

# Superconducting properties of the graphite intercalation compounds $C_8K$

V. V. Avdeev,<sup>1)</sup> O. V. Zharikov, V. A. Nalimova,<sup>1)</sup> A. V. Pal'nichenko,  
and K. N. Smeneko<sup>1)</sup>

*Institute of Solid State Physics, USSR Academy of Sciences*

(Submitted 15 July 1986)

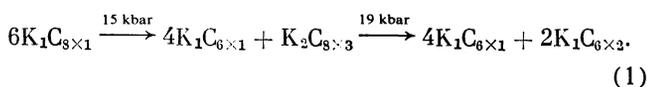
*Zh. Eksp. Teor. Fiz.* **92**, 1423–1432 (April 1987)

The high-pressure method was used to synthesize specimens of the potassium-intercalated graphite compounds  $C_8K$  and  $C_6K$ , and of high-pressure phases  $(C_8K)_P$  quenched to 77 K under pressures  $P = 13$  and 21 kbar. The superconducting transition temperature  $T_c$  and the temperature and angular dependences of the upper critical field  $H_{c2}$  were measured. A considerable increase of  $T_c$  and  $H_{c2}$  was observed in  $C_6K$  and in the high-pressure phases  $(C_8K)_P$  compared with the known compound  $C_8K$ . It is shown that the superconducting properties of the investigated specimens are well described by the model of anisotropic effective mass for the three-dimensional case. The possible trends of further research into the superconducting properties of two-component graphite + alkali metal systems under high pressure are discussed.

## 1. INTRODUCTION

Graphite intercalation compounds (GIC) constitute hexagonal graphite lattices intercalated with monomolecular or monatomic reagent layers. This structure causes the GIC to have a number of new physical properties as well as a high anisotropy. Several hundred GIC are known by now and study of their physical and chemical properties is intensely pursued.<sup>1</sup>

The GIC structure is described in terms of its stages, defined as the number of graphite lattices that separate neighboring layers of the reagent.<sup>1</sup> Ordered systems with up to seven or eight stages are known. In addition, structures are possible constituting combinations of ordered placements of different stages, named fractional. To designate the quantitative ratio of the reagent and graphite atoms in a stage, the formula  $M_n C_{s \times t}$  is used, where  $M$  is the intercalated component,  $C$  is graphite,  $n$  is the number of reagent layers,  $t$  is the number of graphite layers, and  $1/s$  the number of reagent atoms in a layer per graphite atom in a neighboring layer and per element of the GIC, called a layer packet, whose periodic repetition in the direction of the sixfold axis  $c$  makes it possible to construct a picture of the entire sample. The production of a compound of one stage or another is determined by the conditions under which it is synthesized,<sup>1</sup> it is known, however, that in binary GIC with alkali metals phase transitions occur under the influence high pressure, with a stage number increased. For example, a stage-two compound of graphite with potassium  $K_1 C_{12 \times 2}$ , is transformed by a pressure  $P = 6.5$  kbar into a stage-three compound  $K_1 C_{8 \times 3}$  (Ref. 2). Another example is provided by pressure-induced phase transitions in  $C_8K$ , describable by the following reaction:<sup>3</sup>



Thus, application of high pressure to GIC uncovers an additional possibility of obtaining strongly anisotropic and quasi-two-dimensional compounds.<sup>4</sup>

In 1965 was reported<sup>5</sup> observation of a superconducting transition at  $T \approx 0.1$ – $0.5$  K in intercalated alkali-metal compounds of graphite (the values of  $T_c$  were subsequently

made more precise). The superconducting properties of GIC and synthesis of new compounds have been diligently pursued beginning with 1978.<sup>1,4</sup> The superconducting properties of the compounds are highly anisotropic, providing favorable prospects of finding quasi-two-dimensional superconductors among the GIC.

The most investigated compound,  $C_8K$ , corresponds to maximum saturation of graphite with potassium when the synthesis is by the usual gas-phase method.<sup>1</sup> When the potassium concentration is lowered to that of the compound  $C_{14.7}K$ , the critical temperature does not change, and with further decrease of the intercalated metal no superconducting transition is observed down to  $T = 60$  mK.<sup>6</sup> It is therefore concluded that  $T_c$  is independent of the electron density, a fact used essentially in the development of corresponding theoretical models of superconductivity in GIC.<sup>4</sup> In view of the foregoing, it is very important to synthesize GIC with a high concentration of potassium in the layer and to study the superconducting properties of such compounds.

It is known that the intercalation of potassium in graphite is accompanied by a noticeable decrease (by 20–50%) of the volume of the system.<sup>7</sup> This suggested the idea of synthesizing GIC with a higher content of alkali metal than  $C_8K$ , by using high pressure.<sup>7</sup> Preliminary measurements of  $T_c$  of compounds with increased potassium concentration were published in Refs. 8 and 9.

We describe here the synthesis of a GIC with increased potassium content by a high pressure method, determine its composition and stability conditions, and discuss the possible structure. The superconducting characteristics,  $T_c$  and  $H_{c2}$ , are measured. Results are also reported of the superconducting properties of the  $(C_8K)_P$  high-pressure phases at  $P = 13$  and 21 kbar. The results are discussed in the context of the existing models. The possibilities and prospects are considered of additional experiments on the superconductivity of two-component GIC.

## 2. SYNTHESIS OF SPECIMENS AND EXPERIMENTAL PROCEDURE

Owing to the high chemical activity of the potassium, the components for the synthesis of the specimens were as-

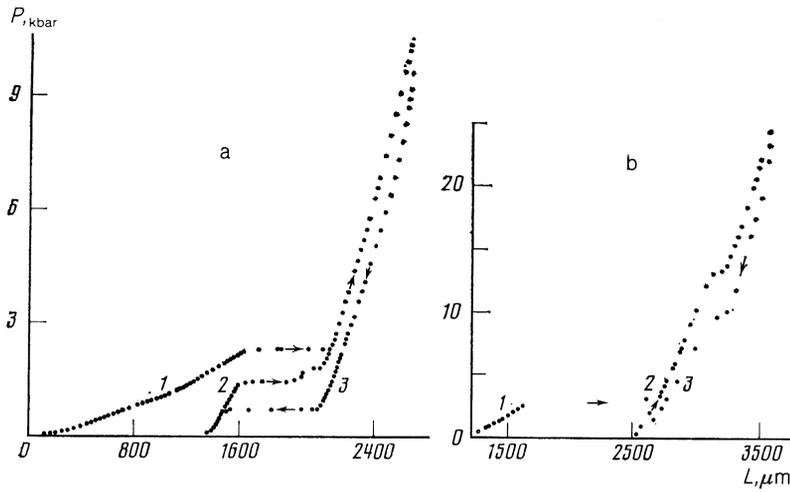


FIG. 1. Compressibility curve  $P(L)$  for synthesis of  $\text{C}_6\text{K}$  (a) and  $\text{C}_8\text{K}$  specimens (explanation in text).

sembled in an inert medium and placed in a self-sealing cell (6 mm in height and diameter) made of thin-wall stainless steel, copper, or teflon. The cell material did not influence the properties of the GIC. The components were quasimonocrystalline pyrolytic graphite (brand UPV-1 TMO) with crystallite disorientation angle  $\approx 70^\circ$ , and potassium 99.999% pure. The composition of the initial system prepared for the synthesis was close to  $\text{C}_6\text{K}$  or  $\text{C}_8\text{K}$ . The final composition of the synthesis products was determined from the compressibility curves. The GIC with potassium was synthesized in a piston-in-cylinder high-pressure unit at quasi-hydrostatic pressure up to 25 kbar and at a temperature 300–500 K. The reaction was monitored by the change of the system volume. Figure 1a shows the dependence of the pressure  $P$  on the piston displacement  $L$ , which is proportional to the change of the system volume, for a synthesized  $\text{C}_8\text{K}$  with increased potassium constant. Initially (curve 1) the pressure was raised to several kbar, the specimen heated to 450–500 K, causing intense penetration of the potassium into the graphite, accompanied by a strong change of the system volume (horizontal plateau on curve 1). The reaction time was 2–5 min. The specimen was then cooled to room temperature and the measurement of  $P(L)$  continued. The amount of intercalated potassium was determined from the difference between the measured change  $\Delta V_{\text{exp}}$  of the system volume before and after the reaction, on the one hand, and the volume change  $\Delta V$  corresponding to an increase of the volume of the intercalated graphite compared with the initial value. In this case  $\Delta V = (d_i/d_j - 1) V_{\text{gr}}$ , where  $V_{\text{gr}}$  is the volume of the initial graphite,  $d_j = 3.35 \text{ \AA}$  is the interplanar distance in the graphite, and  $d_i = 5.35 \text{ \AA}$  is the distance between the graphite planes bounding a monatomic layer of potassium.<sup>1</sup> Following Ref. 3, we have assumed that  $d_i$  is independent of the density of the potassium atoms in the layer, and determined  $\Delta V_{\text{exp}}$  by a least-squares extrapolation of the  $P(L)$  plot regions corresponding to the sections before and after the reaction to zero pressure. The composition of the investigated specimens of GIC with potassium, determined in this manner, was close to  $\text{C}_{6 \pm 0.5}\text{K}$ . The indicated scatter of the calculated composition reflects the leeway in the choice of the segments of the  $P(L)$  curve which were extrapolated to  $P = 0$ . Curves 3 and 2 in Fig. 1a correspond respectively to the cycle of pressure release followed by pressurization at  $T = 300 \text{ K}$ . The plateau observed

in the 0.5–0.8 kbar region on curve 3 and in the 1.5–2.0 kbar region on curve 2 is attributed by us to decomposition and repeated synthesis of the  $\text{C}_6\text{K}$  specimen. Using the method described above to estimate the amount of potassium in the graphite, it can be shown that on relaxation  $\text{C}_6\text{K}$  decomposes into  $\text{C}_8\text{K}$  and potassium (curve 3). Curve 2 reflects the additional penetration of potassium into  $\text{C}_8\text{K}$  to change it to  $\text{C}_6\text{K}$  (see the corresponding plateaus on the curves). Thus, the indicated transitions can correspond to the reaction



We attributed the hysteresis of curves 2 and 3 to the presence of friction in the piston-in-cylinder system. From the fact that  $\text{C}_6\text{K}$  decays on relaxation at  $T = 300 \text{ K}$  it can be concluded that this compound is unstable under normal conditions (see also Ref. 9). The  $\text{C}_6\text{K}$  samples were therefore cooled under pressure directly with liquid nitrogen and were subsequently stored at  $T = 77 \text{ K}$ . The preparation of the specimens for measurement and their entire handling were performed in liquid nitrogen.

Besides  $\text{C}_6\text{K}$  we investigated also  $\text{C}_8\text{K}$  specimens synthesized by the high-pressure method. Figure 1b shows the synthesis of the  $\text{C}_8\text{K}$  (curve 1) and the release and pressurization cycles (curves 3 and 2, respectively). It can be seen that at  $P \approx 13 \text{ kbar}$  the curve reveals a step that can be related to a phase transition in  $\text{C}_8\text{K}$  (this question will be discussed below). We investigated  $\text{C}_8\text{K}$  samples synthesized by high pressure without quenching in liquid nitrogen, as well as samples cooled to 77 K under loads 13 kbar ( $(\text{C}_8\text{K})_{13 \text{ kbar}}$ ), 21 kbar ( $(\text{C}_8\text{K})_{21 \text{ kbar}}$ ) and 8 kbar ( $(\text{C}_8\text{K})_{8 \text{ kbar}}$ ).

The superconducting properties of the GIC were measured in two setups. The  $\text{C}_8\text{K}$  was measured in an  $\text{He}^3/\text{He}^4$  dilution refrigerator at temperatures down to 35 mK. The temperature was measured with a Speer carbon thermometer graduated by measuring the susceptibility of the paramagnetic cerium-magnesium nitrate salt and calibrated against the superconductor standards  $\text{Ir}$  ( $T_c \approx 97 \text{ mK}$ ),  $\text{Cd}$  ( $T_c \approx 0.52 \text{ K}$ ) and  $\text{M}_0$  ( $T_c \approx 0.92 \text{ K}$ ). The error in the determination of  $T$  did not exceed 5%. To measure the anisotropy of the critical field, the apparatus was equipped with a pair of mutually perpendicular coils.

The  $\text{C}_6\text{K}$  and  $(\text{C}_8\text{K})_P$  specimens were investigated in apparatus in which  $\text{He}^3$  vapor was pumped off at tempera-

tures down to 0.7 K, equipped to load the samples in a pre-cooled cryostat without heating them above 77 K. The temperature was also determined with a Speer carbon thermometer calibrated against He<sup>3</sup> vapor pressure at  $T \leq 2.0$  K, and with a semiconductor thermometer at  $T > 2.0$  K. To measure the anisotropy of the critical fields, the apparatus was equipped with an insert that rotated the specimen in a magnetic field produced by a solenoid.

The superconducting properties of the specimens were investigated by measuring the magnetic susceptibility  $\chi$  as a function of the temperature  $T$ , the magnetic field  $H$ , and the angle  $\theta$  between the direction of the magnetic field and the  $c$  axis. The quantity was measured by a contactless inductive method. The investigated specimen was placed in one of the two oppositely wound coils located respectively in the dilution chamber of the refrigerator or in the chamber with the He<sup>3</sup>. The field modulation frequency was 111 Hz and the amplitude  $\approx 0.1$  G. The measured signal was recorded by a standard setup and fed after amplification and detection to an automatic plotter or to a computer.

### 3. EXPERIMENTAL RESULTS

Figure 2 shows the measured temperature dependence of the magnetic susceptibility  $\chi(T)$  of C<sub>8</sub>K or C<sub>6</sub>K specimens synthesized by a high-pressure method. A sharp change of  $\chi$  is observed and is attributed by us to the onset of superconductivity of the specimens. The value of  $T_c$  determined from the midpoint of the transition was  $\approx 0.13$  K for both investigated C<sub>8</sub> specimens, and the width of the transition was  $\approx 30$  mK. For C<sub>6</sub>K we obtained  $T_c = 1.44$ – $1.56$  K (more than 15 specimens were measured), the transition width was usually  $\approx 0.2$  K but also  $< 0.1$  K for several specimens. Thus, the critical temperature in C<sub>6</sub>K is an order of magnitude higher than in C<sub>8</sub>K.

The measured values of  $\chi(T)$  of (C<sub>8</sub>K)<sub>13 kbar</sub> and (C<sub>8</sub>K)<sub>21 kbar</sub> were close to those of C<sub>6</sub>K, i.e.,  $T_c$  was 1.5 K in both cases. A broad superconducting transition starting at 1.5 K was observed in the (C<sub>8</sub>K)<sub>8 kbar</sub> specimens.

The compound C<sub>8</sub>K is stable under normal conditions, as follows from measurements of  $T_c$  performed after prolonged storage of the specimens (3 years). No change in the superconducting properties of the high-pressure phases (C<sub>6</sub>K)<sub>p</sub> was observed in C<sub>6</sub> specimen kept in liquid nitrogen for a year. The (C<sub>8</sub>)<sub>p</sub> specimens are unstable, since no superconducting transition is observed in them (at  $T > 0.7$  K)

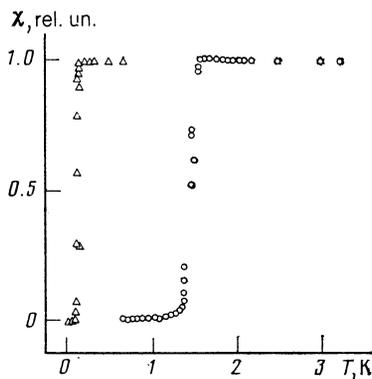


FIG. 2. Temperature dependence of the magnetic susceptibility  $\chi(T)$ :  $\Delta$ —C<sub>8</sub>K specimen,  $\circ$ —C<sub>6</sub>K specimen.

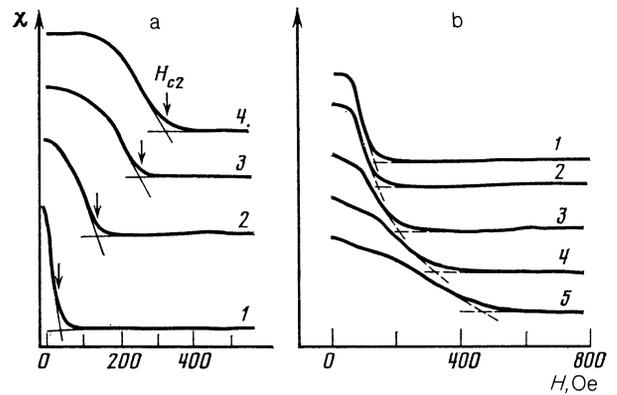


FIG. 3. Magnetic susceptibility  $\chi$  vs the external magnetic field: a) for different temperatures 1—1.44 K; 2—1.205 K; 3—0.95 K, 4—0.77 K. Specimen  $H \perp c$ . b) for different angles  $\theta$  between  $H$  and 1— $0^\circ$ , 2— $31^\circ$ , 3— $63^\circ$ , 4— $78^\circ$ , 5— $90^\circ$ . Specimen (C<sub>8</sub>K)<sub>13 kbar</sub>,  $T = 0.9$  K.

after a one-minute exposure to  $T = 200$  K. The superconducting transition of C<sub>6</sub>K was washed out after a brief heating to  $T = 300$  K and decreased or vanished completely (at  $T \geq 0.7$  K) after prolonged heating. A detailed study of the stability of the high-pressure phases and of the kinetics of their decay is now planned.

The anisotropy for the critical field  $H_{c2}$  and its temperature dependence were investigated by measuring the  $\chi(H)$  curves for given values of  $T$  and  $\theta$ . Figures 3a and 3b show such data. The procedure for determining the upper critical field  $H_{c2}$  is readily understood from this figure. A similar procedure for determining  $H_{c2}$  is traditionally used in the investigation of the superconductivity of GIC (see, e.g., Ref. 10),

Figure 4 shows the measured temperature dependence of  $H_{c2}(T)$  of a C<sub>6</sub>K specimen in the case when  $H \parallel c$  and  $H \perp c$ . Similar measurements were made also for the (C<sub>8</sub>K)<sub>13</sub> and <sub>21 kbar</sub> specimens. The results are gathered in the table. Note that the  $H_{c2}(T)$  dependence of all the investigated specimens is linear in temperature at  $0.7 \leq T \leq 1.5$  K. The experimental data yielded also the values of  $(dH_{c2}/dT)_{T_c}$  and of  $H_{c2}(0)$ . The latter were calculated by linear extrapolation to  $T = 0$ ; the “legitimacy” of this procedure will be discussed below. It follows from the measurements that the values of  $H_{c2}^\perp(0)$  in the  $H_{c2}^\perp(0)$  specimens exceed considerably the corresponding values for C<sub>8</sub>K, but agree with one another in order of magnitude. The value of the anisotropy of the critical field  $\epsilon^{-1} = H_{c2}^\perp/H_{c2}^\parallel$  in C<sub>6</sub>K is somewhat low-

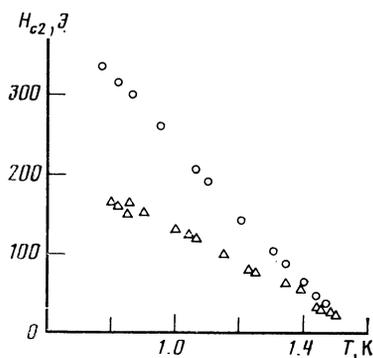


FIG. 4. Temperature dependence of  $H_{c2}(T)$  of C<sub>6</sub>K specimen:  $\circ$ — $H \perp c$ ,  $\Delta$ — $H \parallel c$ .

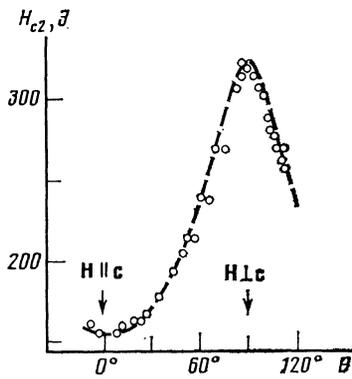


FIG. 5. Angular dependence of  $H_{c2}(\theta)$  for  $C_6K$  sample at  $T = 0.8$  K.

er than in  $C_8K$ , and the maximum value  $\varepsilon^{-1} = 5.43$  is observed for the  $(C_8K)_{13 \text{ kbar}}$  specimens. These data are also given in the table, which contains also the calculated coherence lengths  $\xi^{\perp}(0)$  and  $\xi^{\parallel}(0)$ ; the corresponding calculation procedure will be discussed below.

Figure 5 shows the measured angular dependence of the upper critical field for the  $C_6K$  specimen. In the  $(C_8K)_{13 \text{ kbar}}$  and  $(C_8K)_{21 \text{ kbar}}$  specimens the  $H_{c2}(\theta)$  dependence is qualitatively similar to that shown in Fig. 5.

#### 4. DISCUSSION OF RESULTS

##### 4.1 Synthesis and structure of GIC with potassium under high pressure

The superconducting properties of GIC have up to now been investigated using specimens synthesized by the gas-phase method.<sup>1</sup> Synthesis of GIC by the high-pressure method, proposed in Ref. 7, followed by quenching the specimens under pressure, uncovers new possibilities of discovering new superconducting GIC. It must be ascertained, however, whether the synthesis method affects the properties of the GIC. It follows from the measurements that the values of  $T_c$ ,  $H_{c2}^{\perp}$  and  $H_{c2}^{\parallel}$  for  $C_8K$  obtained by high pressure agree well with the known published data, e.g., Refs. 1, 4, and 10. It can consequently be concluded that the synthesis method does not exert a noticeable influence, at any rate on the superconducting properties of two-component GIC with potassium.

To ascertain the equivalence of the properties of the high-pressure phases  $(C_8K)_P$  quenched under pressure and those in equilibrium, we compare the  $T_c$  data obtained in the present study and in Ref. 11 for a  $C_8K$  specimen located at the instant of the  $\chi(T)$  measurement in a high-pressure

chamber at  $P = 15\text{--}19$  kbar. The value obtained in Ref. 11 was  $T_c \approx 1.8$  K. It can therefore be assumed that the superconducting properties of quenched high-pressure phases and of those in equilibrium (when corrected for the possible dependence of  $T_c$  on  $P$ ) are close or equal. This is also attested by data indicating that  $T_c$  is independent of the time of storage in liquid nitrogen, on the one hand, and on the rapid decay on heating to  $T \approx 200$  K, on the other. In addition, a smeared superconducting transition is observed in  $C_8K$  specimens quenched at  $P = 8$  kbar, which is likewise in agreement with the data of Ref. 11.

We discuss now the phase transitions in the investigated system, and also the possible structure of the phases produced. Measurements of the electric resistance<sup>2</sup> and of elastic neutron scattering<sup>3</sup> revealed phase transitions with change of the staging in  $C_8K$  at  $P < 20$  kbar, and the reaction (1) was suggested. If it is assumed that Eq. (1) describes the transitions correctly, it can be concluded, on the basis of the different values of  $T_c$  of  $C_6K$  and of the high-pressure phases  $(C_8K)_{21 \text{ kbar}}$  and  $(C_8K)_{13 \text{ kbar}}$  (a phase transition in  $C_8K$  was observed in our case at  $P = 13$  kbar) that the superconductivity of the  $(C_8K)_P$  phases is due to the presence in them of the stage-one  $K_1C_{6 \times 1}$ . The difference between the critical fields can then reflect, according to (1), the presence of packets in the specimens, viz,  $K_1C_{6 \times 1}$  and of a second and a fractional stage which are not superconducting at least down to 0.7 K. In addition, it must be emphasized once more that  $C_6K$  differs substantially from the high-pressure phases  $(C_8K)_P$  which contain in their structure a  $K_1C_{6 \times 1}$  intercalated packet.  $C_6K$  becomes synthesized when additional potassium is intercalated at pressures much lower than the pressures of the phase transitions in  $C_8K$ . The entire volume of the sample corresponds then to the stage-one  $C_6K$ , in contrast to the high-pressure  $(C_8K)_P$  phases.

Structures of the  $C_6M$  type are known, for example, for the compounds  $C_6Li$  and  $C_6Eu$  (Ref. 1). We assume that when additional potassium is intercalated in  $C_6K$  a similar structure is formed. The intercalated  $K_1C_{6 \times 1}$  packets in the high-pressure  $(C_8K)_P$  phases also have a similar structure.

##### 4.2. Critical temperature of the compound

It can be seen from the table that the  $T_c$  corresponding to the intercalated  $K_1C_{6 \times 1}$  packet is 1.5 K, much higher than  $T_c = 0.13$  K for the intercalated  $K_1C_{8 \times 1}$  packet. Consequently,  $T_0$  depends strongly on the concentration  $n$  of the alkali metal in the layer. This fact contradicts the conclusion of Ref. 6 that  $T_c$  is independent of  $n$ . We assume that the results of Ref. 6 can be interpreted in another manner. In

TABLE I

CGS	$T_c$ , K	$H_{c2}^{\parallel}(0)$ , Oe	$H_{c2}^{\perp}(0)$ , Oe	$\varepsilon^{-1}(0)$	$\varepsilon^2(0)$	$\xi^{\parallel}(0)$ , Å	$\xi^{\perp}(0)$ , Å	$-\left(\frac{dH_{c2}^{\parallel}}{dT}\right)_{T_c}$ , Oe/K	$-\left(\frac{dH_{c2}^{\perp}}{dT}\right)_{T_c}$ , Oe/K	Remarks
$C_8K$	0.13	8.7	22.1	2.54	0.155	2420	6150	—	—	at $T = 67$ mK
$C_6K$	1.5	315	630	2.0	0.25	510	1020	210	420	—
$(C_8K)_{21 \text{ kbar}}$	1.5	180	870	4.83	0.043	280	1350	120	580	—
$(C_8K)_{13 \text{ kbar}}$	1.5	260	1425	5.43	0.034	205	1125	175	950	—

fact, a sample with composition  $C_xK$  with  $8 < x < 22$  (the concentration interval investigated in Ref. 6) can be regarded as a mixture of two types of intercalated packets—superconducting  $K_1C_{8 \times 1}$  and nonsuperconducting  $K_1C_{12 \times 2}$ , i.e., stages one and two, in amounts corresponding to the initial composition, which may leave  $T_c$  unchanged up to definite values of  $x$ . Thus, these arguments are similar to those advanced above for the case of  $C_6K$  and  $(C_8)_pK$ .

At the present time there exists a single theoretical model that proposes a strong  $T_c(n)$  dependence in two-component superconducting GIC.<sup>13</sup> In Ref. 13 is considered the case of isotropic electron-phonon interaction and an anisotropic electronic structure. The anisotropy of the latter is due to superposition of almost two-dimensional graphite  $\pi$ -bands with a cylindrical Fermi surface and an isotropic almost-spherical Fermi surface of the potassium  $s$ -electrons. It is assumed that a contribution to the superconductivity is made by both graphite and potassium electrons (by analogy with the  $s$ - $p$  hybridization in transition metals). The model leads to the expression

$$T_c \sim \Theta_D \exp \{ -V^{-1} [N_s(0)N_\pi(0)]^{-1/2} \}. \quad (3)$$

Here  $N_\pi(0)$  and  $N_s(0)$  are the state densities connected with the graphite  $\pi$  electrons and the potassium  $s$  electrons, respectively. The model explains the absence of superconductivity in  $C_6Li$  and  $C_{24}K$ , where the respective electron contributions to  $N_s(0)$  and  $N_\pi(0)$  are small,<sup>1</sup> and also provides a correct estimate of  $H_{c2}$  and of its anisotropy in  $C_8K$  (Ref. 13).

An estimate of  $T_c$  for a structure of type  $K_1C_{6 \times 1}$ , made under the assumption (for which there is no basis whatever) that the charge transfer in this structure is 0.8, for which there is no basis whatever (the charge transfer in  $K_1C_{8 \times 1}$  is 0.6, Ref. 14), yields a value 1.5 K (Ref. 13). Thus, a number of simplifying assumptions notwithstanding, the model of Ref. 13 predicts a strong  $T_c(n)$  dependence, in contrast to other theoretical papers.<sup>4</sup>

### 4.3. Anisotropy of critical field

An isotropic effective mass model was proposed<sup>15,16</sup> to describe the temperature and angular dependences of  $H_{c2}$  in intercalated compounds. The model is based on the use of the three-dimensional Ginzburg-Landau equations with anisotropic effective mass for electrons moving inside and across the layers, i.e., respectively  $m_\perp^*$  and  $m_\parallel^*$ . The model predicts the following expressions for the temperature and angular dependences of  $H_{c2}$  (Refs. 10, 16)

$$H_{c2}(\theta) = \frac{\Phi_0}{2\pi(\xi^\perp)^2} (\cos^2 \theta + \varepsilon^2 \sin^2 \theta)^{1/2}, \quad (4)$$

$$\varepsilon = \frac{H_{c2}^\parallel}{H_{c2}^\perp} = \frac{\xi^\parallel}{\xi^\perp} = \left( \frac{m_\perp^*}{m_\parallel^*} \right)^{1/2}, \quad (5)$$

$$H_{c2}^\parallel(T) = \frac{\Phi_0}{2\pi[\xi^\perp(0)]^2} \left( 1 - \frac{T}{T_c} \right) = -T_c \left( \frac{dH_{c2}^\parallel}{dT} \right)_{T_c} \left( 1 - \frac{T}{T_c} \right), \quad (6)$$

$$H_{c2}^\perp(T) = \frac{\Phi_0}{2\pi\xi^\perp(0)\xi^\parallel(0)} \left( 1 - \frac{T}{T_c} \right) = -T_c \left( \frac{dH_{c2}^\perp}{dT} \right)_{T_c} \left( 1 - \frac{T}{T_c} \right). \quad (7)$$

The subscripts  $\perp$  and  $\parallel$  and the angle  $\theta$  are referred here to the  $c$  axis.

It can be seen from Fig. 4 that (6) and (7) describe well the experimentally observed  $H_{c2}$  temperature dependence. This justifies also a linear extrapolation to  $T = 0$  when  $H_{c2}$  is determined or calculated from the equations. The values of  $\xi^\perp$  and  $\xi^\parallel$  were determined from Eqs. (5)–(7) and are listed in the table. Note that for all the investigated superconductors we have  $\xi^\parallel(0) \gg d$ , where  $d = 5.35 \text{ \AA}$  is the distance between the potassium layers (the size of the  $C_6K$  or  $C_8K$  layer packet).

The dashed line of Fig. 5 shows the angular  $H_{c2}(\theta)$  dependence given by Eq. (4). The value of  $\varepsilon^2$  was calculated here from the measured values of  $H_{c2}^\perp$  and  $H_{c2}^\parallel$  at the corresponding temperature. It can be seen that the experimental data agrees well with the predictions of the model.

Thus, recognizing that  $\xi^\parallel(0) \gg d$ , we obtain from the foregoing comparison of the experimental data and the anisotropic-effective-mass model that the GIC investigated in the present study are anisotropic three-dimensional superconductors. An alternative model of quasi-two-dimensional superconductivity in intercalated systems predicts other relations for  $H_{c2}(T, \theta)$  and also stipulates that  $\xi^\parallel \approx d$ .<sup>10,15</sup>

## 5. CONCLUSION

We have thus investigated GIC with potassium,  $C_6K$ , and the high-pressure phases  $(C_8K)_{13 \text{ kbar}}$  and  $(C_8K)_{21 \text{ kbar}}$  which contain  $K_1C_{6 \times 1}$ . The specimens were synthesized by the high-pressure method proposed in Ref. 7. In addition, for comparison with the known data, the method of Ref. 7 was used to synthesize  $C_8K$  specimens. It was shown that  $C_6K$  and the high pressure phases  $(C_8K)_p$  are unstable under normal conditions.

The temperature and angular dependences of the upper critical field was investigated and the critical temperature was determined. It was shown that the superconducting properties of GIC do not depend on the synthesis method, making the high-pressure method promising for obtaining new GIC. A strong dependence of  $T_c$  on the potassium concentration in GIC. It is shown that the investigated superconductors are well described by the phenomenological anisotropic-effective-mass model and are three-dimensional anisotropic superconductors.

The results permit certain suggestions to be made on further research superconductivity of GIC. We propose that the capabilities of binary graphite + alkali metal systems are by far from exhausted and, furthermore, such systems offer definite advantages over ternary and more complicated systems. It will apparently be useful to attempt to synthesize GIC with higher alkali-metal contents. Such experiments can cast light on the understanding of the nature of the superconductivity of GIC and contribute to the development of numerical models. Another important trend may be the search for phase transitions in GIC under pressure and for stronger bonding. Since a significant part of the pressure range  $P > 25 \text{ kbar}$  has not been investigated as yet, one can hope to obtain binary GIC with high anisotropy of the superconducting properties.

In conclusion, the authors are deeply grateful to A. I. Larkin for a discussion of the results and to E. P. Vol'skii for constant interest and support of the research into the super-

conductivity of GIC. The authors are indebted to A. M. Komotin for constructing the insert for rotating the specimens in a magnetic field.

<sup>1)</sup>Moscow State University

<sup>1</sup>M. S. Dresselhaus and G. Dresselhaus, *Adv. Phys.* **30**, 139 (1981).

<sup>2</sup>R. Clarke, N. Wada, and S. A. Solin, *Phys. Rev. Lett.* **44**, 1616 (1980).

<sup>3</sup>C. D. Fuerst, J. E. Fischer, J. D. Axe, J. B. Hastings, and D. B. McWhan, *ibid.* **50**, 357 (1983).

<sup>4</sup>R. Clarke and C. Uher, *Adv. Phys.* **33**, 469 (1984).

<sup>5</sup>N. B. Hannay, T. H. Geballe, B. T. Matthias, *et al.*, *Phys. Rev. Lett.* **14**, 255 (1965).

<sup>6</sup>M. Kobayashi and I. Tsujikawa, *J. Phys. Soc. Jpn.* **50**, 3245 (1981).

<sup>7</sup>K. N. Semenenko, V. V. Avdeev, and V. Z. Mordkovich, *Dokl. Akad.*

*Nauk SSSR* **271**, 1402 (1983).

<sup>8</sup>E. P. Wolski, O. V. Zharikov, A. V. Palnichenko, *et al.*, *Sol. St. Comm.* **57**, 421 (1986).

<sup>9</sup>V. V. Avdeev, O. V. Zharikov, V. A. Nalimova, A. V. Pal'nichenko, and K. N. Semenenko, *Pis'ma Zh. Eksp. Teor. Fiz.* **43**, 376 (1986) [*JETP Lett.* **43**, 484 (1986)].

<sup>10</sup>Y. Iye and S. Tanuma, *Synthetic Metals*, **5**, 257 (1983).

<sup>11</sup>L. E. DeLong, V. Yeh, V. Tondiglia, *et al.* *Phys. Rev.* **B26**, 6315 (1982).

<sup>12</sup>C. D. Fuerst, D. Moses, and J. E. Fischer, *Phys. Rev.* **B24**, 7471 (1981).

<sup>13</sup>R. Al-Jishi, *Phys. Rev.* **B28**, 112 (1983).

<sup>14</sup>T. Ohno, K. Takao, and H. Kamimuru, *J. Phys. Soc. Jpn.* **47**, 1125 (1979).

<sup>15</sup>L. N. Bulaevskii, *Usp. Fiz. Nauk* **116**, 449 (1975) [*Sov. Phys. JETP* **17**, 514 (1975)].

<sup>16</sup>R. C. Morris, R. V. Coleman, and R. Bhandar, *Phys. Rev.* **B5**, 895 (1972).

Translated by J. G. Adashko