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Large anisotropy and stage dependence of the magnetic susceptibility of alkali-graphite intercalation compounds

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We have measured the magnetic susceptibility of alkali-graphite intercalation compounds for $\vec{H}$ parallel to the hexagonal $\vec{c}$ axis (χ^c) and for $\vec{H}\perp\vec{c}$ (χ^a) from 4.2 to 300 K. We find (1) χ^c is large and paramagnetic and (2) the ratio of the molar values of χ^c and the Pauli contribution to the susceptibility (χ_P) as inferred from the specific heat increases rapidly as a function of stage, varying from about 2.4 in stage 1 to 17 in stage 4. The ratio χ^c/χ_P is essentially independent of which alkali metal is intercalated (at least at stage 1). The stage dependence of χ^c/χ_P is in qualitative agreement with the results of a calculation of the π-electron orbital contribution to the susceptibility of graphite intercalation compounds. The orbital part of the susceptibility is shown to be sensitive to the conduction-electron charge distribution from layer to layer in stage 3 and higher compounds, while the spin susceptibility and specific-heat coefficient are less sensitive to this distribution.

The study of graphite intercalation compounds[1] has recently been spurred by the observation of high basal-plane electrical conductivities[2] and by the observation of order-disorder transitions in the intercalant layers.[3] Further, a rich variety of chemical and physical differences are associated with different "stage" compounds of the same intercalant. (The stage of the intercalation compound is equal to the number of graphite layers between each intercalate layer and is denoted by n.) A problem of current interest is the stage dependence of the c-axis conduction-electron charge distribution in these materials.[4-6] Recent calculations[4] and experiments[5,6] indicate that most of the charge is localized in the graphite layers which bound the intercalate, with only a small fraction of the charge in the remaining $n-2$ graphite layers (interior layers). In this paper we report measurements of the magnetic susceptibility in graphite intercalation compounds, an experiment which is sensitive to the c-axis charge distribution.

Recently we measured the temperature dependence of the magnetic susceptibility of the second-stage compound KC_{24}.[7] Since these data showed no anomalies at those temperatures where large resistive anomalies were observed,[8] we concluded that structural effects (order-disorder of intercalant) rather than electronically driven transitions were involved. However, we observed two other interesting features of the susceptibility: (1) The susceptibility shows a large anisotropy; (2) the susceptibility measured with $\vec{H}\parallel\vec{c}$, χ^c, is a factor of 7.5 larger than that expected from the spin-only (Pauli) contribution, χ_P, as calculated from the density of states at the Fermi level derived from specific-heat data. Here, we report on the stage and temperature dependence of a number of alkali-graphite intercalates and show that both the anisotropy and the ratio χ^c/χ_P increase as the compound stage is increased, but that these factors are rather insensitive to which alkali metal is intercalated.

Section I describes the susceptibility experiments and the observed stage and temperature dependence of χ^c. The existence of *paramagnetic* ring currents in organic molecules reduced with alkali metals is discussed in Sec. II, since this fact leads us to study a two-dimensional model which explains the large values of χ^c measured here. In Sec. III, the experimental results are interpreted with the aid of calculations[9] of the orbital and spin susceptibilities of a single graphite layer as a function of the Fermi level μ for $0<\mu<3$ eV. The paramagnetic enhancement of the total susceptibility (χ^c) over the Pauli contribution is related to the two-dimensional band structure. The calculated susceptibility of the sample is sensitive to the c-axis charge distribution in graphite intercalation compounds. The stage dependence of χ^c is discussed in Sec. IV where suggestions for further experiments are presented.

I. RESULTS

The samples were prepared from highly oriented pyrolytic graphite (HOPG) by the usual two-bulb method.[10] The HOPG was previously cut into square 4×4 mm pieces, with thickness 2–3 mm perpendicular to the layers. The stage was checked by sample color and expansion during in-

TABLE I. Room-temperature (295K) susceptibilities χ of graphite and alkali-graphite compounds in cgs units (per gram or mole). The last columns list the estimated core diamagnetic contribution χ_0, the Pauli contribution χ_P, and the ratio $(\chi^c-\chi_0-\chi_P)/\chi_P \equiv \chi^c_{or}/\chi_P$. χ_P is calculated from the linear term in the specific heat.

Material	$10^6\chi_g$ (χ^c_g) $\vec{H}\parallel\vec{c}$	$10^6\chi_g$ $\vec{H}\perp\vec{c}$	$10^6\chi_M$ (χ^c_M) $\vec{H}\parallel\vec{c}$	$10^6\chi_M$ $\vec{H}\perp\vec{c}$	$10\Delta\chi_M$ $\chi_\parallel-\chi_\perp$	$10^6\chi_0$ (Est.)	$10^6\chi_P$	$\frac{\chi^c-\chi_0-\chi_P}{\chi_P}\equiv\frac{\chi^c_{or}}{\chi_P}$
C (Ref. 9)	−21.0	−0.3	− 252	− 3.6	− 248			
C (this exp)	−21.1	−0.43	− 253	− 5.2	− 248			
KC_8	1.02	+0.28	+ 138	+37.9	100	− 52	86 (Ref. 10)	1.2
KC_{24}	1.50	+0.05	+ 491	+16.4	475	−128	83 (Ref. 10)	6.5
KC_{36}	1.75	−0.02	+ 825	− 9.4	835	−188	95 (Ref. 10)	9.7
KC_{48}	1.87	−0.06	+1150	−36.9	1187	−246	82 (est.)	16.0
KC_8	1.02	+0.28	+ 138	+37.9	100	− 52	86 (Ref. 10)	1.2
RbC_8	0.66	+0.05	+ 120	+ 9	111	− 60	...	
CsC_8	0.48	0.00	+ 110	0.0	110	− 77	78 (Ref. 10)	1.4
LiC_6	1.17	+0.38	+ 92.4	+30.0	62.4	− 29	41 (Ref. 12)	1.9

tercalation, and verified after the susceptibility measurements by x-ray diffraction. The samples were removed from the pyrex reaction tubes in an He atmosphere dry box with O_2 and H_2O levels below 1 ppm. They were then loaded and sealed in rectangular quartz tubes so that the hexagonal *c* axes of the pieces were all parallel. The temperature dependent susceptibility was obtained from 4.2 to 300 K for $\vec{H}\parallel\vec{c}(\chi^c)$ and $\vec{H}\perp\vec{c}(\chi^a)$ in a standard Faraday apparatus, modified so that the crystals could not rotate. This method is accurate if the anisotropy is not too large,[11] but *underestimates* the anisotropy if it becomes large. We have previously shown, by comparison to torque measurements, that this method is accurate when the anisotropy (χ^c/χ^a) is about 3.[12] For larger anisotropies, we estimate the experimental accuracy by measuring χ^c and χ^a of pure graphite and compare to the known values.[13] The result is shown in Table I. In a Faraday apparatus the force on the sample when $\vec{H}\parallel\vec{c}$ is given by $F_c=\alpha(\chi^c+k\chi^a)$ where α is a proportionality constant and k is much less than 1.0. The term k is proportional to the secondary gradients in the magnetic field that are usually ignored.[11] A similar expression for $\vec{H}\perp\vec{c}$ shows that if $\chi^c \gg \chi^a$, a large error may result in the value measured for χ^a, i.e., $F_a=\alpha(\chi^a+k\chi^c)$. The apparatus is calibrated by measuring the susceptibility of an *isotropic* standard, so $F_{std}=\alpha(1+k)\chi_{std}$. (The standard susceptibility is known with an *absolute* accuracy of ±2%.) The values listed in Table I were obtained by dividing the measured force by $\alpha(1+k)$, thus $\chi^c_{measured}=(\chi^c+k\chi^a)/(1+k)$ and $\chi^a_{measured}=(\chi^a+k\chi^c)/(1+k)$. That is, the value listed in Table I, $\chi^c_{measured}$, will be slightly less than the true χ^c, and $\chi^a_{measured}$ could be significantly different from χ^a. By comparing our results on pure graphite to published values, we find $k \leq 0.01$. Thus even when the anisotropy ratio $|\chi^c/\chi^a| \approx 50$, we measure χ^c to ±2% and determine χ^a to ±50% or better.

The samples measured were the first-stage compounds LiC_6, KC_8, RbC_8, and CsC_8, and the second-, third-, and fourth-stage potassium compounds KC_{24}, KC_{36}, and KC_{48}. The results are summarized in Table I where the room-temperature susceptibilities per gram χ_g, per formula weight χ_M for $\vec{H}\parallel\vec{c}$ and $\vec{H}\perp\vec{c}$, and also the anisotropy $\Delta\chi_M=\chi^c_M-\chi^a_M$ are given. All these susceptibilities are independent of magnetic field from 2.5 to 13 kG. The susceptibility of LiC_6 is essentially temperature independent. χ^c_g of the other first-stage compounds KC_8, RbC_8, and CsC_8 decreases slightly (and linearly) from 300 to 70 K ($d\chi^c_g/dT$ is approximately -1.0×10^{-10} emu/K g), but below 50K χ_g is temperature independent. The susceptibilities of the first- through fourth-stage potassium intercalates are shown in Fig. 1. It is immediately apparent that the anisotropy as well as the temperature dependence of χ^c_g increase as

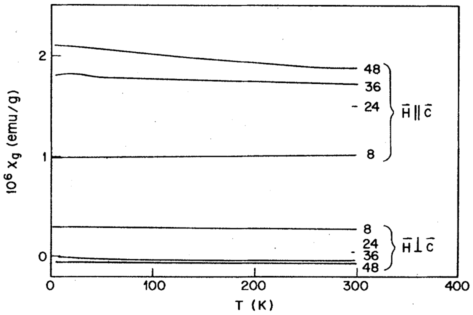

FIG. 1. The temperature dependence of stage 1, 3, and 4 potassium-graphite intercalation compounds (KC_8, KC_{36}, KC_{48}). When $\vec{H}\parallel\vec{c}$ there is a significant increase in the susceptibility of the 4th stage compound as the temperature is decreased.

the stage increases (or equivalently as the alkali concentration decreases). These large anisotropies probably explain the large scatter in the values of previously reported susceptibilities.[14] These experimenters studied powder samples, in which some preferred orientation can occur due to the laminar nature of the particles.

The data in Table I clearly show that the molar anisotropy *increases* with decreasing alkali metal content, and that at constant composition (KC_8, RbC_8, CsC_8) the molar anisotropy is essentially constant. The appropriate susceptibility to compare is indeed the *molar* value, since the *total* conduction electron density (in both the graphite and alkali layers) is determined by the alkali concentration. (The intrinsic carrier density of graphite is only about 1 carrier/10^4 carbon atoms.[15]) Also note that χ_g^c is large and paramagnetic in contrast to graphite, where it is large and diamagnetic.

II. ORIGIN OF THE PARAMAGNETISM IN GRAPHITE INTERCALATES: ORGANIC CHEMICAL PRECEDENTS

It is known that the large diamagnetic susceptibility of certain aromatic organic compounds[16,17] is converted to a paramagnetic susceptibility on reduction of these materials with alkali metals.[18-21] This latter effect (which is *not* associated with the presence of unpaired electrons), is usually referred to as a *paramagnetic* ring current. Diamagnetic ring currents were recognized some time ago and arise from the molecular currents which are induced to flow around the peripheral π-orbital network of aromatic compounds (e.g., benzene) in the presence of a magnetic field.[22,23]

Both [18]annulene[20] and 15,16-dimethyldihydrophyrene[19] undergo alkali-metal reduction to divalent anions in solution, and they show evidence for strong induced paramagnetic ring currents. It has been estimated that the ring current susceptibilities are: −36 (benzene),[21] −274 ([18]annulene),[21] −195 (15,16-dimethyldihydropyrene),[21] 718 ([18]annulene^{2-}),[24,25] 758 ([18]annulene^{2-}),[24,26] and 728 (15,16-dimethyldihydropyrene^{2-}),[21] all $\times 10^{-6}$ emu/mole (where $\vec{H}$ is perpendicular to the plane of the ring). Condensed benzenoid aromatic hydrocarbons show similar effects,[18] although the magnitude of the susceptibilities are smaller than those associated with the monocyclic molecules mentioned above. Paramagnetic ring currents in molecules are brought about by the configurational mixing between the occupied and vacant orbitals which occurs in the presence of a magnetic field and lowers the total energy. Magnetic dipole transitions from the highest occupied molecular orbital (MO) to the lowest unoccupied MO are primarily responsible for the effect.[27] As we discuss below and describe in detail in the following paper, the paramagnetism in graphite intercalates arises in a similar manner.

III. INTERPRETATION OF EXPERIMENTAL RESULTS

The total susceptibility is the sum of several contributions.[28] $\chi = \chi_P + \chi_0 + \chi_{\text{or}}$, where χ_P is the Pauli susceptibility, χ_0 is the core diamagnetism, and χ_{or} is the sum of the intraband and interband contributions to the susceptibility due to the orbital motion of the electrons. We can estimate χ_P by using the density of states at the Fermi level (DOS) computed from the linear term in the measured specific heat. Since the linear term is essentially independent of the stage or the alkali metal intercalculated,[29] and since the specific heat of KC_{48} has not been reported, we use for KC_{48} the value measured for CsC_{48}. In this procedure we neglect the electron-phonon enhancement of the electronic specific heat and also the electron-electron enhancement of χ_P. However, since these compounds are not superconductors or have only very low superconducting T_c, the former is expected to be small (<25%). On the other hand, one might expect a sizable enhancement of χ_P by as much as 50–100%, due to many-body effects in the dilute electron gas. This would result in a reduction of the observed values for χ_{or}^c reported in the last column of Table I. We compute χ_0 by taking the average diamagnetic contribution of a mole of carbon to be -4.8×10^{-6} and of K^+ to be -13×10^{-6}, of Rb^+ to be -21×10^{-6}, and of Cs to be -39×10^{-6}, all in units of emu/mole.[14] Both χ_P and χ_0 are isotropic, since the electron g values are isotropic,[14] and the core diamagnetism is essentially isotropic even in an anisotropic compound. The results are shown in Table I where the ratio $r \equiv (\chi_c - \chi_0 - \chi_P)/\chi_P = \chi_{\text{or}}^c/\chi_P$ is shown in the last column. These ratios increase from about 1.4 in the first-stage compounds to 16 in stage-four compounds.

The two main features of the experimental data, a large paramagnetic value for χ^c and the increase in r as the stage increases (and the concentration of alkali metal *decreases*), can be understood in the light of a recent calculation[9] of the magnetic susceptibility of graphite for $\vec{H} \parallel \vec{c}$. The calculation uses the simple two-dimensional tight-binding π band structure first proposed by Wallace,[30] along with the formula for the orbital susceptibility derived by Fukuyama.[31] Previous calculations of χ_{or}^c for graphite have been performed in the context of the Slonczewski-Weiss model, developed to treat the case of $\approx10^{-4}$ carries per carbon atom (Fermi energy 0.02 eV) appropriate to pure graphite.[32] However, since the charge transfer in graphite intercalation compounds has been estimated to be as large as 10^{-1} carrier/(carbon atom), it is necessary to use a band structure appropriate to a much larger region in energy (Fermi energy as large as 1.5 eV). In the absence of a detailed three-dimensional band structure for stage $n > 1$ intercalation compounds which takes into account the screening of the intercalate layer, the single-layer tight-binding model has been used. This model contains the essential feature of band degeneracy at the K point in the Brillouin zone. Except for the conduction-electron charge density (excess charge) per carbon atom in a given layer (ρ_i, $i = 1, \ldots, n$) which fixes the Fermi level of each layer, the calculation contains no adjustable parameters, since the tight-binding parameter $\gamma_0 = 3.11$ eV is obtained from measurements on pure graphite.[33]

The details of the calculation are given in the following paper. Here, we note that χ^c_{or} contains both interband and intraband terms, with the intraband terms corresponding to the Landau-Peierls susceptibility which dominates away from the degeneracy point. The orbital (χ^c_{or}) and spin (χ_P) contributions to the susceptibility of a single graphite layer as a function of μ_i/γ_0 is shown in Figs. 2 and 3 for $kT/\gamma_0 = 0.0083 = 300$K. Here μ_i represents the contribution to the Fermi energy due to the additional conduction electrons only, so that the Fermi level μ is given by $\mu = \mu_i + V_i$, where V_i is the electrostatic potential of layer i due to the screened intercalate layer. χ_P is proportional to the DOS and thus has a logarithmic singularity at $\mu_i/\gamma_0 = 1$. The orbital susceptibility χ^c_{or} is large and diamagnetic for $\mu_i/\gamma_0 < 0.03$ (Fig. 3), in agreement with previous calculations.[33] However, for $\mu > kT$ the susceptibility becomes less negative, reaching a maximum positive value at $\mu_i \approx 8kT$. For $8kT < \mu_i < \gamma_0$, χ^c_{or} is paramagnetic and always larger than χ_P. In the following paper it is shown that the unusual behavior of χ^c_{or} is due to the peculiar two-dimensional band structure of graphite for $\mu_i/\gamma_0 < 2$, where $m^2/m_{xx}m_{yy} < 0$ ($m_{\alpha\beta}$ is the effective-mass tensor), in contrast to the situation for free electrons in parabolic bands.

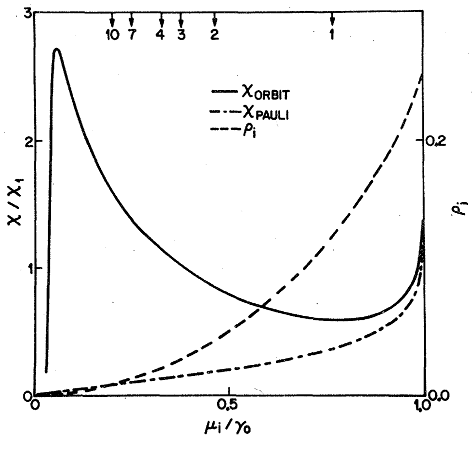

FIG. 2. The calculated orbital and Pauli susceptibility for a tight binding model of a single graphite layer as a function of the Fermi energy μ/γ_0, for $k_BT/\gamma_0 = 0.0083$ (300 K). The constant χ_1 is approximately 2×10^{-6} emu/cm^3. The right hand scale is for ρ_i, the number of electrons per carbon atom in the ith layer. At the top of the figure we indicate the Fermi level for stage 1 through 10 compounds, *assuming* $f = 1$ and a *uniform* charge density in all graphite layers.

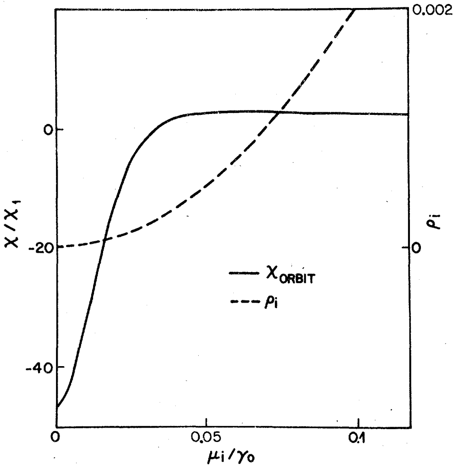

FIG. 3. The calculated orbital susceptibility and conduction-electron concentration ρ_i (electrons per carbon atom) for small values of μ/γ_0.

To compare this theory with the experimental data, we note that in Figs. 2 and 3 the normalizing factor χ_1 is equal to 6.7×10^{-14} emu/cm^2 when $\gamma_0 = 3$ eV. Experiments[34] and band calculations[35] for LiC$_6$ suggest that the Li is completely ionized (i.e., the charge transfer f is 1.0), and we calculate $\chi_P = 30 \times 10^{-6}$ emu/mole and $\chi_{\mathrm{or}} = 39 \times 10^{-6}$ emu/mole from Fig. 2 (i.e., $\rho_i = 0.167$ fixes the Fermi energy at which χ_{or} and χ_P are obtained). The theoretical Pauli susceptibility is about 25% smaller than the experimentally derived value, but the theoretical orbital contribution is a factor of 2.0 smaller than the experimentally derived value. Since in this case the evidence for $f = 1$ is quite strong, we use this as a quantitative test of our simple two-dimensional model. While the agreement between the model and more sophisticated calculations is quite good at small μ/γ_0, the results on LiC$_6$ suggest that at high μ/γ_0 the model is quantitatively correct within perhaps a factor of 1.5 to 2.0. The situation for the other first-stage compounds is less satisfactory. We calculate from Fig. 2, assuming $f = 1$, that $\chi_P = 31 \times 10^{-6}$ emu/mole and $\chi_{\mathrm{or}} = 50 \times 10^{-6}$ emu/mole. These values are about a factor of 2.5 too small. This discrepancy must be due in part to our assumption that $f = 1$, since calculations and experiments suggest that $f \approx 0.5$. In that case we have neglected the susceptibility of the electrons remaining in the potassium layer, and these apparently account for at least half of the overall susceptibility. The present model with the choice of $\gamma_0 = 3$ eV always *underestimates* the experimental data. Inclusion of higher-order overlaps changes the band structure to some extent, the logarithmic singularity in the DOS occurs at $\mu/\gamma_0 \approx 0.6$ instead of at $\mu/\gamma_0 = 1.0$ in our simpler model. This would produce higher values of the DOS and hence results for the χ_P in stage 1 compounds in better agreement with experiment. However, the value of our simplified model lies in its ability to describe the trends in $\chi^c_{\rm or}$ as a function of stage, in qualitative agreement with experiment.

IV. STAGE DEPENDENCE OF χ^c AND c-AXIS CHARGE DISTRIBUTION

The stage dependence of the susceptibility of graphite intercalation compounds ($n \geq 2$) can also be estimated from our model. In particular, the measured ratio $r \equiv \chi^c_{\rm or}/\chi_P$ per mole of intercalant is given by $r = \sum_{i=1}^n \chi^c_{\rm or}(i)/\sum_{i=1}^n \chi_P(i)$, where the index i labels the n graphite layers between the alkali layers. This expression assumes that the Pauli susceptibility is due *only* to conduction electrons in the graphite (or equivalently that the charge transfer from the alkali to the graphite is complete, $f = 1.0$). NMR measurements in CsC_{24} suggest that $f = 1.0$ in second- or higher-stage compounds.[36]

The electron distribution for second-stage compounds ($n = 2$) is uniform by symmetry, so $\rho_i = 0.0417$ (i.e., $\frac{1}{24}$). We then calculate from Fig. 2 that $\chi^c = 47 \times 10^6$ emu/mole and $\chi_{\rm or} = 218 \times 10^6$ emu/mole. These values are about a factor of 2 smaller than the experimentally derived values (Table I). Interestingly the ratio r is 4.6, close to the experimental value of 6.5. We are presently uncertain as to the source of the discrepancy between the theoretical and experimental estimates. It is possible that $f < 1.0$, and neglect of the interlayer overlap between adjacent graphite layers may be oversimplified. Also there is possibly some error in the estimated χ_P due to enhancements previously discussed. However, the trend shown in Fig. 2 of $\chi_{\rm or}/\chi_P$ increasing with increasing n is in obvious agreement with the data of Table I. This indicates that while more realistic band-structure calculations are necessary for a quantitative comparison with experiment, the single-layer model of Figs. 2 and 3 does account for the two main features of the data: (1) the large *paramagnetic* contribution of $\chi^c_{\rm or}$ and (2) the enhancement of $\chi^c_{\rm or}/\chi_P$ due to the decrease in ρ_i as a function of stage.

For stage n ($n > 2$) compounds there are two bounding layers (on each side of the alkali layer) and $n - 2$ interior layers. The theoretical value for r will depend sensitively upon the charge distribution in the interior layers. To illustrate this we consider two cases: (1) the conduction-electron density is the same in each graphite layer (bounding and interior) and (2) the conduction-electron density decreases on the interior layers due to a screening of the alkali layers. The latter model is supported by recent theoretical[4] and experimental[5,6] work, while the former was assumed in earlier work.[37] If the electron density remains uniform, then ρ_i for all layers decreases with increasing n and theoretical values of r ($n = 3$) and r ($n = 4$) are 7.0 and 9.0, respectively. These values are within factors of 2 of the actual data and show the correct trend. Owing to the present uncertainties concerning the charge transfer and the simplicity of the two-dimensional calculation, our data *alone* can not eliminate the uniform charge-density model. This model, however, predicts that r will continue to increase with increasing stage to $r_{\rm max} \approx 100$ at $n_{\rm max} \approx 80$ (from Fig. 2). On the other hand the screening model will lead to smaller maximum r occuring at a lower stage. As an extreme example consider the case in which all the conduction-electron density resides in the bounding layers only. Then for $n \geq 3$ the interior layers would be similar to graphite and have an enormous diamagnetic susceptibility (see Table I). The *total* susceptibility for $n \geq 3$ would be diamagnetic and r would be negative. Consequently r would reach a maximum value at $n = 2$. The data do not support such a short screening length.[38] However, if the conduction-electron density in the interior layers is only a few percent of the bounding layer density so that $\chi^c_{\rm or}$ is near the peak shown in Fig. 2, the theoretical values of r would be 11 and 20 for $n = 3$ and 4, respectively. These values are closer to the actual data (9.7 and 16, respectively) and show the observed trend with stage. Further, the 12% increase of χ^c in KC_{48} as the temperature is lowered is consistent with $\mu_i/\gamma_0 \approx 0.05$ in the interior layers, as estimated from the model calculation at 30 and 300 K (see the following paper). That is, we roughly estimate that the conduction-electron density in the interior layers is only several percent of that of the bounding layers (assuming $f \approx 1$) and the ratio of the Fermi energy to room temperature in the interior layers μ/kT is 6. This result does give a low value of μ, but this may not be low enough to explain the presence of an infrared mode apparent in $n \geq 3$ stage compounds which occurs at the same frequency in graphite.[5]

V. CONCLUSIONS

We have experimentally shown that the magnetic susceptibility χ^c as well as the anisotropy χ^c/χ^a increase with increasing stage. At the same time, χ^c becomes much larger than χ_P estimated from specific heat measurements. We present a simple tight-binding model that semiquantitatively explains these results. The central result of this model will be unchanged in more sophisticated calculations: as the screening length decreases from infinity (uniform charge density) both $r_{\max}$ and $n_{\max}$ will decrease. Consequently the calculated value of χ^c vs stage is a sensitive function of the assumed screening length. While this conclusion is independent of the particular model assumed, the exact functional form of r vs n will also depend upon, for example, the band parameters (such as γ_0), the *interlayer* wave-function overlap, and the fractional charge transfer f. Recent experiments[5,6] and theory[4] indicate that this screening length is indeed rather short. If this is so, we should see r decrease (or become negative) at some stage between about 5 and 10. Further experiments on samples of higher stage ($n > 4$) are underway to test these ideas.

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