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FERMI SURFACE, TRANSPORT AND SUPERCONDUCTING PROPERTIES OF GRAPHITE INTERCALATION COMPOUNDS

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Résumé.- On a construit la surface de Fermi du composé intercalaire graphite-potassium $C_{48}K$ et $C_{36}K$ afin qu'elle soit adaptée au cycle observé de Haas-van Alphen. L'étude de la résistance magnétique a permis de présenter l'orbite ouverte prévue. On observe la supra-conductivité du composé C_8K à 134 mK ; on trouve une forte anisotropie du H_{c2} . On étudie aussi les composés graphite-brome par des méthodes similaires.

Abstract.- The Fermi surfaces of graphite-potassium intercalation compounds, $C_{48}K$ and $C_{36}K$, were composed in such a way that the observed de Haas-van Alphen periods were fitted. The predicted open orbits were proved by the magneto-resistance study. Superconductivity of C_8K compound was observed at 134 mK. A large anisotropy of H_{c2} was found. Graphite-bromine compounds were also studied by a similar method.

Intercalation of atoms or molecules into graphite attracts recent attention [1] in the view points of electronic structure, transport properties, electronic phase changes of superconductivity of CDW possibility and phonon modes. We have investigated low temperature properties of C_xK and CBr_y as the typical intercalation compounds of donor and acceptor types respectively. We prepared pseudo-single crystals of $C_{12n}K$ ($n = 4, 3, 2$) and $CBr_{0.021-0.045}$ using highly oriented pyrolytic graphite given by Dr. Moore of Union Carbide Co.. The number n means that n hexagonal carbon layers exists between adjacent intercalated layers to make a superlattice structure along the c -axis, and n is called the stage number.

The de Haas-van Alphen (dHvA) effect was observed at 1.3 K in most of the prepared crystals. Figure 1 shows the field angle dependence of the dHvA periods. The dashed lines ($\cos \theta$) correspond to cylindrical Fermi surfaces (FS). The lines are adjusted with the experimental points at $\theta = 0^\circ$. For the 4th stage compound $C_{48}K$, five branches α , β , γ , δ and ϵ are found and their values at 0° are smaller by two orders of magnitudes than the values of pure graphite ($1.60 \times 10^{-5} \text{ Oe}^{-1}$ for electron and $2.16 \times 10^{-5} \text{ Oe}^{-1}$ for hole). Except the ϵ -branch which has not enough observed points, every branch suggests rather thin FS. For the most intercalated compound C_8K only one value of $3.49 \times 10^{-8} \text{ Oe}^{-1}$ is observed at present, which agrees fairly with the calculated value $2.8 \times 10^{-8} \text{ Oe}^{-1}$ corresponding to the cylindrical FS in the band calculation by

Inoshita et al. [2]. No less dHvA period than the α -branch is considered to exist in $C_{48}K$ because

much less period is found in C_8K sample of which quality should be worse than high stage compounds ; therefore the α -branch should correspond to the largest FS in $C_{48}K$. We adopted the rigid band model of graphite and let the observed period $2.96 \times 10^{-7} \text{ Oe}^{-1}$ at $\theta = 0^\circ$ in the α -branch to fit the sectional area at K-point of the Brillouin Zone (BZ) and we obtained the Fermi energy of 0.42 eV which is compared to 0.018 eV in pure graphite. The calculated FS is much like an ellipsoid in the extended BZ, and the hole FS in graphite disappears. The 4th stage compound has twice the c-axis period of the pure graphite, i.e., the BZ has half the thickness of the original one. We made the FS of $C_{48}K$ by folding the rigid band FS into the half thick BZ and introducing energy gaps at the new zone edge. Figure 2 shows the electron FS thus constructed. The figure is drawn as the extended zone scheme and thick line

shows the FS in the unit zone $\tilde{H}\tilde{K}\tilde{H}$. The three kinds of FS appears ; the smallest one is a closed FS and the other two are open. By fitting the sectional area S_1 at K-point, the observed values of S_2 to S_5 are fairly compatible with the rigid band model if we ignore the separations of S_2 and S_3 and of S_4 and S_5 , as is shown in the inserted table in figure 2. The FS of $C_{36}K$ was constructed in a similar way. There were predicted open orbits in $C_{12}K$ ($n=4,3,2$) as well as in C_8K /2/. We measured the field angle dependence of the transverse magneto-resistance at low temperatures and found a hump or a peak centered at $\theta = 90^\circ$ ($H \perp c$ -axis) in contrast to the zero magneto-resistance at $\theta = 90^\circ$ for pure graphite. This fact proves the existence of the open orbits at this configuration.

The superconductivity of C_8K was observed on similar samples to the above one. The transition

temperature was 134 and 130 mK for two samples. The samples are square shaped lamellar plates of which edge length do depth ratio are about 4. The values of H_{c1} , (H_{c1} without the correction of demagnetization factor) and H_{c2} are 6.0 Oe and about 50 Oe for $H \parallel c$ -axis, and 20 Oe and $\sim 1 \text{ kOe}$ for $H \perp c$ -axis respectively (Fig. 3). The measured T_c in these rather well defined C_8K compounds is lower than the

early reported value 550 mK in the sample wet with potassium metal /3/ and higher than the value 80 mK in the powder samples /4/.

By the similar experimental investigations on CBr_y intercalation compounds, we concluded that the residue compounds are multipase. The main compound is probably $C_{32}(Br_2)$ irrespective to the y -value. This compound makes islands in the original highly oriented graphite, and the y -value determines the mol. ratio of intercalated to pure graphite.

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