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Paramagnetic Susceptibility of Disordered N-Methyl-Phenazinium Tetracyanoquinodimethanide*

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The organic charge-transfer salt N-methyl-phenazinium tetracyanoquinodimethanide is described in terms of a one-dimensional disordered Hubbard model. For low temperatures and small transfer integrals this model reduces to a disordered Heisenberg antiferromagnet. The magnetic susceptibility of the latter can be described adequately by the disordered classical Heisenberg model. Fitting of susceptibility data by the one-dimensional classical Heisenberg model provides us with values of $t = 0.055$ eV, $U_{\text{eff}} = 0.130$ eV, and $\sigma = 0.136$ eV for the parameters of the original Hubbard Hamiltonian.

The paramagnetic susceptibilities, χ_p, of the high-conductivity charge-transfer salts[1-5] N-methyl-phenazinium tetracyanoquinodimethanide (NMP-TCNQ), quinolinium tetracyanoquinodimethanide [Qn(TCNQ)$_2$], and acridinium tetracyanoquinodimethanide [Ad(TCNQ)$_2$] depend weakly on temperature at high temperatures, but behave[1] as $\chi_p \propto 1/T^\gamma$ with $\gamma < 1$ at low temperatures. Figure 1 shows various experimental results for NMP-TCNQ, whose magnetic properties are the subject of this Letter. The crystal structure[6,7] of NMP-TCNQ consists of chains of closely stacked $TCNQ^-$ anions separated by chains of NMP^+ cations. The small intrachain $TCNQ^-$ spacing and large interchain distances lead to pseudo one-dimensional motion of electrons along the individual stacks. Bloch, Weisman, and Varma[8] first recognized that structural disorder is important for the conductivity of NMP-TCNQ. X-ray studies showed that the orientation of the asymmetric NMP^+ cations can be either random,[6,7] with a variable degree of disorder, or ordered.[9] We attribute the large variability in susceptibility throughout the whole temperature region, Fig. 1, to the intrinsic structural disorder.

Epstein *et al.*[3] have argued that at low temperatures their data can be quantitatively described by the half-filled periodic Hubbard model. Their explanation, however, cannot account for the rapid growth of the susceptibility observed by others. Butler, Wudl, and Soos[10] found their NMR data to be consistent with the assumption of partial charge transfer, and attributed the low-temperature growth of χ_p to electrons localized on 5% of the NMP sites. This picture cannot explain the variability in the susceptibility and does not give the $1/T^\gamma$ behavior. Bulaevskii *et al.*[1] proposed a phenomenological model which they based on the disordered Heisenberg model with a nonsingular probability distribution $P(J)$ of the coupling constant J. A canonical transformation reduces this model to one of interacting spinless fermions. They assumed that the Fermi-liquid theory holds for the interacting spinless fermions and that the

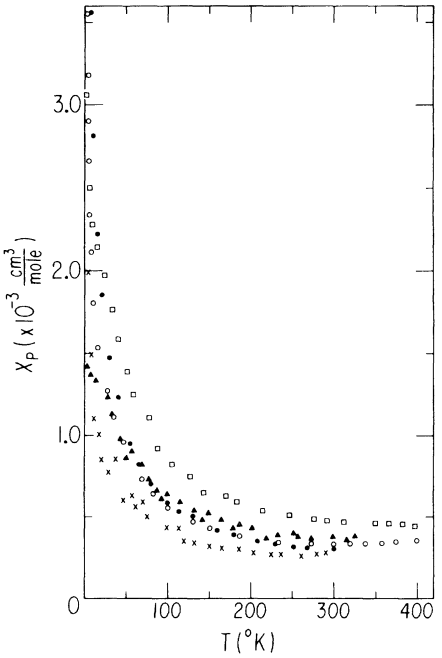

FIG. 1. Paramagnetic susceptibility data of NMP-TCNQ as a function of temperature. □, from Ref. 4; ●, from Ref. 2; ○, from Ref. 1; ▲, from Ref. 3; and x, from Ref. 5.

density of states has a singularity of the form $\rho(E) \propto |E|^{-\gamma}$. They were then able to explain the low-temperature magnetic and thermodynamic properties of NMP-TCNQ. However, they did not justify the applicability of the Fermi-liquid theory, and their justification of the singularity in the density of states is incorrect. A singularity in $\rho(E)$ cannot exist without a singularity in $P(J)$ for the Heisenberg model.

We use the disordered Hubbard model to describe NMP-TCNQ. Conductivity data suggest that for $T < 200$°K the electron-phonon interaction is small compared with static disorder. Thus the disordered Hubbard Hamiltonian can be written as

$$H = \sum_{l,\sigma} \epsilon_l A_{l\sigma}^{\dagger} U \sum_{l} N_{l\uparrow} N_{l\downarrow} + t \sum_{l,\sigma} (A_{l\sigma}^{\dagger} A_{(l+L)\sigma} + A_{(l+1)\sigma}^{\dagger} A_{l\sigma}), \quad (1)$$

where the ϵ_l are the single-site energies, U the on-site Coulomb repulsion, and t the hopping matrix element. The energies ϵ_l of the unpaired electrons on $TCNQ^-$ are random because of their dependence on the random orientation of the NMP^+ dipoles. We assume that the ϵ_l are uncorrelated with a Gaussian probability distribution having rms σ.[11] Studies of (1) without hopping show[12] that at $kT \ll U$ sites with $\epsilon_l < \frac{1}{2}U$ are doubly occupied, those with $-\frac{1}{2}U < \epsilon_l < \frac{1}{2}U$ are singly occupied, and sites with $\epsilon_l > \frac{1}{2}U$ are empty. This model gives a susceptibility[12,13,8] $\chi(T) \propto U/kT$ for $kT \ll U$ and constant for $U \ll kT \ll \sigma$. It is roughly consistent with the data for NMP-TCNQ but does not provide the detailed low-temperature behavior. We examined the case $t \neq 0$ but $\sigma \gtrsim U \gg t$ because the other limiting relations between the parameters of the Hubbard Hamiltonian do not give results similar to experiment. Treating the hopping term as a perturbation gives a random exchange J between localized spins, and the Hubbard Hamiltonian (1) reduces to a disordered Heisenberg antiferromagnet. We note that the susceptibility data also indicate antiferromagnetic coupling between localized spins. In the lowest order of perturbation, $J(n)$ is proportional to t^{2n} for large n, where n is the random separation between the spins. A detailed numerical analysis of perturbation theory[13] shows that $J(n)$ can be accurately represented by $f(n)\beta^{2n}$ with $\beta = t/(0.92\sigma - 0.26U)$ and $f(n)$ a function of n, U, t, and σ. For $J \ll \sigma$, $P(J)$ has the behavior

$$P(J) \propto 1/J^{1-c} \quad (2)$$

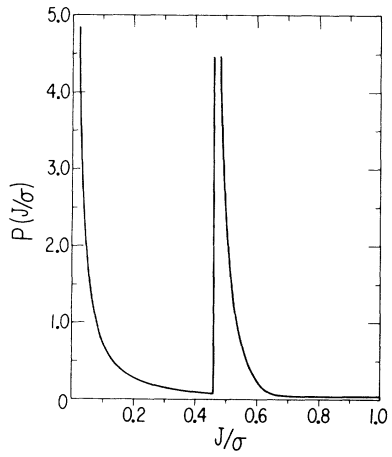

FIG. 2. Probability distribution of J/σ as a function of J/σ for $\sigma = 0.136$ eV, $t = 0.055$ eV, and $U = 0.130$ eV.

with $c = p/2|\ln\beta|$ and p the probability for a site to be singly occupied. Equation (2) follows directly from $J(n) \propto \beta^{2n}$ and probability distribution of n, pe^{-pn}. The distribution (2) is singular for $c < 1$. Monte Carlo calculations of $P(J)$ for $n = 0$ and 1 were connected by interpolation to the asymptotic behavior (2) to give the entire probability distribution which is shown in Fig. 2 for $\sigma = 0.136$ eV, $U = 0.130$ eV, $t = 0.055$ eV.

We now must solve the problem of the random Heisenberg antiferromagnet with $S = \frac{1}{2}$. There is no exact solution for the periodic one-dimensional (1-D) Heisenberg model, let alone for the disordered one. Studying instead six exactly soluble 1-D disordered models[1,14,15] with $P(J)$ given by (2), we found that the low-temperature susceptibility for the quantum Ising model with magnetic field $\vec{H} \| \hat{z}$, the classical Ising, the classical planar with $\vec{H}$ in the plane, and the classical Heisenberg models behaves as $1/T^{1-c}$ while for the quantum Ising model with $\vec{H} \perp \hat{z}$ the behavior is $1/T^{1-2c}$ and for the XY model $1/T$. We can understand the $1/T^{1-c}$ behavior via a cluster argument. The coupling between spins is strong if $J > kT$ and weak if $J < kT$. We ignore all weak couplings and are left with a system of decoupled clusters in their ground states. Only odd clusters contribute to χ_p. The magnetic susceptibility of the system is then $\chi_p \propto N_{\text{odd}}(T)/T$, with N_{odd} the number of odd clusters. Using $J = f(n)\beta^{2n}$ to calculate N_{odd}, we obtain

$$\chi_p \propto 1/T^{1-c}. \quad (3)$$

We can thus account for the $1/T^{1-c}$ behavior of the four simple models. The Ising model with perpendicular magnetic field has the property

that only clusters of size one contribute to the susceptibility because it is energetically unfavorable for larger clusters to rotate from the z axis towards the direction of the magnetic field. We thus find $\chi_p \propto 1/T^{1-2c}$. The disordered XY model is equivalent[16] to spinless fermions with nearest-neighbor interaction and off-diagonal disorder. The state in the middle of the band has such strong fluctuations that it is not possible to decompose the spins cleanly into separate clusters.[17] On the other hand, diagonal disorder in the 1-D Heisenberg model restores the applicability of the cluster argument. Thus the low-temperature behavior of the disordered quantum Heisenberg model is $1/T^{1-c}$, the same as that of the classical Heisenberg model. The classical χ_p constitutes an upper bound on the quantum χ_p, since the zero-point motion lowers the latter. Moreover the susceptibility given by the formula

$$\chi_p = \chi_0 \frac{1 + \langle (\chi_{per} - \chi_0)/(\chi_{per} + \chi_0) \rangle}{1 - \langle (\chi_{per} - \chi_0)/(\chi_{per} + \chi_0) \rangle}, \quad (4)$$

where $\chi_0 = Np\mu^2 g^2/4kT$ and χ_{per} is the susceptibility of the periodic quantum Heisenberg model, calculated numerically by Bonner and Fisher,[18] bounds from below the disordered Heisenberg susceptibility. The difference in χ_p between the upper and lower bounds, for $P(J)$ given by Fig. 2, is $\simeq 10\%$ throughout the whole temperature region and therefore the difference between the classical and the quantum χ_p is less than 10%. We conclude that the magnetic susceptibility data for NMP-TCNQ can be fitted by the disordered classical 1-D Heisenberg model,[15]

$$\chi_p = \frac{Np g^2 \mu^2}{4kT} \frac{1 + \langle u \rangle}{1 - \langle u \rangle}, \quad (5)$$

with $U = 4kT/3J - \coth(3J/4kT)$. Fitting the low-temperature data fixes the ratios t/σ and U/σ and fitting the high-temperature data fixes σ. The fitting of Di Salvo's data,[2] shown in Fig. 3, gives $\sigma = 0.136$ eV, $U_{eff} = 0.130$ eV, $t = 0.055$ eV, $p = 0.367$, and $c = 0.36$. X-ray analysis[7] of crystals from the same batch as Di Salvo's showed that they were disordered.

Molecular orbital calculations of t for NMP-TCNQ do not exist. However, such calculations for tetrathiafulvalene tetracyanoquinodimethane (TTF-TCNQ), which has an internal structure of the $TCNQ^-$ stacks similar to that of NMP-TCNQ, give $t = 0.1$[19] or 0.05 eV.[20] Also analysis of reflectivity data of TTF-TCNQ gives $t \simeq 0.1$.[21] Our value for t is therefore in the same range as existing estimates. In disordered systems the wave

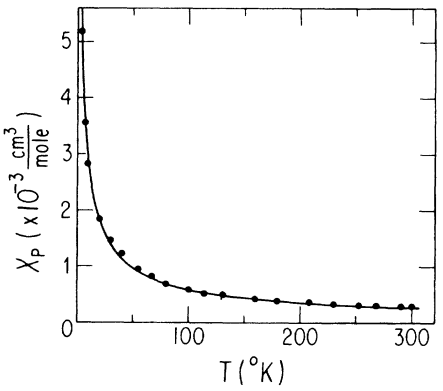

FIG. 3. Paramagnetic susceptibility of NMP-TCNQ. ●, Di Salvo's data (Ref. 2); solid curve is the present theory with $U_{eff} = 0.130$ eV, $t = 0.055$ eV, and $\sigma = 0.136$ eV.

function of an electron will be approximately constant over a region of L_e sites and then will decay exponentially with a decay length L_d.[22] Thus the effective Coulomb repulsion will be equal to $U_{eff} \simeq U/(L_e + 2L_d)$, with U the "bare" Hubbard repulsion.[11,13] Experiments done at frequencies higher than the plasma frequency will yield values of U, while experiments at low frequencies will yield values of U_{eff}. L_e and L_d can be calculated[22] for $U = 0$. For our σ and t we have $L_e \simeq 3$ and $L_d \simeq 2$ intermolecular distances. Then the "bare" U according to our calculations is equal to $U \simeq 0.9$ eV. Optical measurements give[23] $U \simeq 1$ eV. We note that Papatriantafillou and Cohen[11] analyzed microwave properties and dc conductivity data with the disordered Hubbard model and obtained values for t, U, and σ in the same range as ours.

Examining the heat capacity, C, and strong field magnetization, M, within the framework of our model gives $M \propto H^c$ and $C \propto T^c$ at low temperatures, as is observed and given by the model of Bulaevskii *et al.*[1,24]

In conclusion, our analysis provides an excellent fit of the experimental data for χ_p of NMP-TCNQ in the whole temperature region and gives values for the parameters, t, U, and σ in good agreement with independent estimates. Our picture gives the observed behavior of M and C as well. If the validity of the Fermi-liquid theory used by Bulaevskii and co-workers[1,24] were established for the present singular distribution of coupling constants, our work would constitute a derivation of their assumed density of states. We should point out that the use of the Hubbard model with a half-filled band is not a requirement for obtaining relation (2). A system with the follow-

ing two features would be sufficient: (1) random distribution of localized spins along a line, and (2) an exponential decay of the exchange coupling with separation. (1) follows from disorder if the net electron-electron coupling is repulsive and (2) then follows automatically from localization.

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Asymmetric Scattering and the Spin-Glass Transition in *Au*Fe and *Au*Mn Alloys

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We have measured the isomagnetic temperature dependence of the anomalous Hall effect that arises from the asymmetric scattering of the conduction electrons by the localized moments in two alloys of Au containing ~8.1 at.% Fe or Mn. The experiment is evidently a sensitive way to detect the magnetic rearrangement in a spin-glass. It shows clearly the spin-glass transition and features that are tentatively ascribed to the presence of magnetic clusters and "loose spins."

We report a sensitive way to detect the rearrangement of localized moments in a metallic spin-glass.[1] We measure the anomalous part of the Hall effect that arises from the spin-orbit coupling between the conduction electrons and a solute's moment in the resonant scattering by the virtual bound state.[2] This coupling gives to each elastic scattering event an asymmetric probability with respect to the plane containing the solute's moment and the electron's incident velocity.[3] In an applied magnetic field $\vec{B}$ the effects of these events for those moments aligned by the field are combined additively and, when $\vec{B}$ is normal to the current flow, appear as the "skew component" of the transverse electric field.[3] Moments that are randomly arranged throughout