Model for superconductivity in graphite intercalation compounds

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The observed superconductivity in the stage-1 graphite—alkali-metal intercalation compounds (GIC's) 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 GIC's.

INTRODUCTION

Superconductivity in stage-1 alkali-metal—graphite intercalation compounds (GIC's) (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 has been reported for these compounds. For example, 13 samples of stage-1 K-intercalated graphite prepared from highly oriented pyrolytic graphite (HOPG) were investigated by Koike *et al.*[2] for which the transition temperature ranged from 0.128 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 GIC's, 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 date[5] 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 GIC's 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 GIC's, but it is only for state-1 alkali-metal GIC's 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 state-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 Tanuma[7] and by Pendrys *et al.*[8] through the observation of a Meissner effect. A superconducting transition was also discovered in stage-2 C_8RbHg at 1.44 K by Pendrys *et al.*[8] and Alexander *et al.*[9] The stage-1 compounds C_4KHg and C_4RbHg were found by Iye and Tanuma[10] to undergo a superconducting transition at 0.73 and 0.99 K, respectively. Recent experiments by Tedrow and Timp[11] 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 GIC's 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 $0<\theta<65°$, C_8K behaves as a type-I superconductor which shows magnetic-flux exclusion, whereas for $65°<\theta<90°$, 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 C_8K is $\xi_\perp/\xi_{||}\sim 5$. The anisotropy in the graphite—potassium-amalgam compounds is even higher, with the ratio of the basal to c-axis coherence length $\xi_\perp/\xi_{||}$ being greater than 10 for stage-1 compounds and greater than 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 $\xi_\perp/\xi_{||}\sim 1.3$, which is considerably smaller than the experimental value of ~ 5.

In the next section, we present a different model for superconductivity in alkali-metal GIC's 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 GIC's

In the superconducting GIC's 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-intercalated graphite.[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 surface[13] 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 GIC's.[15] 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 C_6Li would have a superconducting transition temperature approximately 10 times higher than that of C_8K. This estimate is based on the higher density of states at the Fermi surface in C_6Li. However, C_6Li does not show superconductivity down to temperatures ~ 0.1 K.[4]

Superconductivity in GIC's 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

$$H=2\sum_{k_s}\epsilon_{ks}C_{ks}^{\dagger}C_{ks}+2\sum_{K_\pi}\epsilon_{k\pi}C_{k\pi}^{\dagger}C_{k\pi} -\lambda\sum_{k_s,k_\pi}(C_{k\pi\uparrow}^{\dagger}C_{-k\pi\downarrow}^{\dagger}C_{-ks\downarrow}C_{ks\uparrow}+\text{H.c.}) , \tag{1}$$

where ϵ_{ks} and $\epsilon_{k\pi}$ 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 and is assumed to be a constant, and H.c. stands for the Hermitian conjugate. The finite-temperature Green's functions are defined by[17]

$$g_i(k,\tau)=-\langle\mathcal{T}[C_{ki\uparrow}(\tau)C_{ki\uparrow}^{\dagger}(0)]\rangle , \tag{2}$$

$$F_i(k,\tau)=-\langle\mathcal{T}[C_{-ki\downarrow}^{\dagger}(\tau)C_{ki\uparrow}^{\dagger}(0)]\rangle , \tag{3}$$

where $C_{ki\sigma}(\tau)$ $[C_{ki\sigma}^{\dagger}(\tau)]$ is the annihilation (creation) operator for an electron of wave vector k_i and spin σ, $i=s,\pi$, $\langle\ \rangle$ represents thermal averaging, $\mathcal{T}$ is the time-ordering operator, and τ is an "imaginary" time, defined by the equation

$$C_{ki\sigma}(\tau)=\exp[(H-\mu N)\tau/\hbar]\times C_{ki\sigma}(0)\exp[-(H-\mu N)\tau/\hbar] , \tag{4}$$

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 Green's functions defined in Eq. (2) are given by

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

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

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

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

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

in which F is defined by Eq. (3).

The form of the Green's-function equations (5) and (6) implies that the system could be decoupled in terms of s and π Fermi surfaces, each having its own Cooper pair 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

$$\Delta_s=\lambda k_BT\sum_{\omega_n,k_\pi}\frac{\Delta_\pi}{\hbar^2\omega_n^2+\delta\epsilon_{k\pi}^2+|\Delta_\pi|^2} , \tag{9}$$

$$\Delta_\pi=\lambda k_BT\sum_{\omega_n,k_\pi}\frac{\Delta_s}{\hbar^2\omega_n^2+\delta\epsilon_{ks}^2+|\Delta_s|^2} . \tag{10}$$

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

$$kT_c\approx\hbar\omega_c\exp\{-1/|\lambda|[N_s(0)N_\pi(0)]^{1/2}\} , \tag{11}$$

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. We would like to note that neither pristine graphite nor potassium is superconducting. This fact implies that the intraband electron-phonon interaction in potassium and graphite leads only to a renormalization of the electrons' energies. It is the assumption of this model that the intraband electron-phonon coupling in the intercalate system can still be treated as giving rise to only a renormalization of the electrons' energies as in pristine potassium and graphite. The interband electron-phonon coupling, however, exists only in the intercalate system. The interband scattering is then that between the s and π quasielectrons. According to Eq. (11), $T_c\to 0$ as $N_s(0)\to 0$ or $N_\pi(0)\to 0$, 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-intercalated graphite, the density of states $N_\pi(0)$ is lower than that in stage 1 by a factor es-

timated to be $\sim 8.7/5.35$, thus giving a transition temperature an order of magnitude smaller than that in C_8K even if the s band is considered to be appreciably occupied in these stage-2 compounds.

ELECTRODYNAMICS OF SUPERCONDUCTIVITY IN GIC's

In this section we apply the microscopic theory presented in the preceding section to calculate the superconducting coherence length. Based on this estimate, standard results of phenomenological Ginzburg-Landau (GL) theory[18] are used to calculate the experimental parameters of the superconductivity in GIC's.

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

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

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

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

$$\frac{\Delta_s^2}{\Delta_\pi^2}\approx\frac{N_\pi(0)}{N_s(0)}\frac{\ln(2\omega_c/\Delta_\pi)}{\ln(2\omega_c/\Delta_s)}\ , \tag{14}$$

where the cutoff frequency $\omega_c\gg\Delta_s,\Delta_\pi$. For stage-1 K-intercalated graphite, the s band is treated as spherical with a Fermi radius $k_F\approx 4.7\times10^7$ cm^{-1} and the π electrons have a linear dispersion given by

$$\delta\epsilon_{k\pi}=v_F p-\epsilon_F\ , \tag{15}$$

where the Fermi velocity $v_F\approx 9.7\times10^7$ cm/sec and p is the electron momentum.[12] The π electron Fermi cylinder has a c-axis length of $2\pi/I_c$, where $I_c=5.35$ Å for stage-1 K-intercalated graphite. For this model, we have $N_s(0)\approx N_\pi(0)\approx 2\times10^{33}$ cm^{-3}erg^{-1}. Equation (14) then implies that $\Delta_s\approx\Delta_\pi\approx 2k_BT_c$. The Pippard coherence lengths of the s and π bands are estimated[19] as $\xi_{0s}\approx 0.15\hbar v_s/k_BT_c\approx 40\,000$ Å in which v_s is the s-electron Fermi velocity. Similar estimates give $\xi_{0\pi}\approx 70\,000$ Å.

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 $\sim 10^5\ (\Omega\,\text{cm})^{-1}$. 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 $l_s\approx m_s v_s\sigma/n_s e^2\approx 540$ Å 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 l_s to be isotropic. Thus if the magnetic field is applied perpendicular to the c axis, the superconductor is in the dirty limit because $l_s\ll\xi_{0s}$. The London penetration depth is given by $\lambda_L(0)=(m_sc^2/4\pi n_se^2)^{1/2}\approx 1000$ Å. For dirty superconductors, the GL parameter κ is given by[18] $\kappa\approx 0.715\lambda_L(0)/l\approx 1.3$. Since $\kappa>1/\sqrt{2}$, the superconductor is type II for magnetic fields in the plane of the graphite. The GL coherence length at $T=0$ is $\xi(0)\approx 0.9\sqrt{\xi_0 l}$, where ξ_0 is the Pippard coherence length and l is the electron mean free path.[18] Then the upper critical magnetic field H_{c2} is

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

in which $\phi_0\approx 2.07\times10^{-7}$ G cm^2 is the flux quantum.

Using the approximation[18]

$$\xi(T)\approx 0.855[\xi_0 l/(1-T/T_c)]^{1/2}\ , \tag{17}$$

which holds for temperatures near T_c, we find that at $T=2T_c/3$ the critical magnetic field is $H_{c2}(T=0.67T_c)\approx 8.5$ G. Experimentally, the value of $H_{c2}(T=0.67T_c)$ is found to be ~ 12–19 G for C_8K when the magnetic field is applied perpendicular to the c axis.[2]

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 C_8K at 4 K is[20] $\sigma\approx 10^7\ (\Omega\,\text{cm})^{-1}$, and it is mainly due to π electrons, the mean free path of the π electrons l_π is very large and is comparable to the coherence length ξ_π. Thus in the field orientation $H\|c$ axis the superconductor is not in the dirty limit. Because $l_\pi\gg l_s$, it follows that the π-electron supercurrent is dominant. The penetration depth is then determined by the π-electron parameters. Therefore, in this case, $\lambda_L(0)\approx(m_\pi c^2/4\pi n_\pi e^2)^{1/2}\approx 400$ Å, where m_π is taken as $\sim 0.25m_0$, 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

$$H_c(0)^2=4\pi[N_s(0)\Delta_s^2+N_\pi(0)\Delta_\pi^2]\ . \tag{18}$$

By using $N_s(0)\approx N_\pi(0)=2\times10^{33}$ cm^{-3}erg^{-1}, $\Delta_s\approx\Delta_\pi\approx 2k_BT_c$ where $T_c\approx 0.15$ K, $H_c(T=0)$ is found to be ~ 9.3 G. At $T=0.67T_c$, the critical field is given by

$$H_c(T=0.67T_c)\approx H_c(0)[1-(T/T_c)^2]\approx 5.2\ ,$$

measured in G. This value for $H_c(T=0.67T_c)$ agrees very well with the experimental values of 5–7 G.[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 GIC's.

DISCUSSION AND CONCLUSIONS

Although the detailed estimates carried out in the preceding section were specific to C_8K, the model presented in this paper is generally applicable to other superconducting GIC's, such as potassium- and rubidium-amalgam GIC's. At present, however, there are no detailed band-structure calculations for these compounds. Experimental work is in progress[21] 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 fac-

tor 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 $p(\sqrt{3}\times\sqrt{3})R30°$ 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 tenfold increase in T_c.

In the discussion to follow, all primed quantities refer to the situation where the intercalate layer has the $p(\sqrt{3}\times\sqrt{3})R30°$ structure, and the unprimed quantities refer to the $p(2\times 2)R0°$ 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 $n_s' = (\frac{4}{3}\times\frac{1}{2})n_s$ and consequently $\epsilon_F' = (\frac{2}{3})^{2/3}\epsilon_F \approx 0.75\epsilon_F$. The s-electron density of states is estimated as $N_s'(0) = (\frac{2}{3})^{1/3}N_s(0) \approx 0.87N_s(0)$. In contrast for the π electrons, the dispersion is linear and is given by

$$\epsilon' = \hbar v_F' k_\perp' - \epsilon_F' \ . \tag{19}$$

The Fermi wave vector of the π electrons $k_{F\perp}'$ is $k_{F\perp}' \approx \frac{4}{3}k_{F\perp}$; thus we estimate $v_F' \approx 0.56v_F$. Since the single-spin density of states at the Fermi surface of the π electrons is given by

$$N_\pi'(0) = (k_c'/2\pi^2)(k_{F\perp}'/\hbar v_F') \approx 2.4N_\pi(0) \ ,$$

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

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

If the cutoff frequency is $\omega_c \approx 250$ K, then for $T_c \approx 0.15$ 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 $T_c' \approx 10T_c \approx 1.5$ 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-intercalated graphite than in C_8K. X-ray measurements show that the intercalate concentration is lower in stage-1 Cs-intercalated graphite than in stage-1 Rb-intercalated graphite, which in turn is lower than in C_8K.[24] Moreover, Knight-shift measurements[25] show that the fractional charge transfer in C_8K is higher than in stage-1 Rb- and Cs-intercalated graphite. Consequently, the π-electron density of states in stage-1 Rb- and Cs-intercalated graphite 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-intercalated graphite[5] 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 GIC's 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 GIC's 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. By 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 $T_c \approx 0.22$ 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 Refs. 1–3.

We conclude by noting that the model presented above explains the most important features of the superconducting GIC's. It explains the absence of superconductivity in C_6Li and higher-stage alkali-metal GIC's. 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 $p(\sqrt{3}\times\sqrt{3})R30°$ 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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[1]N. B. Hannay, T. H. Geballe, B. T. Matthias, K. Andres, P. Schmidt, and D. MacNair, Phys. Rev. Lett. 14, 225 (1965).

[2]Y. Koike, H. Suematsu, K. Higuchi, and S. Tanuma, Solid State Commun. 27, 623 (1978); J. Phys. Chem. Solids 41, 1111 (1980).

[3]M. Kobayashi and I. Tsujikawa, J. Phys. Soc. Jpn. 46, 1945 (1979).

[4]Y. Iye and S. Tanuma, Solid State Commun. 44, 1 (1982); Y. Iye, in *Materials Research Society Symposium Proceedings on Intercalated Graphite, Boston, 1982,* edited by M. S. Dresselhaus, G. Dresselhaus, J. E. Fischer, and M. J. Moran (North-Holland, New York, 1983).

[5]M. Kobayashi and I. Tsujikawa, Physica 105B, 439 (1981); J. Phys. Soc. Jpn. 50, 3245 (1981).

[6]M. G. Alexander, D. P. Goshorn, D. Guerard, P. Lagrange, M. El-Makrini, and D. G. Onn, Synth. Met. 2, 203 (1980).

[7]Y. Koike and S. Tanuma, J. Phys. Soc. Jpn. 50, 1964 (1981).

[8]L. A. Pendrys, R. Wachnik, R. L. Vogel, P. Lagrange, C. F. Furdin, M. El-Makrini, and A. Herold, Solid State Commun. 38, 677 (1981).

[9]M. G. Alexander, D. P. Goshorn, D. Guerard, P. Lagrange, M. El-Makrini, and D. G. Onn, Solid State Commun. 38, 103 (1981).

[10]Y. Iye and S. Tanuma, Phys. Rev. B 25, 4583 (1982).

[11]P. Tedrow and G. Timp (private communication).

[12]Y. Takada, J. Phys. Soc. Jpn. 51, 63 (1982).

[13]T. Inoshita, K. Nakao, and H. Kamimura, J. Phys. Soc. Jpn. 43, 1237 (1977); 45, 689 (1978).

[14]T. Ohno, K. Nakao, and H. Kamimura, J. Phys. Soc. Jpn. 47, 1125 (1979).

[15]Y. Iye, in *Materials Research Society Symposium Proceedings on Intercalated Graphite, Boston, 1982,* edited by M. S. Dresselhaus, G. Dresselhaus, J. E. Fischer, and M. J. Moran (North-Holland, New York, 1983).

[16]H. Suhl, B. T. Matthias, and L. R. Walker, Phys. Rev. Lett. 3, 552 (1959).

[17]See, for example, A. A. Abrikosov, L. P. Gorkov, and I. E. Dzyaloshinski, *Methods of Quantum Field Theory in Statistical Physics* (Dover, New York, 1975).

[18]M. Tinkham, *Superconductivity* (Gordon and Breach, New York, 1966).

[19]A. L. Fetter and J. D. Walecka, *Quantum Theory of Many Particle Systems* (McGraw-Hill, New York, 1971).

[20]H. Suematsu, K. Higuchi, and S. Tanuma, J. Phys. Soc. Jpn. 48, 1541 (1980).

[21]G. Timp, B. S. Elman, M. S. Dresselhaus, and P. Tedrow, in *Proceedings of the Materials Research Society Annual Meeting, Boston, 1982,* edited by M. S. Dresselhaus, G. Dresselhaus, J. E. Fischer, and M. J. Moran (North-Holland, New York, 1983).

[22]L. E. De Long, V. Yeh, P. C. Eklund, S. E. Lambert, and M. B. Maple, in *Proceedings of the Materials Research Society Annual Meeting, Boston, 1982,* edited by M. S. Dresselhaus, G. Dresselhaus, J. E. Fischer, and M. J. Moran (North-Holland, New York, 1983).

[23]C. E. Fuerst, D. Moses, A. Devenstein, A. J. Heeger, and J. E. Fischer, Bull. Am. Phys. Soc. 26, 451 (1981).

[24]S. Y. Leung, C. Underhill, T. Krapchev, D. Dresselhaus, M. S. Dresselhaus, and B. Wuensch, Phys. Rev. B 24, 3505 (1981).

[25]J. Conard, H. Estrade, P. Lauginie, H. Fuzellier, G. Furdin, and R. Vosse, Physica 99B, 521 (1980).