Superconductivity in graphite intercalation compounds

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Alkali-metal graphite intercalation compounds undergo a normal-to-superconducting transition at a critical temperature T_c that increases with increasing alkali-metal concentration. Furthermore, the temperature dependence of the critical magnetic field H_{c2} is linear down to very low temperatures. A two-band model, which considers coupling between a three-dimensional band and an almost two-dimensional electronic energy band, and which was successfully applied to explain superconductivity in C_8K, is used to interpret recently reported data. In particular, we show that the increase in T_c as the alkali-metal concentration increases, the linear temperature dependence of H_{c2}, and the anisotropy in its value, are consistent with the two-band model.

I. INTRODUCTION

The observation of superconductivity in alkali-metal graphite intercalation compounds (GIC's) was reported years ago by Hannay *et al.*[1] Intensive research work in this area ensued and other GIC's were subsequently found to exhibit superconductivity.[2–9] An interesting property of the superconducting alkali-metal GIC's is that they are formed from constituents which are not superconducting, yet upon intercalation they undergo normal-to-superconducting transitions. A similar recent observation has been made of superconductivity in alkali-metal doped C_{60} (Ref. 10) and this work has attracted a good deal of attention because of the relatively high T_c in K_3C_{60}.

The superconducting GIC's display a large degree of anisotropy (by an order of magnitude) with regard to their behavior in a magnetic field. Large variations in the value of the critical field are obtained as the orientation of the applied magnetic field is varied.[3,7–9,11–14]

Until recently, only alkali-metal GIC's with relatively low metal concentrations have been studied. Synthesis of graphite and potassium by the standard gas-phase two-zone technique[15] yields C_8K as the compound with the maximum metal concentration possible. Intercalation under high pressure, up to 50 kbar, on the other hand, has been used to synthesize alkali-metal GIC's, such as C_6K, C_3K, C_4Na, C_3Na, C_2Na, and C_2Li with a relatively high metal concentration.[16–21] It is also found that the superconducting transition temperature increases with increasing metal concentration, reaching a value of 5 K for C_2Na. Furthermore, the anisotropic behavior in the presence of a magnetic field is still evident, although it becomes less pronounced as the alkali-metal concentration increases. In C_6K, for example, the value of the critical magnetic field, H_{c2}, increases by a factor of 2 as the orientation of the applied magnetic field changes from $\mathbf{H} \parallel c$ axis to one in which $\mathbf{H} \perp c$ axis. In C_3K, however, the corresponding increase is only 10%. Another common feature of all the alkali-metal GIC's is that the critical magnetic field, H_{c2}, exhibits a linear dependence on temperature T which persists down to low values of T.[9,18,21] It is essential that any model for superconductivity in GIC's explain this critical field phenomenon.

In considering a theoretical model that would explain the superconducting properties of alkali-metal GIC's, it is important to consider the nature of the energy bands in these compounds. The intercalate species, i.e., the alkali metal, acts as a donor, and hence there is a charge transfer from the intercalate layer to the host carbon layers, resulting in partially filled intercalate s bands and graphite π bands. Thus the Fermi surface has two components: mostly two-dimensional graphite π bands with a cylindrical Fermi surface parallel to the HKH axis of the graphite Brillouin zone, and an alkali metal-derived s band with an approximately spherical Fermi surface centered at the Γ point which represents the center of the hexagonal Brillouin zone. If one argues that it is the s-band electrons which are responsible for superconductivity, then isotropic behavior should be expected in C_8K. One may invoke the possibility of an anisotropic-electron-phonon interaction[22] but the calculated anisotropy in the behavior of the superconductor in a magnetic field is much smaller than that observed. If it is assumed, on the other hand, that the π electrons are solely responsible for superconductivity, then we would expect that C_6Li, in which the charge transfer from the intercalate to the graphite host is believed to be complete, would exhibit superconductivity at a transition temperature ten times larger than that in C_8K, on account of the larger density of states in C_6Li at the Fermi level. However, C_6Li is not superconducting at all.

Several years ago we proposed a two-band model for superconductivity in C_8K whose predictions[23] seemed to be consistent with experimental observations available at that time.[2–4] It was assumed that superconductivity arises from a coupling between the s and π bands, in analogy with a model proposed over three decades ago for the s-d coupling in transition metals.[24] The anisotropic behavior of the superconducting state of C_8K was explained in terms of the anisotropic properties of the electronic energy bands.

At this point we should note that there has been some controversy concerning the nature of the electronic energy bands in C_8K. According to tight-binding[25] and self-consistent pseudopotential[26] calculations, the Fermi surface at the center of the Brillouin zone was taken to have K $4s$ character. Later it was suggested[27,28] that the three-dimensional conduction bands at the Γ point of C_8K have the character of interlayer states of graphite rather than the K $4s$ states. More recently, a calculation of the electronic energy bands in C_8K using the self-consistent numerical-basis-set LCAO method within the local-density-functional scheme[29,30] suggests that the 3D Fermi surface at the Γ point originates from graphite π states; zone folding brings equivalent M points in the Brillouin zone of graphite to the Γ point of the smaller Brillouin zone of C_8K.

It is believed that in C_8K the intercalate layer has the $p(2\times2)$ structure, i.e., the potassium atoms form a lattice in the plane commensurate with the graphite lattice but with a lattice constant which is twice as large as that of graphite.[31] Thus the Brillouin zone of C_8K looks like that of graphite except that the distance from Γ to a zone edge point is half the corresponding distance in graphite and the six M points in graphite are folded to the Γ point in C_8K, giving rise to six almost degenerate states just above the Fermi energy if the charge transfer is negligible. In the presence of charge transfer, two of these states move down in energy to below the Fermi energy, thus forming the 3D bands.

Although detailed calculations were made only for C_8K, one may envision a similar situation in C_6K where a $p(\sqrt{3}\times\sqrt{3})R30°$ superlattice structure for the intercalate layer exists.[31] In such a case, zone folding would bring the K points of the graphite Brillouin zone to the Γ point of the C_6K Brillouin zone, and then we could anticipate that two of these states at Γ could move down in energy as the charge transfer takes place. The extension of that idea to compounds of larger metal concentration, such as C_3K, C_4Na, etc., is not clear due to the absence of a commensurate superlattice structure.

Despite the controversy, there is general agreement that a charge transfer from the potassium atoms to the carbon layers does indeed take place, and that it gives rise to a 3D band centered at the Γ point and almost cylindrical bands centered around the HKH axes of the Brillouin zone and we shall simply refer to these below as the s and π bands, respectively. In the following we show that the proposed two-band model for superconductivity in C_8K (Ref. 23) is indeed consistent with recent experimental observations[18,21] in GIC's with higher alkali-metal concentrations.

II. THE TWO-BAND MODEL AND EXPERIMENTAL OBSERVATIONS

Within the BCS framework, the two-band model results in the following expression for T_c:

$$T_c \sim \theta_D \exp\left(\frac{-1}{|V|\sqrt{N_s(0)N_\pi(0)}}\right), \tag{1}$$

where θ_D is the Debye temperature, and $N_s(0)$ and $N_\pi(0)$ are the densities of states at the Fermi surface for the s and π bands, respectively. The product $\sqrt{N_s(0)N_\pi(0)}$ defines an effective density of states, and V is a measure of the strength of the effective electron-electron interaction that causes scattering of pairs of electrons with opposite spins and wave vectors from the s band to the π band or vice versa. The interaction V is mediated by the emission and absorption of virtual phonons. The phonons involved are expected to have nonvanishing components of the wave vector $\mathbf{q}$, in the directions both parallel and perpendicular to the graphite planes.

Since we need to consider the dependence of the effective density of states on the intercalate concentration, and since band-structure calculations have been reported only for C_8K relative to the many compounds recently measured by Belash and co-workers,[19,18,21] we will need to make simplifying approximations that keep the problem tractable, yet still retaining its essential ingredients. Since the in-plane arrangement of the intercalate atoms is not known except for C_8K and possibly for C_6K, we do not consider explicitly the lattice structure in the x-y plane, but we take into account only the layer structure in the z direction. The Brillouin zone is taken to be bounded by the planes $z=-\pi/d$ and $z=\pi/d$, where d is the distance between adjacent graphite layers between which the intercalate layer is sandwiched and is given by 5.3 Å for the C_xK system, and 3.98 Å for the C_xNa system. We will assume that in the case of C_8K, the 3D band is spherical.

The fractional charge transfer in C_8K is $f=0.6$ per potassium atom, which corresponds to $0.075e$ per carbon atom. In the absence of any reported band-structure calculation, for the other C_xK compounds, and for the C_xNa compounds, the fractional charge transfer is not known. As the alkali-metal concentration increases, the distance between the adjacent alkali atoms in the plane decreases;[18] consequently, we expect that the dispersion in the intercalate-derived band would increase, with the bottom of this band at the Γ point moving down to a lower energy. It is then expected that f will decrease as the intercalate concentration increases.

A reasonable assumption to make is that on the average, each carbon atom still receives an approximate charge of $0.075e$ from the intercalate layer so that $N_\pi(0)$ remains essentially unchanged, while $N_s(0)$ increases as the metal concentration is increased. It then follows that if the effective density of states for C_4Na at the Fermi level has the value D, then the effective density of states will have the values $1.067D$ and $1.16D$ for C_3Na and C_2Na, respectively. To choose a value for θ_D in the graphite-sodium system, we note that in C_8K a Debye temperature of 234 K is determined from specific-

heat measurements.[32] Consequently it is expected that a somewhat higher value exists in C_xNa. Choosing $\theta_D \sim 300$ K, we can determine the value of T_c for two of the three compounds C_4Na, C_3Na, and C_2Na if we know T_c for one of them. Using the above arguments, we obtain the following values for T_c: 5 K for C_2Na, 3.5 K for C_3Na, and 2.6 K for C_4Na. These values are in excellent agreement with the experimental values of 5, 3.5, and 2.8 K, respectively.[18,21]

Even if the opposite assumption is made, namely, that the fractional charge transfer per metal atom increases or remains constant as the metal density increases, similar results will be obtained because the effective density of states, which determines T_c, is the geometric mean of the densities of states of the two bands. Thus the two-band model for superconductivity readily explains the functional dependence of T_c on the metal concentration in C_xNa.

As for C_xK, it is not easy except for C_8K, to calculate the density of states on the basis of the model for the Fermi surface that we described before. This has to do with the fact that in the case of C_8K, if the lattice structure in the x-y plane is not considered, then π/d is 5.8×10^7 cm^{-1}, while the Fermi radius of the spherical band is 4.7×10^7 cm^{-1}. Upon increasing the potassium concentration, the density of electrons increases and the Fermi surface gets very close to the Brillouin zone edge, causing a large increase in the density of states due to the flattening of the bands near the zone edge. The calculated[29,30] density of states in C_8K shows that a small increase in the Fermi energy, which could result from increasing the density of electrons, as in going from C_8K to C_6K, does indeed lead to a large increase in the density of states, far more than what would be predicted by simply increasing the Fermi radius of the Fermi sphere centered at the Γ points. In addition, the values of the density of states for C_8K, C_6K, and C_3K, as calculated from the measured critical magnetic fields, concur with the above statement.

The increase in the calculated density of states as we go from C_8K to C_6K is consistent with a tenfold increase in the transition temperature in agreement with the observed increase in T_c.[21] It was suggested by Belash *et al.*[21] that C_3K is a strong coupling superconductor so that the expression for T_c given in Eq. (1) no longer holds since it is based on a weak coupling approximation. It is shown that if McMillan's formula is used, the electron-phonon parameter λ turns out to be equal to 0.52 so that the validity of Eq. (1) breaks down. This explanation may account for the relatively small increase in T_c observed in C_3K relative to C_6K.

III. CRITICAL-FIELD PREDICTIONS AND OBSERVATIONS

The critical magnetic field H_{c2}, which destroys superconductivity through flux penetration, usually increases with decreasing temperature T, first linearly in the vicinity of T_c, but then saturating for low values of T.[33] The reported data on superconducting GIC's, on the other hand, suggest that the linear dependence of H_{c2} on T persists to low values of the reduced temperature T/T_c.[7–9,18,21] Furthermore, a large degree of anisotropy exists with regard to the behavior of C_8K in the presence of a magnetic field. In the superconducting state C_8K behaves as a type-I superconductor for fields applied parallel to the c axis, while it behaves as a type-II superconductor for fields applied perpendicular to the c axis.[3] In the case of C_6K and C_3K, the behavior is that of type-II superconductors for all directions of the applied field,[18,21] which indicates a decrease in the coherence distance ξ caused by an increase in disorder and impurity scattering of electrons as the metal density increases.

In the two-band model for superconductivity,[23,34] it was shown that the dependence of the critical field H_{c2} on temperature is obtained by solving the equation

$$1 = V^2 k_B^2 T^2 \sum_n \left(S_n^1 - \frac{\hbar}{2\pi N_\pi(0)\tau_\pi} \right)^{-1} \times \sum_m \left(S_m^{-1} - \frac{\hbar}{2\pi N_s(0)\tau_s} \right)^{-1} , \quad (2)$$

where k_B is the Boltzmann constant, τ_s and τ_p are the lifetimes of the s and π electrons at the Fermi surface, respectively, and

$$S_n = \frac{\pi N_\pi(0)}{\hbar\tilde{\omega}_n} \sqrt{\pi} y_\pi \exp(y_\pi^2)\mathrm{erfc}(y_\pi) , \quad (3)$$

$$S_m = \frac{\pi N_s(0)}{\hbar\tilde{\omega}_m} \sqrt{\pi} y_s \exp(y_s^2)\mathrm{erfc}(y_s). \quad (4)$$

Here, erfc stands for the complementary error function, and

$$y_s = \frac{\hbar\tilde{\omega}_m}{V_{s\perp}} \left(\frac{2c}{e\hbar H_{c2}} \right)^{1/2} , \quad (5)$$

$$y_\pi = \frac{\hbar\tilde{\omega}_n}{V_{\pi\perp}} \left(\frac{2c}{e\hbar H_{c2}} \right)^{1/2} , \quad (6)$$

$$\tilde{\omega}_m = (2m+1)(\pi k_B T/\hbar) + 1/2\tau_s , \quad (7)$$

$$\tilde{\omega}_n = (2n+1)(\pi k_B T/\hbar) + 1/2\tau_\pi , \quad (8)$$

where $V_{s\perp}$ and $V_{\pi\perp}$ are the Fermi velocities of the s and π electrons in the plane perpendicular to the applied magnetic field.[34] Equation (2) is an implicit relation for H_{c2}. It is possible to write an explicit expression for H_{c2} only in the vicinity of T_c for which case H_{c2} is very small, thus making y_s and y_π large, which in turn enables us to replace erfc(y) by only a few terms in its series expansion.

For C_8K, the dependence of H_{c2} on T has been measured for both $H \parallel c$ axis and $H \perp c$ axis and it is found that C_8K behaves as a type-I superconductor for $H \parallel c$ axis. For C_6K the temperature dependence for H_{c2} was also measured for both orientations $H \parallel c$ axis and $H \perp c$ axis.[18,21] To calculate H_{c2} from Eq. (2) we choose reasonable values for the various parameters that appear in this equation.

In the case of C_8K we take τ_s and τ_π to be approximately 10^{-13} s, and $V_{s\perp} = 5.7 \times 10^7$ cm/s. which is the

value for $V_{s\perp}$ obtained if the s band is assumed to be spherical. If the π electrons are taken to be strictly two dimensional, the $V_{\pi\perp}$ will be zero for motion in the plane perpendicular to the magnetic field, since in this case, the field is parallel to the graphite planes. However, due to s-π hybridization at the Fermi surface, we expect $V_{\pi\perp}$ to be small but nonzero. The results of the calculation agree well with experimental observations.[34]

For C_6K, we take $\theta_D \simeq 300$ K, τ_s and τ_p are both taken as 0.5×10^{-13} s, and for an applied field perpendicular to the c axis we again take $V_{s\perp} \simeq 5.7\times10^7$ cm/s and $V_{\pi\perp} = 1.2\times10^7$ cm/s. This is reasonable since one expects $V_{s\perp}$, in going from C_8K to C_6K, to increase on account of the increase in the density of electrons, but to decrease due to the fact that the Fermi surface is now very close to the Brillouin zone edge. As for the case when the field is applied parallel to the c axis, we take $V_{s\perp} \simeq 7\times10^7$ cm/s, which is the value calculated from the increase in the Fermi radius due to the increase in the density of electrons on going from C_8K to C_6K. We further assume that $V_{\pi\perp} \sim 1\times10^8$ cm/s for C_6K, which is approximately the same as that in C_8K. With regard to τ_s and τ_p, we note that for motion of electrons parallel to the graphene layers, the lifetime of the Bloch state is determined by boundary scattering, since the intercalate is expected to form domains with a diameter of $\sim$ 80–100 Å. This gives a value of $\sim 1.2\times10^{-14}$ s for τ_s and τ_p. Note that these values are smaller than those for motion in a plane parallel to the c axis, a consequence of the fact that in an ordered stage compound, the mean free path along the c axis could extend much beyond 100 Å. The calculated results for $H_{c2\|}$ and $H_{c2\perp}$ are plotted in Fig. 1 and are compared with the experimental values; good agreement is achieved. In this notation, $\|$ and $\perp$ stand for magnetic field directions parallel and perpendicular to the c axis.

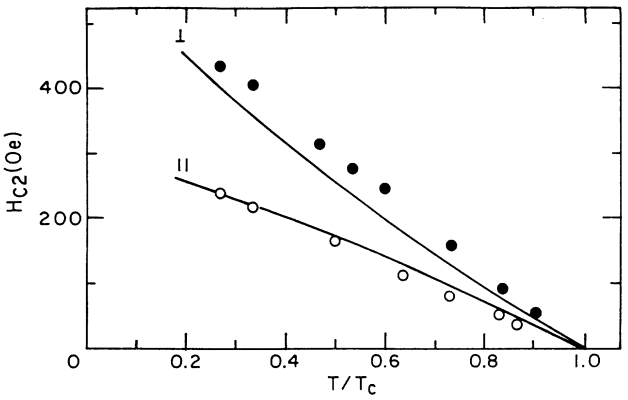

FIG. 1. The calculated results for $H_{c2\|}$ and $H_{c2\perp}$ are plotted and compared with the experimental results of Belas *et al.* (Refs. 18 and 21).

IV. DISCUSSION AND SUMMARY

Recent experiments by Belash *et al.*[18,21] have shown that by using high pressures, high concentrations of alkali metals can be intercalated into graphite, yielding increases in T_c by more than a factor of 20 and increases in critical field by 3 orders of magnitude relative to C_8K. We have shown that the two-band model[23] that was previously used to explain the superconductivity in C_8K could be applied also to explain superconductivity in the higher density alkali-metal compounds, including the approximately linear dependence of $H_{c2}(T)$ over a broad temperature range and the decrease in the anisotropy in H_{c2} with increasing alkali-metal concentration. In particular, the calculated $H_{c2}(T)$ agrees well with experiment with decreasing temperature down to reduced temperatures of $T/T_c \sim 0.3$ for directions of the applied magnetic field both parallel and perpendicular to the c axis. The two-band model successfully accounts for the relative T_c values for the sodium compounds C_4Na, C_3Na, and C_2Na. The corresponding calculation for the C_xK compounds is complicated by the proximity of the Brillouin zone boundary to the Fermi surface. This proximity would tend to make the 3D band less spherical, which in turn, makes the calculation of H_{c2} more difficult. More detailed calculations are needed in this case, possibly using strong coupling theories. Furthermore, Eqs. (1) and (2) that determine T_c and H_c will have to be modified for strong coupling superconductors.

The success of this two-band model hopefully will stimulate further study of the high density alkali-metal GIC's, including measurements of $H_{c2}(T)$ for the C_xNa materials.

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