Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Fermi Surface of Electrons and Holes in C_8K: First-Principles Study

Satoshi Amamiya [a], Shinichi Higai [a], Shugo Suzuki [a] & Kenji Nakao [a]

[a] Institute of Materials Science, University of Tsukuba, Tsukuba, Ibaraki, 305-8573, Japan

Version of record first published: 24 Sep 2006

To cite this article: Satoshi Amamiya, Shinichi Higai, Shugo Suzuki & Kenji Nakao (2000): Fermi Surface of Electrons and Holes in C_8K: First-Principles Study, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 340:1, 53-58

To link to this article: http://dx.doi.org/10.1080/10587250008025442

Mol. Cryst. and Liq. Cryst., 2000, Vol. 340, pp. 53-58
Reprints available directly from the publisher
Photocopying permitted by license only

Fermi Surface of Electrons and Holes in C_8K: First-Principles Study

SATOSHI AMAMIYA, SHIN'ICHI HIGAI, SHUGO SUZUKI and KENJI NAKAO

Institute of Materials Science, University of Tsukuba, Tsukuba, Ibaraki 305–8573, Japan

The band structure and Fermi surface of C_8K are studied by the first-principles calculation using two different types of basis sets to resolve the disagreements in the results of both experimental and theoretical studies. It is concluded that C_8K is a compensated metal with the same number of holes and electrons. The Fermi surface of C_8K is composed of the hole cylinders and electron prisms. The hole cylinders originated from the state in which the graphite interlayer state, π state, and potassium 4*s* state are hybridized have the simply connected topology. On the other hand, the topology of the electron prisms originated from the π state is multiply connected with the electron tube. Furthermore, we calculate the cross sections of these Fermi surfaces and compare them with the dHvA frequencies. The observed two dHvA frequencies can be assigned to the maximum and minimum cross sections of the electron prisms. We also predict that four dHvA frequencies originated from the hole cylinders should be observed.

Keywords: graphite intercalation compound; potassium; Fermi surface; interlayer state; first-principles calculation

INTRODUCTION

The first-stage graphite intercalation compound (GIC) of potassium, C_8K, is a typical material of the donor-type GIC's. In the last two decades, its electronic structure has been actively studied. However, there still remain several serious unsettled problems among the results of both experimental and theoretical studies.

The most controversial point is whether a three-dimensional (3D) carrier pocket exists or not at the center of the Brillouin zone (BZ) besides graphitic

π carrier pocket at the corners of BZ. Moreover, if it exists, there is another controversial point, that is, what features the 3D carrier pocket has.

In experimental studies, it has not been elucidated whether the 3D carrier pocket exists or not. Oelhafen *et al.*[1] have measured the ultraviolet photoelectron spectra and reported that the band originated from the potassium 4*s* state exists just below the Fermi level (E_F). This result suggests that the 3D carrier pocket exists and its character is the potassium 4*s* state. Although only one dHvA frequency has been observed formerly in the dHvA experiments, Wang *et al.*[2] recently reported two dHvA frequencies and suggested that the stronger dHvA signal corresponds to the 3D carrier pocket. On the other hand, there is an opposite experimental result that the 3D carrier pocket does not exist. Ritsuko and Bruckner [3] have measured the x-ray photoemission and electron energy loss spectra and reported that the band originated from the potassium 4*s* state is above E_F, that is, the 3D carrier pocket does not exist.

In theoretical studies, it has also not been elucidated whether the 3D carrier pocket exists or not. Inoshita, Nakao, and Kamimura[4] have shown that the spherical 3D carrier pocket exists at the center of the BZ and the character of this pocket is the potassium 4*s* state. The result by Tatar and Rabii[5] almost agrees with these results although the character of the 3D carrier pocket is quite different; they have concluded that the 3D carrier pocket originates from the graphite π band. On the other hand, there are opposite results that the 3D carrier pocket does not exist[6,7].

In this paper, we examine the electronic structure and the characteristics of the Fermi Surface (FS) of C_8K to resolve the above unsettled points. Furthermore, we calculate the cross section of FS and compare them with the dHvA frequencies.

RESULTS AND DISCUSSION

We have performed the first-principles all-electron full-potential calculations based on the density functional theory within the local density approximation. Furthermore, we have used two different types of basis sets, localized and delocalized basis sets, to estimate the reliability of the present calculations; one is the linear-combination-atomic orbitals (LCAO) method and the other is the mixed-basis (MB) method. We consider the results of our

calculation to be reliable if these obtained by both methods is the same. The details will be given elsewhere[8]. Also, we have used the same crystal structure of C_8K as Inoshita *et al.*

We first summarize the characteristics of the band structure of C_8K obtained by our calculations[8]. We have found that the free-electron-like band with a large dispersion along the c-axis crosses E_F, which is quite similar to the graphite interlayer (IL) state[9]. We call this band as the C_8K IL band. The C_8K IL band consists of the potassium $4s$ state, graphite IL state, and the graphite π state. This means that the electrons in the C_8K IL band spread in the IL region. Also, a band originated from the graphite π band crosses E_F in agreement with the results of all the other theoretical studies. We refer to this band as the π band.

We now show the FS of the C_8K IL band and the π band in Fig.1. The FS is composed of the hole and electron pieces as mentioned below.

An important point to be emphasized is that the FS of the C_8K IL band does exist. We believe that the present result settles the controversy about this point. However, the FS of the C_8K IL band obtained by the present study differs from the electron pocket, which has been reported to exist at the center of the BZ by several experimental and theoretical studies. The present result shows that the FS of the C_8K IL band is composed of the hole cylinders at the boundary of the BZ, which appear as a consequence of the merger of the electron components at the center and corners of the BZ. There are two kinds of hole cylinder because of the symmetry of C_8K. Furthermore, the topology of the hole cylinders is simply connected. That is, all of the closed orbits of the C_8K IL band are hole orbits while there exist open orbits extending in the c-axis. Moreover, this hole cylinders are curved substantially along the c-axis near the center of the BZ. On the other hand, the portion of the hole cylinders near the boundary of the BZ is flat along the c-axis. This reflects the fact that the character of the C_8K IL band changes gradually from the 3D character near the center of the BZ to the 2D character near the boundary of the BZ due to mixing with the graphite π state.

We next describe the FS of the π band. This FS is dominated by a component enclosing the electrons around the corners of the BZ, which is a triangular prism extending in the c-axis. In contrast to the hole FS, there is only one kind of electron prism. In addition to the electron prisms, there

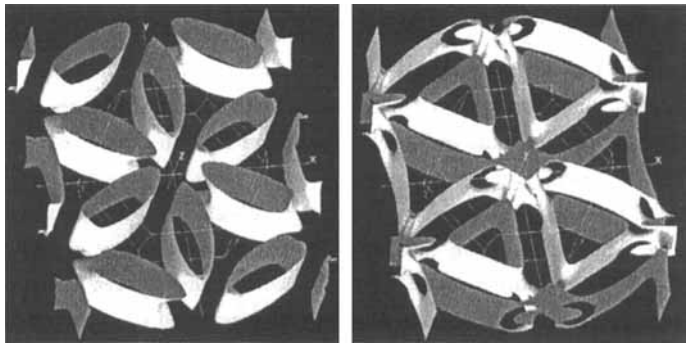

Figure 1: FS originated from (a)the C_8K IL band and (b)the π band.

is a tubular component enclosing the electrons around the Γ-A lines. These two components are slightly connected with each other and therefore the topology of the FS of the π band is multiply connected. Consequently, almost all of the closed orbits of the π band are electron orbits although there are a few hole orbits at the connected regions of the FS. Also, the FS of the π band is curved substantially along the c-axis near the center of the BZ and the electron FS is flat along the c-axis near the boundary of the BZ as well as the hole FS.

The above-mentioned characteristics of FS lead to one very important result. It is that C_8K is a compensated metal. That is, the number of holes in the C_8K IL band is equal to that of electrons in the π band.

Also, for each of the hole cylinders and the electron prisms, we obtained six dHvA frequencies by calculating the cross section areas of the FS. The calculated dHvA frequencies are shown in Table 1. We obtained four dHvA frequencies of the hole cylinders; these frequencies correspond to the minimum and maximum values for the two kinds of hole cylinder. On the other hand, we obtained two dHvA frequencies of the electron prisms; these frequencies correspond to the minimum and maximum values for the only one kind of electron prism. The maximum value is, however, obtained by assuming that the magnetic breakdown occurs at the multiply connected portion.

We now compare the present results with the results of dHvA experiments. Higuchi *et al.*[10] have reported one dIIvA frequency, 2870T, and

Wang *et al.*[2] have reported two dHvA frequencies, 3126T and 4250T, although Wang *et al.* reported only one dHvA frequency, 3070T in the earlier work[11]. The dHvA signal observed by Higuchi *et al.* and the lower frequency dHvA signal observed by Wang *et al.* are very strong; these are most likely originated from the same cross section of the FS. In contrast to this, since the higher frequency dHvA signal measured by Wang *et al.* is very weak, earlier experiments have not observed it[10,11].

We assign the strong and weak signals to the minimum and maximum cross sections of the electron prisms, respectively, by the following reason. Firstly, the observed signals cannot be of the hole FS because the four hole FS cross sections have almost the same character and the signals from them accordingly have almost the same intensity. Secondly, the agreement between the observed and calculated frequencies is good for the electron prisms. Finally, we can understand the weakness of the higher frequency dHvA signal by considering that the signal may be observed as a result of the magnetic breakdown at the slightly connected portion of the electron prisms and tube.

A possible reason why the signals from the electron prisms are observed and the signals from the hole signals are not observed is as follows. It should first be noted that the homogeneity of the arrangement of the alkali atoms between the graphite sheets might not be good while the homogeneity of the arrangement of the carbon atoms in the graphite sheet might be good. It is then most likely that the relaxation time of the holes is shorter than that of the electrons because the holes in the C_8K IL band have the substantial contribution of the potassium $4s$ state and graphite IL state while the electron in the π band have predominant contribution of the graphite π state. Consequently, the signals of the hole cylinders are expected to be weaker than the signals from the electron prisms. It is however possible to

Table 1: Calculated dHvA frequencies in T from the hole and electron pocket. The maximum value of electron pocket is caused by the magnetic breakdown.

Method	hole cylinder (M)		hole cylinder (M)		electron prism (K)	
	min	max	min	max	min	max
LCAO	2540	2780	2590	2700	3240	4050
MB	2410	2850	2520	2690	3170	3970

observe the four dHvA frequencies of the hole cylinders in a crystal with good quality. This is prediction of the present study.

CONCLUSIONS

We have examined the electronic structure of C_8K using both the LCAO and MB methods. Since both methods have given the identical results, we consider them to be reliable. We have obtained the following results. Firstly, C_8K is a compensated metal. Secondly, the C_8K IL band crosses E_F and it forms the simply connected hole cylinders at the boundary of BZ. On the other hand, the electron prisms formed by the π band are multiply connected although the degree of connection is very slight. Thirdly, we have calculated the six dHvA frequencies and assigned the two of them, which are the minimum and maximum frequencies of the electron prisms, to the two experimentally observed frequencies. Furthermore, we have predicted that the four dHvA frequencies of the hole cylinders should be observed.

Acknowledgements
We wish to thank T. Enoki, A. J. Freeman, T. Ohno, A. Oshiyama, M. Posternak, M. Takashita, and S. Tsuneyuki for helpful discussions.

References

[1] P. Oelhafen, P. Pfluger, E. Hauser, and H.-J. Güntherodt: Phys. Rev. Lett. **44,** 197(1980).

[2] G. Wang, W. R. Datars, and K. Ummat: Phys. Rev. B **44,** 8294(1991).

[3] J. J. Ritsuko and C. F. Brucker: Solid State Commun. **44,** 889(1980).

[4] T. Inoshita, K. Nakao, and H. Kamimura: J. Phys. Soc. Jpn. **43,** 1237(1977).

[5] R. C. Tatar and S. Rabii: *Extended Abstract of the First Symposium of the Materials Research Society,* eds. P.C. Eklund, M.S. Dresselhaus, and G. Dresselhaus (Mater. Res. Soc., Pittsburgh, 1984), p. 36.

[6] D. P. DiVincenzo, and S. Rabii: Phys. Rev. B **25,** 4110(1982).

[7] M. Saito and A. Oshiyama: J. Phys. Soc. Jpn. **55,** 4341(1986).

[8] S. Amamiya, S. Higai, S. Suzuki, and K. Nakao (to be published).

[9] M. Posternak Balderschi, A. J. Freeman, E. Wimmer, and M. Weinert : Phys. Rev. Lett. **50,** 761(1983).

[10] K. Higuchi, H. Suematsu, and S. Tanuma: J. Phys. Soc. Jpn. **48,** 1532(1980).

[11] G. Wang, K. Ummat, and W. R. Datars: *in Extended Abstract of the Symposium of the Materials Research Society on Graphite Intercalation Compounds,* eds. P. C. Eklund, M. S. Dresselhaus, and G. Dresselhaus (Mater. Res. Soc., Boston, 1988), p. 217.