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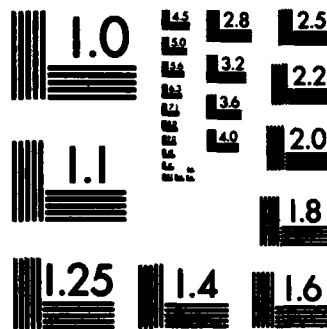
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A MODEL FOR SUPERCONDUCTIVITY IN GRAPHITE INTERCALATION COMPOUNDS.

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ABSTRACT

The observed superconductivity in the stage 1 graphite-alkali metal intercalation compounds (GICs) is modeled using both graphite π -bands and intercalate s-bands. The anisotropy observed in the superconducting properties is explained in terms of the anisotropy of the Fermi surfaces of the GICs.

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INTRODUCTION

Superconductivity in stage 1 alkali-metal graphite intercalation compounds (GICs) (C_8K , C_8Rb , C_8Cs) was first reported by Hannay et al.¹ The highest transition temperatures reported by these authors were 0.55 K for C_8K , 0.15 K for C_8Rb , and 0.135 K for C_8Cs . Superconductivity in C_8K was more recently reexamined in a detailed study by Koike et al.² and by Kobayashi et al.³ A range of transition temperatures have been reported for these compounds. For example, 13 samples of stage 1 K-GICs prepared from HOPG were investigated by Koike et al.² for which the transition temperature ranged from 0.128 K to 0.198 K, with T_c values considerably lower than those reported previously by Hannay et al.¹ Kobayashi et al.³ found a transition temperature of 0.15 K for their C_8K samples prepared from HOPG. The higher stage alkali-metal GICs, as well as stage 1 C_6Li , have been investigated for superconductivity but no superconducting transition has yet been reported.⁴ The dependence of the transition temperature on in-plane intercalate concentration has not yet been studied in detail, but evidence to date⁵ indicates that T_c decreases slowly with decreasing intercalate concentration until some critical concentration at which T_c vanishes. The most important feature of alkali-metal GICs is that they are formed from components that are not by themselves superconducting but nonetheless upon intercalation the compound exhibits superconductivity. Superconductivity has also been reported for other GICs, but it is only for stage 1 alkali-metal GICs that the intercalant is not by itself superconducting.

More recently, Alexander et al.⁶ observed anomalous behavior in the temperature dependence of the specific heat of stage 2 potassium-amalgam GIC, C_8KHg , at 1.93 K. This anomaly was interpreted as the onset of a superconductive transition. The superconducting state was later confirmed by Koike and

Tanuma⁷ and by Pendrys et al.⁸ through the observation of a Meissner effect. A superconducting transition was also discovered in stage 2 C₈RbHg at 1.44 K by Pendrys et al.⁸ and Alexander et al.⁹ The stage 1 compounds C₄KHg and C₄RbHg were found by Iye and Tanuma¹⁰ to undergo a superconducting transition at 0.73 K and 0.99 K, respectively. Recent experiments by Tedrow and Timp¹¹ observed $T_c = 1.65$ K for a well ordered ($\sqrt{3} \times \sqrt{3}$)R30° stage 1 potassium-amalgam GIC. The difference in superconducting transition temperature in the stage 1 compounds is attributed to differences in the in-plane stoichiometry.¹¹

The superconducting GICs exhibit a high degree of anisotropy with regard to their behavior in an applied magnetic field. The anisotropic properties are well described in terms of an effective mass model for superconductivity. By measuring the magnetic susceptibility as a function of the magnitude and direction of the applied magnetic field (θ is the angle between the applied magnetic field and the c-axis), Koike et al.² found that for $0 < \theta < 65^\circ$, C₈K behaves as a type I superconductor which shows magnetic flux exclusion, whereas for $65^\circ < \theta < 90^\circ$, it behaves as a type II superconductor which allows magnetic flux penetration. The estimated ratio of the in-plane coherence length to the c-axis coherence length for C₈K is $\xi_{\perp}/\xi_{\parallel} \sim 5$. The anisotropy in the graphite-potassium amalgam compounds is even higher, with the ratio of the basal to c-axis coherence length $\xi_{\perp}/\xi_{\parallel}$ being > 10 for stage 1 compounds and > 20 for stage 2 compounds.¹⁰

Recently, a model for superconductivity in graphite-alkali metal compounds was presented by Takada.¹² In the Takada model, the mechanism for superconductivity was assumed to be the electron-polar phonon interaction, and the

anisotropy of the coherence length was ascribed to anisotropy in the electron-phonon interaction. The calculated anisotropy in the Takada model is $\xi_{\perp}/\xi_{\parallel} \sim 1.3$ which is considerably smaller than the experimental value of ~ 5 .

In the next section, we present a different model for superconductivity in alkali-metal GICs which can explain the large anisotropy in the superconducting behavior. In our model, the known anisotropic electronic band structure is included and the electron-phonon interaction is assumed isotropic. We shall show that the anisotropy of the electronic band structure is the main factor contributing to the observed anisotropy of the superconducting behavior in an applied magnetic field. The model also explains the absence of superconductivity in C_6Li and in the higher stage alkali-metal compounds.

MODEL FOR SUPERCONDUCTIVITY IN GICs

In the superconducting GICs reported to date, the intercalate species acts as a donor and hence there is a transfer of electrons to the graphite layers. The value of the fractional charge transfer is estimated to be ~ 0.6 in first stage compounds of K-GIC.^{13,14} This incomplete charge transfer results in an electronic band structure which can be regarded as a superposition of approximately two dimensional graphite π -bands with a cylindrical Fermi surface along the HKH axis and an almost spherical Fermi surface associated with the alkali-metal s-band centered at the Γ point of the pristine graphite Brillouin zone. The small hybridization of the graphite π -orbitals with intercalant orbitals at the Fermi surface¹³ suggests a role for the highly anisotropic π -electrons in the superconductivity mechanism.

The identity of the band electrons which contribute to superconductivity is the central issue in understanding the mechanism for superconductivity in GICs¹⁵. The s-band is nearly isotropic so that if only the s-electrons were responsible for superconductivity then a nearly isotropic behavior would be expected. On the other hand, if the π -electrons are solely responsible for superconductivity then C₆Li would have a superconducting transition temperature approximately ten times higher than that of C₈K. This estimate is based on the higher density of states at the Fermi surface in C₆Li. However, C₆Li does not show superconductivity down to temperatures ~ 0.1 K.⁴

Superconductivity in GICs has not yet been fully characterized experimentally so that a unique model cannot yet be firmly established. However, the model discussed in this paper is shown to account for the experimental data available at this time. More complete experimental characterization of the superconducting state may require some modification of the model.

the experimental observations summarized above suggest a model which assumes that the coupling between the intercalate s- and graphite π -electrons gives rise to the observed superconducting transition. The model for superconductivity is based on a coupling of Cooper pairs on different Fermi surfaces, as was previously developed by Suhl et al.¹⁶ who considered the effect on superconductivity of the interaction between s- and d-electrons in transition metals. According to our modification of the Suhl model, the dominant terms in the Hamiltonian for this interaction is given by

$$H = 2 \sum_{k_s} \epsilon_{k_s} C_{k_s}^\dagger C_{k_s} + 2 \sum_{k_\pi} \epsilon_{k_\pi} C_{k_\pi}^\dagger C_{k_\pi} + \lambda \sum_{k_s, k_\pi} \{ C_{k_\pi}^\dagger C_{-k_s}^\dagger C_{-k_s} C_{k_s} + \text{H.C.} \} \quad (1)$$

where ϵ_{k_s} and ϵ_{k_π} are the energies of electrons in the s- and π -bands

respectively whose wave vector is k , and λ is the coupling parameter between the s - and π -electron pairs, λ is assumed to be a constant, and H.C. stands for the hermitian conjugate. The finite temperature Greens functions are defined by:¹⁷

$$g_i(k, \tau) = - \langle T \{ C_{k_i \uparrow}(\tau) C_{k_i \uparrow}^\dagger(0) \} \rangle \quad (2)$$

$$F_i(k, \tau) = - \langle T \{ C_{-k_i \downarrow}^\dagger(\tau) C_{k_i \uparrow}^\dagger(0) \} \rangle \quad (3)$$

where $C_{k_i \sigma}(\tau)$ ($C_{k_i \sigma}^\dagger(\tau)$) is the annihilation {creation} operator for an electron of wave-vector k_i and spin σ , $i = s, \pi$ and $\langle \dots \rangle$ represents thermal averaging, T is the time ordering operator and τ is an 'imaginary' time, defined by the equation

$$C_{k_i \sigma}(\tau) = \exp[(H - \mu N) \tau / \hbar] C_{k_i \sigma}(0) \exp[-(H - \mu N) \tau / \hbar] \quad (4)$$

in which μ is the chemical potential, N is the total number of electrons, and H is the Hamiltonian given in Eq. 1.

For the Hamiltonian of Eq. 1, the Fourier transforms of the finite temperature s - and π -Greens functions defined in Eq. 2 are given by

$$g_s(k, \omega_n) = \frac{-\hbar (i\hbar\omega_n + \delta\epsilon_{ks})}{\hbar^2 \omega_n^2 + \delta\epsilon_{ks}^2 + |\Delta_s|^2} \quad (5)$$

$$g_\pi(k, \omega_n) = \frac{-\hbar (i\hbar\omega_n + \delta\epsilon_{k\pi})}{\hbar^2 \omega_n^2 + \delta\epsilon_{k\pi}^2 + |\Delta_\pi|^2} \quad (6)$$

where $\delta\epsilon_{ks} = \epsilon_{ks} - \mu$, $\delta\epsilon_{k\pi} = \epsilon_{k\pi} - \mu$ and $\omega_n = (2n+1)\pi k_B T / \hbar$, k_B being the Boltzmann constant and T is the temperature. The superconducting energy gaps

Δ_s and Δ_π are given by

$$\Delta_s = \lambda \sum_{k_\pi} F_\pi^\dagger(k_\pi, 0) \quad (7)$$

$$\Delta_\pi = \lambda \sum_{k_s} F_s^\dagger(k_s, 0) \quad (8)$$

in which F is defined by Eq. 3.

The form of the Greens functions Eqs. (5) and (6) implies that the system could be decoupled in terms of s- and π -Fermi surfaces, each having its own Cooper pairs and own energy gap. This decoupling results from the functional form of the Hamiltonian and leads to a two gap system where the gap conditions are coupled and are given by

$$\Delta_s = \lambda k_B T \sum_{\omega_n, k_\pi} \frac{\Delta_\pi}{h^2 \omega_n^2 + \delta \epsilon_{k_\pi}^2 + |\Delta_\pi|^2} \quad (9)$$

$$\Delta_\pi = \lambda k_B T \sum_{\omega_n, k_s} \frac{\Delta_s}{h^2 \omega_n^2 + \delta \epsilon_{k_s}^2 + |\Delta_s|^2} \quad (10)$$

At the superconducting transition temperature T_c , both Δ_s and Δ_π vanish simultaneously, and the expression for T_c is found to be

$$kT_c = h \omega_c \exp\{-1/|\lambda| [N_s(0)N_\pi(0)]^{1/2}\} \quad (11)$$

where ω_c is a cutoff frequency (the Debye frequency), and $N_s(0)$ and $N_\pi(0)$ are respectively the densities of states at the Fermi surface of the s- and π -bands.

It should be mentioned that in this model, superconductivity exists even if the net coupling between electron pairs is repulsive. Moreover, neglecting the intra-band interactions does not mean that they are weaker than the inter-band interactions, but merely that they do not give rise to superconductivity, and can thus be accounted for by renormalizing the electron mass in the s- and π -bands separately. The interband scattering is then that between the s- and π -quasi-electrons. According to Eq. (11), $T_c \rightarrow 0$ as $N_s(0) \rightarrow 0$ or $N_\pi(0) \rightarrow 0$, which implies that the absence of superconductivity in C_6Li is due to the complete charge transfer to the graphite that makes $N_s(0)$ vanish. In stage 2 K-GIC, the density of states $N_\pi(0)$ is lower than in stage 1 by a factor estimated to be $\sim 8.7/5.35$, thus giving a transition temperature an order of magnitude smaller than in C_8K even if the s-band is considered to be appreciably occupied in these stage 2 compounds.

ELECTRODYNAMICS OF SUPERCONDUCTIVITY IN GICs

In this section we apply the microscopic theory presented in the previous section to calculate the superconducting coherence length. Based on this estimate, standard results of phenomenological Ginzburg-Landau (GL) theory¹⁸ are used to calculate the experimental parameters of the superconductivity in GICs.

At $T = 0$, the coupled gap equations, Eqs. (9) and (10) reduce to

$$\Delta_s = \lambda/2 \sum_{k_\pi} \frac{\Delta_\pi}{(\delta\epsilon_{k_\pi}^2 + |\Delta_\pi|^2)^{1/2}} \quad (12)$$

$$\Delta_\pi = \lambda/2 \sum_{k_s} \frac{\Delta_s}{(\delta\epsilon_{k_s}^2 + |\Delta_s|^2)^{1/2}} \quad (13)$$

In Eqs. (12) and (13) the sum over k -space is converted to an integral over energy which is taken up to a maximum cut-off energy $\hbar\omega_c$ (e.g. $\omega_c \sim$ Debye frequency). After integration we divide Eq. (12) by Eq. (13) to get

$$\frac{\Delta_s^2}{\Delta_\pi^2} = \frac{N_\pi(0)}{N_s(0)} \frac{\ln(2\omega_c/\Delta_\pi)}{\ln(2\omega_c/\Delta_s)} \quad (14)$$

where the cut-off frequency $\omega_c \gg \Delta_s, \Delta_\pi$. For stage 1 K-GIC, the s -band is treated as spherical with a Fermi radius $k_F = 4.7 \times 10^7 \text{ cm}^{-1}$ and the π -electrons have a linear dispersion given by

$$\delta\epsilon_{k\pi} = v_F p - \epsilon_F \quad (15)$$

where the Fermi velocity $v_F = 9.7 \times 10^7 \text{ cm/sec}$ and p is the electron momentum.¹² The π -electron Fermi cylinder has a c -axis length of $2\pi/l_c$, where $l_c = 5.35 \text{ \AA}$ for stage 1 K-GIC. For this model, we have $N_s(0) = N_\pi(0) = 2 \times 10^{33} \text{ (cm}^{-3} \text{ erg}^{-1}\text{)}$. Equation (14) then implies that $\Delta_s = \Delta_\pi = 2k_B T_c$. The Pippard coherence lengths of the s - and π -bands are estimated¹⁹ as $\xi_{0s} = 0.15 \hbar v_s / k_B T_c = 40,000 \text{ \AA}$ in which v_s is the s -electron Fermi velocity. Similar estimates give $\xi_{0\pi} = 70,000 \text{ \AA}$.

If a magnetic field is applied perpendicular to the c -axis, then the superconducting current is the s -band current since the π -electrons are two-dimensional and thus cannot contribute to a current in the z -direction. The critical field is thus totally determined by the s -band parameters. To calculate the electron mean free path in the s -band, we note that the c -axis conductivity in C_8K at 4 K is estimated to be $\sim 10^5 \text{ (\Omega cm)}^{-1}$. Since the π -electrons do not contribute to the c -axis conductivity, we assume that this contribution is due only to the s -electrons. Thus, the s -electron mean free path, l_s is given by $l_s = m_s v_s c / n_s e^2 = 540 \text{ \AA}$ where m_s , v_s and n_s are the

s-electron mass, Fermi velocity and density, respectively. Since the s-band is nearly isotropic, we can take λ_s to be isotropic. Thus, if the magnetic field is applied perpendicular to the c-axis, the superconductor is in the dirty limit because $\lambda_s \ll \xi_{0s}$. The London penetration depth is given by $\lambda_L(0) = \{m_s c^2 / 4\pi n_s e^2\}^{1/2} \approx 1000 \text{ \AA}$. For dirty superconductors, the Ginzburg-Landau parameter κ is given by¹⁸ $\kappa \approx 0.715 \lambda_L(0) / \xi \approx 1.3$. Since $\kappa > 1/2$, the superconductor is type II for magnetic fields in the plane of the graphite. The GL coherence length at $T=0$ is $\xi(0) \approx 0.9 \sqrt{\xi_0 \lambda}$, where ξ_0 is the Pippard coherence length and λ is the electron mean free path.¹⁸ Then the upper critical magnetic field H_{c2} is:

$$H_{c2} = \phi_0 / [2\pi \xi_s(0)^2] \approx \phi_0 / [(0.9)^2 2\pi \xi_{0s} \lambda_s] \quad (16)$$

in which $\phi_0 = 2.07 \times 10^{-7} \text{ gauss cm}^2$ is the flux quantum.

Using the approximation¹⁸

$$\xi(T) \approx 0.855 \{(\xi_0 \lambda) / (1 - T/T_c)\}^{1/2} \quad (17)$$

which holds for temperatures near T_c , we find that at $T = 2T_c/3$ the critical magnetic field is $H_{c2}(T=0.67T_c) \approx 8.5 \text{ gauss}$. Experimentally the value of $H_{c2}(T=0.67T_c)$ is found to be $\sim 12-19 \text{ gauss}$ for C₆K when the magnetic field is applied perpendicular to the c-axis².

On the other hand, if the magnetic field is applied parallel to the c-axis, then the current is basal and both s- and π -electrons contribute to the current. Since the in-plane conductivity of C₆K at 4 K is²⁰ $\sigma \approx 10^7 \text{ (Qcm)}^{-1}$, and it is mainly due to π -electrons, the mean free path of the π -electrons λ_π is very large and is comparable to the coherence length ξ_π . Thus in the field orientation $H \parallel c$ -axis the superconductor is not in the dirty limit. Because $\lambda_\pi \gg \lambda_s$, it follows that the π -electron supercurrent is

dominant. The penetration depth is then determined by the π -electron parameters. Therefore, in this case, $\lambda_L(0) \approx \{m_\pi c^2 / 4\pi n_\pi e^2\}^{1/2} \approx 400 \text{ \AA}$ where m_π is taken as $\sim 0.25 m_0$, m_0 being the free electron mass. Since $\lambda_L(0) \ll \xi_\pi$, the superconductor behaves as type I. The critical field is then calculated by

$$H_C(0)^2 = 4\pi [N_S(0) \Delta_S^2 + N_\pi(0) \Delta_\pi^2] . \quad (18)$$

Using $N_S(0) \approx N_\pi(0) \approx 2 \times 10^{33} \text{ cm}^{-3} \text{ erg}^{-1}$, $\Delta_S \approx \Delta_\pi \approx 2k_B T_C$ where $T_C \approx 0.15 \text{ K}$, $H_C(T=0)$ is found to be ~ 9.3 gauss. At $T = 0.67 T_C$, the critical field is given by $H_C(T = 0.67 T_C) \approx H_C(0)[1 - (T/T_C)^2] \approx 5.2$ gauss. This value for $H_C(T=0.67 T_C)$ agrees very well with the experimental values of 5 to 7 gauss.² The results of the above analysis thus show that our model explains very well the observed anisotropy in the critical field in terms of the anisotropy of the electronic Fermi surfaces of alkali-metal GICs.

DISCUSSION AND CONCLUSIONS

Although the detailed estimates carried out in the previous section were specific to C_8K , the model presented in this paper is generally applicable to other superconducting GICs, such as potassium- and rubidium-amalgam GICs. At present, however, there are no detailed band structure calculations for these compounds. Experimental work is in progress²¹ to determine the shape of the Fermi surface in potassium-amalgam GIC and the analysis of these data indicates cylindrical Fermi surfaces for the π -bands and nearly spherical surfaces for the intercalate bands.

Recently there have been reports that the superconducting transition temperature T_C in C_8K is increased by a factor of ~ 10 under a hydrostatic pressure of 15 kbar.²² It is known that in most cases T_C decreases slightly as pressure increases due to a small decrease in the electron-phonon coupling

parameter. We attribute the large increase in T_c in the case of C_8K under pressure to a structural phase transition resulting from the application of pressure. We propose that the in-plane ordering of the intercalate layer changes under pressure to a $p(\sqrt{3} \times \sqrt{3})R30^\circ$ superlattice structure, to interpret the pressure dependent resistivity measurements.²³ The increase in overlap between the intercalate and bounding graphite layers may also lead to an increase in the charge transfer from the intercalate to these bounding graphite layers. We estimate below that such structural changes lead to the observed ten fold increase in T_c .

In the discussion to follow, all primed quantities refer to the situation where the intercalate layer has the $p(\sqrt{3} \times \sqrt{3})R30^\circ$ structure, and the unprimed quantities refer to the $p(2 \times 2)R0^\circ$ structure. If we assume (for the sake of argument) that the fractional charge transfer increases under pressure from ~ 0.6 at atmospheric pressure to ~ 0.8 (at the pressure where the phase transition occurs), the s-electron density n_s' is given by $n_s' = (4/3 \times 1/2)n_s$ and consequently $\epsilon_F' = (2/3)^{2/3} \epsilon_F \approx 0.75 \epsilon_F$. The s-electron density of states is estimated as $N_s'(0) = (2/3)^{1/3} N_s(0) \approx 0.87 N_s(0)$. In contrast for the π -electrons, the dispersion is linear and is given by

$$\epsilon' = \hbar v_F' k_{\parallel}' - \epsilon_F' \quad . \quad (19)$$

The Fermi wave-vector of the π -electrons, $k_{F\parallel}'$ is $k_{F\parallel}' \approx (4/3) k_{F\parallel}$; thus we estimate $v_F' \approx 0.56 v_F$. Since the single spin density of states at the Fermi surface of the π -electrons is given by $N_{\pi}'(0) = (k_c'/2\pi^2) (k_{F\parallel}'/\hbar v_F') \approx 2.4 N_{\pi}(0)$, where k_c' is the c-axis length under pressure of the π -Fermi surface cylinders, and $k_c' \approx k_c$. Assuming that

the s- and π -band coupling parameter is unchanged under pressure, we have

$$|\lambda'| [N_s'(0)N_\pi'(0)]^{1/2} \approx 1.44 |\lambda| [N_s(0)N_\pi(0)]^{1/2} . \quad (20)$$

If the cut off frequency is $\omega_c \sim 250$ K, then for $T_c \sim 0.15$ K, it follows that $1/|\lambda| [N_s(0)N_\pi(0)]^{1/2} \approx 7.5$, and therefore $1/|\lambda'| [N_s'(0)N_\pi'(0)]^{1/2} \approx 5.2$, giving a transition temperature $T_c' \approx 10 T_c \approx 1.5$ K.

This model shows that the value of the superconducting transition temperature is more sensitive to changes in the π -band electronic density than to changes in the s-band. This makes it possible to explain the lower T_c in the case of stage 1 Rb- and Cs-GIC than in C_8K . X-ray measurements show that the intercalate concentration is lower in stage 1 Cs-GIC than in stage 1 Rb-GIC, which in turn is lower than in C_8K .²⁴ Moreover, Knight shift measurements²⁵ show that the fractional charge transfer in C_8K is higher than in stage 1 Rb- and Cs-GIC. Consequently, the π -electron density of states in stage 1 Rb- and Cs-GIC could be considerably lower than in C_8K resulting in an appreciably lower T_c .

The weak dependence of T_c on the intercalate concentration in stage 1 K-GIC⁵ is explained by our model if we assume that the fractional charge transfer increases with the decrease of the intercalate concentration. Such behavior is expected because we know that the fractional charge transfer is larger in stage 2 alkali-metal GICs than in the corresponding stage 1 compounds. For example, consider $C_{12}K$ and assume that the fractional charge transfer increases from 0.6 in C_8K to 0.7 in $C_{12}K$ and that the compound $C_{12}K$ is stage 1, which implies that k_c is unchanged. A calculation of the s- and π -electron densities of states, as done above, shows that the change in T_c is less than 5%. However if the intercalate concentration is further reduced,

the compound becomes dominantly stage 2 leading to a lowering of the π -electron density of states, or to complete charge transfer, thus making T_c vanish. At this point we would like to point out that while a model in which the s -electrons are solely responsible for superconductivity in alkali-metal GICs is incompatible with the observed weak dependence of T_c on intercalate concentration, our model also explains this phenomenon in a simple manner.

Another question we like to consider here is how T_c will be affected if we increase the intercalate concentration rather than decrease it. We illustrate this by considering the stoichiometric compound C_7K . Assuming that the fractional charge transfer in C_7K is the same as in C_8K , it can be shown, using the same arguments as given above, that $T_c \sim 0.22$ K. These arguments provide an explanation for the sample dependence of T_c observed by Koike et al.², and the discrepancy in measured T_c among references 1, 2 and 3.

We conclude by noting that the model presented above explains the most important features of the superconducting GICs. It explains the absence of superconductivity in C_6Li and higher stage alkali-metal GICs. The observed anisotropic behavior of C_8K in an applied magnetic field is explained in terms of the anisotropic band structure. The large increase in transition temperature under pressure is explained by assuming that the more dense intercalate phase of C_8K under pressure is a $p(\sqrt{3} \times \sqrt{3})R30^\circ$ structure and an increase in the fractional charge transfer from the intercalate to the graphite layer under pressure. The model also explains the transition temperature dependence in stage 1 potassium-graphite on sample stoichiometries.

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