PHYSICAL REVIEW B VOLUME 25, NUMBER 3 1 FEBRUARY 1982

Absolute spin susceptibility of LiC_6: Density of states and orbital paramagnetism

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(Received 6 July 1981)

We have measured the absolute spin (Pauli) susceptibility χ_p of the stage-1 graphite donor intercalation compound LiC_6 using the ESR-NMR method pioneered by Shumacher and Slichter. The Fermi-level density of states agrees well with a simple two-dimensional rigid-band prediction assuming complete charge transfer. The agreement is less good with the value derived from a rigorous band calculation by Holzwarth *et al.* Comparing χ_p with the total susceptibility χ_{tot}^c (measured via Faraday balance with $\vec{H} \parallel c$) and correcting for core diamagnetism using Pascal's constants, we find an orbital (Landau-Peierls) contribution which is *para*magnetic and comparable in magnitude to χ_p. This confirms the theory of Safran and DiSalvo predicting that the large, anisotropic orbital diamagnetism of graphite becomes small and paramagnetic when the Fermi energy is raised. The LiC_6 data are contrasted with similar results for a typical stage-1 acceptor compound C_8AsF_5.

I. INTRODUCTION

Measurements of the total static susceptibility χ_{tot} are often used to determine the overall metallic behavior of conducting materials. The usual procedure for nonmagnetic substances is to assume $\chi_{\text{tot}} = \chi_p + \chi_{\text{orb}} + \chi_0$ where χ_p is the spin, or Pauli, susceptibility, χ_{orb} is the inter- and intraband orbital susceptibility (often referred to as Landau diamagnetism), and χ_0 is the diamagnetism of the atomic cores. The Pauli term is given by $\chi_p = \mu_B^2 N(E_F)$ where $N(E_F)$ is the density of states at the Fermi energy (including both signs of spin) and is the quantity of fundamental interest characterizing the metal. To obtain this quantity, χ_{tot} must be corrected for χ_{orb} and χ_0. We note that χ_0 is isotropic by definition, χ_p is usually essentially isotropic (any anisotropy arises from anisotropy in the g value), while χ_{orb} and χ_{tot} are anisotropic if the crystal is noncubic.

Graphite and its derivatives provide interesting applications of this approach. For pure single-crystal graphite χ_p is negligible since $N(E_F) \sim 10^{-2}$ states/eV per C atom, thus χ_{tot} is dominated by the huge, anisotropic Landau diamagnetism χ_{orb} associated with the degeneracy of valence and conduction bands[1] (i.e., graphite is almost a zero-gap semiconductor). Defects and disorder have a drastic effect on the electron states near E_F; therefore deviations from the ideal χ_{orb} are used to characterize pregraphitic carbons, fibers, irradiated graphite, etc.[2]

Intercalation compounds of graphite[3] provide a large class of anisotropic synthetic metals by virtue of the fact that the ionized intercalant atom or molecule is compensated by delocalized charge of appropriate sign. To a very good first approximation the electronic structure of most compounds can be deduced from a rigid-band approach. The energy bands near E_F are graphitelike, and E_F is raised or lowered by an appropriate amount according as the intercalant acts as an electron donor or acceptor. Screening of the ionized intercalant layer by the delocalized charge complicates the situation in high-stage compounds (those in which three or more contiguous carbon layers separate nearest-neighbor intercalant layers), because the displacement of E_F is maximum for "bounding" carbon layers (those next to an intercalant layer) and small for "interior" carbon layers.[4]

Powder measurements of χ_{tot} (notation χ_{tot}^c henceforth denotes oriented specimen with $\vec{H} \parallel c$) for many compounds have been published over the last 30 years; these have been reviewed by Delhaes,[5] Fischer,[6] and Dresselhaus and Dresselhaus.[7] The usual procedure in analyzing these data has been to correct χ_{tot} for χ_0 and to assume χ_{orb} negligible, the argument being that displacing E_F raises χ_p and lowers χ_{orb} relative to the graphite values.[5] The surprising results of this procedure are that χ_p greatly exceeds the value inferred from the linear-T heat-capacity coefficient $\gamma = \pi^2 k_B^2 N(E_F)/3$ (k_B, Boltzmann's constant), and that χ_p per intercalant atom or molecule increases with decreasing concentration.

It turns out that both discrepancies can be attributed to incorrect treatment of χ_{orb}. Safran and DiSalvo[8] showed that χ_{orb} becomes paramagnetic for displacements of E_F greater than $\sim$0.05 eV, and that the resulting orbital *para*magnetism can exceed χ_p in magnitude. Furthermore, the unusual concentration dependence of χ_{tot} results from the highly nonuniform charge distribution perpendicular to the layers; the positive χ_{orb} has a maximum value for small E_F

shifts, so the innermost layers in a high-stage compound dominate this contribution to χ_{tot} while bounding layers dominate χ_p.

DiSalvo *et al.*[9] applied the above theory to a series of experimental results on stages-1–4 potassium and stage-1 lithium compounds. With values of χ_p estimated from previously published specific-heat data, they extracted χ^c_{orb}, the orbital susceptibility with $\vec{H} \parallel c$, from their measurements of χ^c_{tot}. In comparing this result with theory, the biggest uncertainty comes from the estimate of χ_p, which neglects all many-body interactions as well as other potential sources of linear-T heat capacity. We were thus motivated to perform a more quantitative test of the theory by actually measuring χ_p directly. We had previously done this for the acceptor compound $\mathrm{C_8AsF_5}$,[10] but the theory as it exists applies only to donor compounds. Probably the only stage-1 donor for which absolute values of χ_p can be obtained is $\mathrm{LiC_6}$, as discussed below. The purposes of this paper, then, are to present an experimental value of χ_p for $\mathrm{LiC_6}$, to compare $\mathrm{LiC_6}$ and $\mathrm{C_8AsF_5}$ as typical donor and acceptor compounds, respectively, and to test the Safran-DiSalvo theory of orbital paramagnetism in "doped" graphite.

II. EXPERIMENTAL

The absolute spin susceptibility χ_p was measured using the ESR/NMR technique pioneered by Shumacher and Slichter.[11] The principles have been described elsewhere.[10] Briefly, one measures the integrated intensity of the conduction electron spin resonance *relative to* the integrated nuclear resonance intensity of a constituent atom of known concentration. To avoid rf gain uncertainties, both resonances are obtained at the same frequency (in our case 10 MHz). This means that the resonant magnetic field for CESR scales down to a few gauss if the NMR resonant field is several kilogauss, because the electronic and nuclear gyromagnetic ratios differ by 3 orders of magnitude. The experiment is thus limited to materials in which the CESR linewidth is $\lesssim 1$ G. As with the pure alkali metals, the primary ESR relaxation mechanism is spin-orbit coupling which scales with atomic mass,[5] so only the lightest elements give sufficiently small ESR linewidths for the Shumacher-Slichter technique to be feasible. Motional narrowing is also beneficial in this regard.

Data analysis is straightforward. The NMR is represented by a Curie-Weiss term for the nuclear spins, $\chi_n = N\gamma_n^2\hbar^2 I(I+1)/3k_BT$ and χ_p is given by $\chi_n\gamma_e I_e/\gamma_n I_n$ where γ_e, γ_n and I_e,I_n are the gyromagnetic ratios and integrated intensities for the ESR and NMR, respectively; N is the number of resonating nuclei per unit volume (or per mole) of sample, and I is the nuclear spin. The fundamental requirements for the technique to be applicable are that the ESR be dominated by conduction electrons (no local moments) and that the ESR line be Lorentzian in shape.

$\mathrm{LiC_6}$ is a good conductor in both principal directions,[12] so powdered samples were required in order to achieve sufficient sensitivity. Chunks of highly oriented pyrolytic graphite were intercalated by immersion in liquid Li at 350 °C,[12] ground into powder with 80 grit emery paper and loaded into 8-mm diameter Pyrex tubes. Mineral oil was added to one sample to reduce intergrain electrical contact. This sample provided the best ^{7}Li NMR signal. The sample mass was typically a few hundred milligrams. All these operations were performed in an argon-filled glove box. A simple *Q*-meter cw spectrometer with small-amplitude field modulation was employed to give absorption-mode spectra.

III. RESULTS AND DISCUSSION

Figure 1 show a field sweep (through $H=0$) for both signs of H of the CESR in $\mathrm{LiC_6}$ at 300 K. The recorded signal is proportional to $d\chi''/dH$, the field derivative of the imaginary part of the electronic susceptibility. The first integral of the resonant structure gives a Lorentzian line for $\chi''(H)$, and the second integral is proportional to I_e. Similar ^{7}Li NMR spectra were obtained. The ESR and NMR linewidths were the same within experimental error: $\Delta H = 1.1 \pm 0.1$ G and 1.2 ± 0.2 G, respectively. Previous work[5,13] shows that both lines are motionally narrowed at 300 K. The final result is $\chi_p = 25 \pm 8 \times 10^{-6}$ emu/mole $\mathrm{LiC_6}$ for the oil-coated sample. A dry sample gave $(30 \pm 15) \times 10^{-6}$ emu/mole. The major uncertainty comes from poor signal-to-noise ratio of the ^{7}Li NMR. The error bars on our earlier measurement[10] of $\mathrm{C_8AsF_5}$ were only ±18% because the ^{19}F resonance was motionally narrowed to less than 0.5 G, and the signal was therefore much stronger.

Comparisons between theory and experiment for $\mathrm{LiC_6}$ and $\mathrm{C_8AsF_5}$ are given in Table I. We begin with $\mathrm{LiC_6}$. The experimental χ_p (first row) agrees well

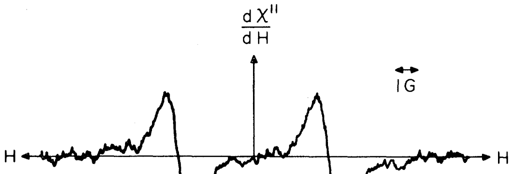

FIG. 1. Conduction electron spin resonance of powdered $\mathrm{LiC_6}$ in mineral oil, at 300 K and 10 MHz. The magnetic field is swept from positive to negative through zero, the resonant field $H_0 \sim 3.5$ G.

TABLE I. Tabulation of the various components of static susceptibility for LiC_6 and C_8AsF_5; comparison of theory and experiment. Units are 10^{-6} emu/mole of compound.

	LiC_6	C_8AsF_5
1. χ_p(expt)	25 ± 8[a]	16 ± 3[b]
2. χ_p(theor)	31[c]	14[c]
	47[d]	27[e]
3. χ_p(sp.ht.)	41[f]	. . .
	48[g]	
4. χ_p	−29	−113
5. $\chi^c_{\rm tot}$	92 ± 2[h]	-93 ± 10[i]
6. $\chi^c_{\rm orb}({\rm expt}) = \chi^c_{\rm tot} - \chi_0 - \chi^p$	90 ± 10	4 ± 13
7. $\chi^c_{\rm orb}$(theor)	41[c]	. . .

[a] This work.
[b] Weinberger, Ref. 10.
[c] Safran, Ref. 8.
[d] Holzwarth, Ref. 14.
[e] Campagnoli, Ref. 21.
[f] Delhaes, Ref. 15.
[g] Ayache, Ref. 16.
[h] Di Salvo, Ref. 9.
[i] Weinberger, Ref. 19.

with Safran's model[8] based on the simplest two-dimensional (2D) graphite bands and a nearest-neighbor overlap integral $\gamma_0 = 3$ eV. The experimental upper bound is significantly below the second theoretical value, obtained by Holzwarth[14] using a more elaborate Korringa-Kohn-Rostoker (KKR) technique. Both theories are based on completely ionized Li, so the discrepancy does not arise from uncertainties in the charge transfer. Many-body corrections to χ_p would increase the discrepancy with the KKR band model prediction.[10]

The third row of Table I presents χ_p values inferred from specific-heat measurements. In contrast to previous analysis[5] (in which $\chi_{\rm orb}$ was neglected in extracting χ_p from $\chi_{\rm tot}$) which implied that χ_p was too large in relation to γ, we find from the actual χ_p that γ is "too large." Both Dehaes' specific-heat value[15] and the more recent data from Ayache *et al.*[16] significantly exceed our χ_p suggesting that γ is enhanced by electron-phonon interaction. Taking rows 1 and 3 at face value would imply electron-phonon enhancement factors of 64% and 92% for the two specific-heat values, respectively. Superconductivity occurs in related compounds such as KC_8 and $KHgC_8$,[17] but has not been reported to date in LiC_6.

The fourth row lists the core diamagnetism corrections as estimated from Pascal's constants. The fifth row gives experimental $\chi^c_{\rm tot}$ values obtained by the Faraday method with $\vec{H} \parallel c$. The experimental orbital susceptibility $\chi^c_{\rm orb} = \chi^c_{\rm tot} - \chi_0 - \chi_p({\rm expt})$ is presented in row six and the theoretical value[8] $\chi^c_{\rm orb}$(theor), again based on Li^+, is given in the last row. The most striking feature of these numbers is that $\chi^c_{\rm orb}$ is positive and *exceeds* χ_p by a factor of 2–3, demonstrating immediately that previous analyses of $\chi_{\rm tot}$ are meaningless. The agreement between theory and experiment for $\chi^c_{\rm orb}$ is considerably poorer than for χ_p, which is curious since both calculations are based on the same band model and the formalism used to calculate $\chi^c_{\rm orb}$ works well for pure graphite.[1] One possibility is that the contribution to χ_0 from the carbon atomic $2s$ and $2p$ orbitals is a poor representation of the sp^2-hybridized in-plane bonding orbitals of graphite.[18]

A similar analysis of our previous data[10,19] for C_8AsF_5 is presented in the second column of the table. The experimental χ_p per mole is slightly smaller for the acceptor compound. The difference is more pronounced on a per C atom basis. For LiC_6 the excess charge per C atom is 0.167. If C_9AsF_5 were "$C_8{}^+AsF_5{}^-$" one would have 0.125/C atom. The maximum possible excess charge is only $\frac{2}{3}$ this value, according to the equilibrium redox reaction $3AsF_5 + 2e^- \rightleftharpoons 2AsF_6{}^- + AsF_3$. Recent evidence[20] shows that the equilibrium goes less far to the right as the total concentration increases, and that the excess charge at stage 1 is 0.034/C atom, i.e., a formal composition $C_{30}{}^+AsF_6{}^- \cdot \frac{1}{2}AsF_3 \cdot 2\frac{1}{4}AsF_5$. The χ_p value from Safran's calculation corresponding to this charge is in very good agreement with our experimental result, confirming the result that the excess charge per C atom is much smaller in acceptor compounds relative to donors.[10] Differences per unit volume are even more dramatic since the volume per C atom in C_8AsF_5 is only 0.46 that in LiC_6. This in turn underscores the importance of carrier scattering in determining the electrical conductivity, which is 50% greater for C_8AsF_5 than for LiC_6.[3,12]

A second theoretical value for χ_p of $\mathrm{C_8AsF_5}$ comes from the recent band calculation of Campagnoli and Tosatti.[21] They assumed 0.049 electrons removed per C atom, so it is not surprising that their χ_p is somewhat large. On the other hand, the same assumption produces a good fit to the reflectivity spectrum.

The total susceptibility of $\mathrm{C_8AsF_5}$ (Ref. 19) is the same in magnitude but opposite in sign relative to $\mathrm{LiC_6}$. This is primarily due to the large core diamagnetism of $\mathrm{AsF_5}$ (in calculating χ_0 we assume that all the $\mathrm{AsF_5}$ equivalents are $\mathrm{AsF_5}$; none of the species actually present have unpaired spins).[19] The resulting $\chi^c_{\mathrm{orb}}(\mathrm{expt})$ is indeed paramagnetic, but just barely. We cannot compare this with Safran's theory, which was only carried out in detail for donors. Unlike χ_p, χ_{orb} is a sum of three terms whose signs vary with $N(E)$ and its energy derivative, so the acceptor result is no longer the simple mirror image of the donor result.[8] Thus, extending the calculation to the acceptor case would provide a critical test of the model.

For $\mathrm{LiC_6}$ the uncertainty in $\chi^c_{\mathrm{orb}}(\mathrm{expt})$ is clearly dominated by the error bars on $\chi_p(\mathrm{expt})$. χ_0 is fairly certain since the electronic configuration of the intercalant is well established, and the measurement of χ^c_{tot} is good to ±2%. Despite the better precision on $\chi_p(\mathrm{expt})$ for $\mathrm{C_8AsF_5}$, the uncertainty in $\chi^c_{\mathrm{orb}}(\mathrm{expt})$ is somewhat greater than $\mathrm{LiC_6}$, due to the lesser precision in χ^c_{tot}. There is also an additional uncertainty in χ_0 due to the lack of knowledge of the detailed nature of the "$\mathrm{AsF_5}$" intercalant, in particular the possibility of fluorine bridging bonds among the several species present. The net result is that χ^c_{orb} and χ_p may indeed be comparable in magnitude for $\mathrm{C_8AsF_5}$, as they are for $\mathrm{LiC_6}$.

IV. SUMMARY

By measuring directly the Pauli susceptibility of $\mathrm{LiC_6}$, we have shown that the orbital contribution from inter- and intraband transitions is large and paramagnetic, as predicted by Safran and DiSalvo. Previous interpretations of χ_{tot} which neglected χ_{orb} relative to χ_p are therefore incorrect. This phenomenon is quite general, so it applies to all donor compounds. For $\mathrm{C_8AsF_5}$, the orbital contribution is much smaller; within the uncertainty of the experiment $\chi_{\mathrm{orb}} \simeq 0$. Extension of the theory of χ_{orb} to include acceptor compounds should therefore provide an important test of the model.

The relative χ_p values for $\mathrm{LiC_6}$ and $\mathrm{C_8AsF_5}$ indicate that the excess charge per C atom is ~5 times larger in the former, for which the oxidation of Li to $\mathrm{Li^+}$ is complete. The basal plane conductivities at 300 K are in the ratio $\sigma_a(\mathrm{LiC_6})/\sigma_a(\mathrm{AsF_5}) \simeq \frac{2}{3}$, while the C atom densities are in the ratio 2.2. If we assume $\sigma_a \simeq n\bar{\mu}e$ where n = charge/volume and $\bar{\mu}$ is an effective mobility, then we have $\bar{\mu}(\mathrm{LiC_y})/\bar{\mu}(\mathrm{C_8AsF_5}) = 0.06$ at 300 K. This ratio becomes even smaller at low T. It is thus apparent that the high conductivity of acceptor compounds relative to donors is not due to a greater carrier density, but rather to higher mobility.

ACKNOWLEDGMENTS

We acknowledge useful discussions with F. J. DiSalvo and S. A. Safran, and thank E. Tosatti for communicating his results prior to publication. This work was supported by the NSF MRL Program, Grant No. DMR 79-23647.

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