.[11] It is very difficult to make a pure stage-2 K GIC because the amount of potassium absorbed into graphite has to be controlled carefully. Otherwise, a mixture of stage 2 with stage 1 occurs.

Highly oriented pyrolytic graphite (HOPG) and potassium metal are used as initial reagents. The slabs of HOPG were cut into pieces with a cross section of about 2.5×3.5 mm^2 and a thickness of about 0.5–0.7 mm. The HOPG and potassium were loaded into the Pyrex tube in a dry box and then the tube was vacuum sealed after being taken from the dry box. The potassium metal at one end of the Pyrex tube was heated at a temperature of about 245 °C and the HOPG at the other end was about 335 °C, which is higher than the potassium in the reaction ampoule to avoid condensation of the potassium on to the sample surface. The period of the reaction was between 4 h and 1 d, depending on the size of the HOPG, the size of the ampoules, the amount of potassium metal, and the distance between the HOPG and potassium.

The color of stage-2 K GIC, which is a rich bluish

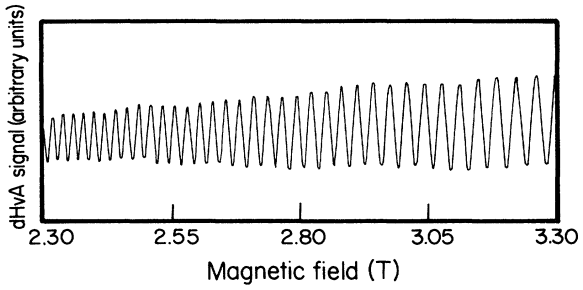

FIG. 1. de Haas–van Alphen oscillations of stage-2 K-GIC at 4.2 K.

green, disappears when the sample is exposed to air for just a few seconds. This is due to the instability of the alkali-metal samples in the presence of air and moisture. Therefore, after the reaction was completed, the tube was transferred into a dry box and the samples were sealed in sample holders for both the x-ray examination and the dHvA experiment.

The sample stage number was determined by (001) x-ray diffraction with Cu-Kα radiation. The c-axis identity period for our stage-2 K GIC was $I_c = 8.67$ Å. This value is consistent with 8.73 Å obtained by Nixon and Parry[11] and 8.77 Å obtained by Rudorff and Schulze.[12] Therefore, well-staged, stage-2 K-GIC samples were obtained for the dHvA experiments.

The dHvA effect was observed with the low-frequency, field-modulation technique in magnetic fields up to 5.5 T. The sample was cooled down slowly from room temperature to 77 K in about 4 d and oriented for measurement with the c axis parallel to the direction of the magnetic field. Data were taken as a function of magnetic field with the sample temperature in the range of 1.3 to 4.2 K.

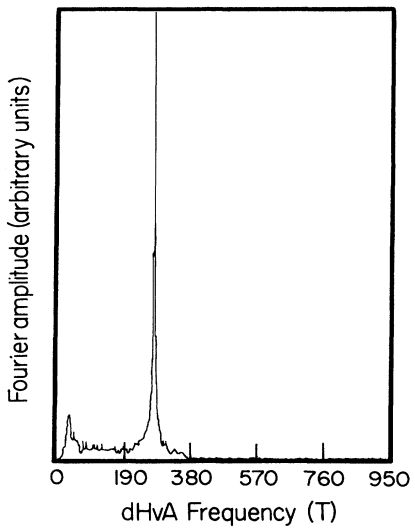

FIG. 2. Fourier transform of the de Haas–van Alphen oscillations in $C_{24}K$ from 1.55 to 3.25 T at 4.2 K.

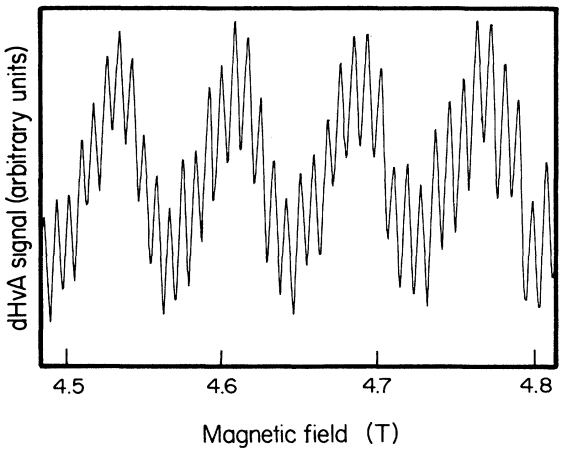

FIG. 3. de Haas–van Alphen oscillations of stage-2 K-GIC at 1.4 K.

III. RESULTS

The dHvA signal in stage-2 $C_{24}K$ obtained at a temperature of 4.2 K is shown in Fig. 1. The Fourier transform of the oscillation from 1.55 to 3.25 T gives only one dHvA frequency, 286 T, as shown in Fig. 2. This frequency is the same as one of the SdH frequencies, 282 T, observed by Dresselhaus *et al.*[1]

When the temperature was decreased to 1.4 K, the dHvA signal became much stronger and different. Figure 3 is the part of the dHvA oscillation obtained at 1.4 K from 4.50 to 5.41 T. This oscillation shows that there is more than one dHvA frequency. From the Fourier transform, as shown in Fig. 4, one can see two dominant dHvA frequencies in the spectrum; one is the low-frequency 286 T, another one is 2570 T. These measurements were repeated two weeks later and all results were reproducible. For different ranges of magnetic field

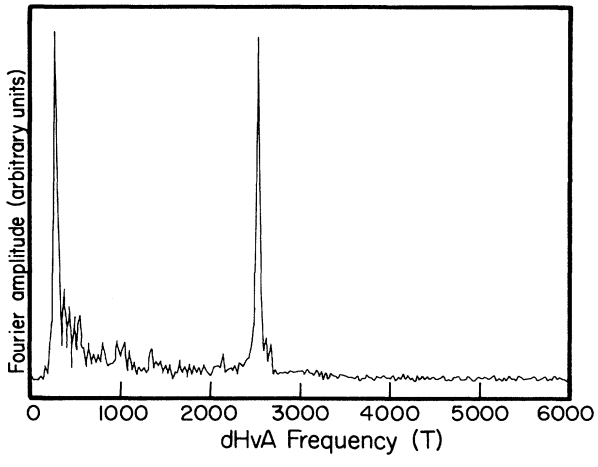

FIG. 4. Fourier transform of the de Haas–van Alphen oscillations in $C_{24}K$ from 4.5 to 5.41 T at 1.4 K.

chosen to take data, the low frequency was between 270 and 286 T and the high frequency was between 2540 and 2570 T.

IV. DISCUSSION

A. Band structures

The tight-binding model proposed by Blinowski *et al.*[5] (BR) assumes that the in-plane unit vectors of GIC are the same as in graphite and the *c*-axis unit vector is equal to the intercalate-intercalate spacing. This gives n valence-conduction pairs of bands for a stage-n compound. The electron dispersion (i.e., the band equation) is assumed to be independent of the intercalated species and the number of electrons transferred to or from the graphite. The band parameters in this model can be adjusted for different intercalated species, and the Fermi level depends on the number of electrons when the band parameters are fixed.

For the stage-2 donor GIC, the two conduction bands are given as

$$E=[(\gamma_1^2+3\gamma_0^2a^2k^2)^{1/2}\pm\gamma_1]/2 , \quad (1)$$

where k is the wave vector measured from the corner of the Brillouin zone, a is the length of the translation vector in graphite, γ_0 is the in-plane nearest-neighbor interaction, and γ_1 is the interaction energy of nearest atoms in the two layers. The Fermi areas of the bands are given by

$$A_{F1}=4\pi(E^2-E\gamma_1)(3\gamma_0^2a^2)^{-1} , \quad (2)$$

$$A_{F2}=4\pi(E^2+E\gamma_1)(3\gamma_0^2a^2)^{-1} . \quad (3)$$

The model is used in the following way. First, the band parameters γ_0 and γ_1 are assumed to be 2.4 and 0.38 eV, respectively, because these values were used for other stage-2 GIC's.[13,14] Then the value of the Fermi areas obtained from the equation

$$A_F=(2\pi e/\hbar)F \quad (4)$$

by

$$E_F=(3/8\pi)^{1/2}\gamma_0a(A_{F1}+A_{F2})^{1/2} . \quad (5)$$

The Fermi energy and the band parameters (γ_0,γ_1) are then used to calculate the Fermi areas and dHvA frequencies, which are compared with the experimental values. This procedure was repeated several times and the band parameters γ_0 and γ_1 were determined to be 1.12 and 0.39 eV, respectively, for the stage-2 $C_{24}K$. The Fermi energy was then calculated to be 0.5 eV. A comparison of the experimental data with the model is shown in Table I.

The value of γ_0, 1.12 eV, for stage-2 $C_{24}K$ is less than 2.4 eV, the value of γ_0 for the stage-2 $SbCl_5$ GIC.[13] This deviation is consistent with the model that predicts that the larger the Fermi surface the lower the value of γ_0.[5] In fact, the largest Fermi area is 0.1136 $Å^{-2}$ for the stage-2 $SbCl_5$-GIC,[13] and 0.2453 $Å^{-2}$ for stage-2 $C_{24}K$. Therefore, it is reasonable that $C_{24}K$ has a smaller value of γ_0 than the $SbCl_5$ GIC. In addition, one can see from Table I that the predicted area and frequency of the higher frequency are perfectly matched with the observations and the lower one is within 10%.

TABLE I. Comparison of experimental data with the BR model (Ref. 5) for $C_{24}K$.

Area ($Å^{-2}$)		Frequency (T)	
Expt.	Calc.	Expt.	Calc.
0.0273	0.0301	286	316
0.2453	0.2455	2570	2572

Figure 5 shows the energy bands for the stage-2 C_2K according to Eq. (1) with $\gamma_0=1.12$ eV and $\gamma_1=0.39$ eV. There are two valence bands and two conduction bands. The conduction bands are partially filled with electrons which are transferred to graphite from the donor intercalate species. The Fermi energy is positive with a value of 0.5 eV and is shown by the dashed line in Fig. 5.

We now compare the calculation for $C_{24}K$ by Yang and Eklund[9] (YE) with the dHvA experimental results. Their calculation for $C_{24}K$ is based on the two-dimensional, tight-binding model of Saito and Kamimura (SK),[10] but the parameters in the model of SK are adjusted by comparison with the calculated interband dielectric function with YE experimental optical data.[9] A simple k dependence of the nearest-neighbor carbon transfer integral parameter γ_0 is introduced in the model as well. The energy-band structure of YE also has two conduction and two valence bands for $C_{24}K$ and both conduction bands are partially filled with electrons.

The calculated Fermi areas and dHvA frequencies according to YE energy bands for $C_{24}K$ are compared with the dHvA experimental data in Table II. One can see that the theory predicts the right number of dHvA frequencies for $C_{24}K$ but the values of the frequency do not match the experimental data very well. One is higher and the other one is lower. However, this theory is in good agreement with YE optical data.[9] Therefore, the theory could be improved for $C_{24}K$ if the right parameters in the energy bands could be obtained to describe

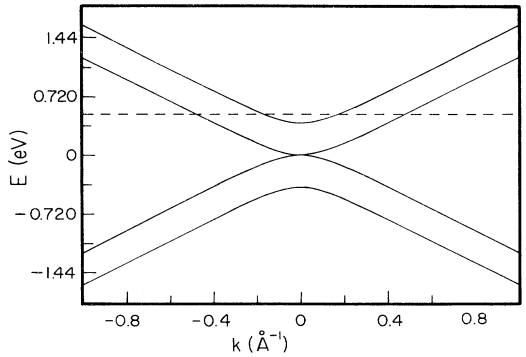

FIG. 5. The band structure of stage-2 K-GIC with the band parameters $\gamma_0=1.12$ eV and $\gamma_1=0.39$ eV. The dashed line is the Fermi level of 0.5 eV.

TABLE II. Comparison of experimental data with YE model (Ref. 9) for $C_{24}K$.

Area ($Å^{-2}$)		Frequency (T)	
Expt.	Calc.	Expt.	Calc.
0.0273	0.1335	286	1399
0.2453	0.1735	2570	1820

both the optical data and the dHvA data.

B. Charge transfer

The dHvA effect measures the charge transfer directly by the following relation for two-dimensional energy bands:

$$f_c=[(a^2\sqrt{3})/(4\pi^2 n)]\sum_i A_{Fi} , \quad (6)$$

where n is the stage number, a is the length of the primitive lattice translation vector, and A_{Fi} are the Fermi surface cross-sectional areas perpendicular to the k_z direction. The areas A_{Fi} are directly proportional to the dHvA frequencies.

For $C_{24}K$, n is equal to 2; the sum of the dHvA frequencies is 2856 T. The charge per carbon atom, f_c, is then 0.0362 according to Eq. (6). Thus, the charge f_k, transferred from each potassium atom to 24 carbon atoms, is found to be 0.87.

From Blinowski's model, the charge transfer for a stage-2 GIC can be calculated with the equation

$$f_c=(E_F/\gamma_0)^2/(\pi\sqrt{3}) . \quad (7)$$

It should be noted that the expression for f_c here is the one corrected by Zhang and Eklund,[8] since the one in Ref. 5 is in error (with an extra $\sqrt{2}$).

For $C_{24}K$, E_F and γ_0 are found to be 0.5 and 1.12 eV, respectively. Thus, f_c is 0.0367 according to Eq. (7) and f_k is 0.88. This value is in very good agreement with the experimental result.

Other experiments, the optical reflectance,[6,7] the optical transmission,[8] the Knight shift of the ^{13}C NMR,[4] and the specific heat,[2] all derived a complete intercalate ionization ($f_k=1$) for $C_{24}K$. The present work is consistent with these experiments and suggests that the potassium s band lies almost totally above the Fermi level in $C_{24}K$.

V. CONCLUSIONS

The dHvA measurement with the magnetic-field direction parallel to the c axis shows two dominant frequencies in $C_{24}K$. The predictions of Blinowski's theoretical model[5] for a stage-2 GIC are in agreement with the experimental data when the band parameters, γ_0 and γ_1, are chosen as 1.12 and 0.39 eV, respectively. The Fermi energy in $C_{24}K$, determined from the dHvA frequencies by using Blinowski's model, is 0.5 eV.

The theoretical calculation for the energy bands of $C_{24}K$ by Yang and Eklund[9] predicts two dHvA frequencies but the values of the frequencies do not agree with the dHvA data very well.

The charge transfer per potassium atom is determined from both the dHvA measurements and Blinowski's model. The value $f_k \sim 0.88$ suggests that the potassium s band is above the Fermi level in $C_{24}K$.

ACKNOWLEDGMENTS

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

[1]G. Dresselhaus, S. Y. Leung, M. Shayegan, and T. C. Chieu, Synth. Met. **2**, 321 (1980).
[2]U. Mizutani, T. Kondow, and T. B. Massalski, Phys. Rev. B **17**, 3165 (1978).
[3]M. S. Dresselhaus and G. Dresselhaus, Adv. Phys. **30**, 139 (1981).
[4]J. Conard, H. Estrade, P. Lauginie, H. Fuzellier, G. Furdin, and R. Vosse, Physica B **99**, 521 (1980).
[5]J. Blinowski, N. Hy Hau, C. Rigaux, J. P. Vieren, R. Toullec, G. Furdin, A. Herold, and J. Melin, J. Phys. (Paris) **41**, 47 (1980).
[6]P. C. Eklund, M. H. Yang, and G. L. Doll, in *Intercalation in Layered Materials,* edited by M. S. Dresselhaus (Plenum, New York, 1986), p. 257.
[7]G. L. Doll, M. H. Yang, and P. C. Eklund, Phys. Rev. B **35**, 9790 (1987).
[8]J. M. Zhang and P. C. Eklund, J. Mater. Res. **2**, 858 (1987).
[9]M. H. Yang and P. C. Eklund, Phys. Rev. B **38**, 3505 (1988).
[10]R. Saito and H. Kamimura, Synth. Met. **12**, 295 (1985).
[11]D. E. Nixon and G. S. Parry, J. Phys. D **1**, 291 (1968).
[12]W. Rudorff and E. Schulze, Z. Anorg. Allg. Chem. **277**, 156 (1954).
[13]H. Zaleski, P. K. Ummat, and W. R. Datars, Phys. Rev. B **35**, 2958 (1987).
[14]H. Zaleski, P. K. Ummat, and W. R. Datars, J. Phys. C **1**, 369 (1989).