Enhancement of the magnetic susceptibility of TTF-TCNQ (tetrathiafulvalene-tetracyanoquinodimethane) by Coulomb correlations

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In order to gain some insight into the nature of the interactions in TTF-TCNQ (tetrathiafulvalene-tetracyanoquinodimethane), we compare the magnitude of the observed magnetic susceptibility χ with the predictions of two simple models. First we consider a tight-binding band of noninteracting electrons and find that the magnitude of the observed high-temperature χ is large compared to that calculated using the expected bandwidth. The same conclusion is also reached by a more general consideration of the magnitude of the product $T\chi$. It is concluded that *at high temperatures* χ *is enhanced*. We then compare the observed χ to calculations using a Hubbard model with on-site Coulomb repulsion energy U. χ is calculated in *both* the low-U and large-U limits and, in either limit, the large magnitude of χ can be readily accounted for. Using these two results, a relationship between the two parameters U and the bandwidth $4t$ is obtained, knowing the magnitude of χ at 300 K. From independent estimates of $4t$, it is concluded that U is comparable or larger than $4t$, at least on one stack. Additional evidence for and against the presence of Coulomb interactions in TTF-TCNQ is summarized.

I. INTRODUCTION

During the last three years, there has been considerable experimental and theoretical work attempting to understand the unusual electronic and magnetic properties of the organic metal TTF-TCNQ (tetrathiafulvalene-tetracyanoquinodimethane). While some progress has been made, many of the most basic questions remain the subject of active controversy. For example, a number of workers have suggested[1-13] that Coulomb correlations are significant in TTF-TCNQ and might even be the strongest interactions in this material. On the other hand, these interactions have been widely assumed to play only a minor role; in fact, they have been neglected by a majority of workers in the field. The question of whether Coulomb correlations are the strongest interactions or whether they may be neglected is a rather fundamental issue, which should be resolved before we can have any confidence in more detailed explanations of the properties of TTF-TCNQ.

The purpose of the present paper is to examine and analyze the measured magnetic susceptibility χ of TTF-TCNQ in order to determine the significance or insignificance of Coulomb correlations. This experimental quantity χ is in principle quite sensitive, since Coulomb interactions are expected to enhance the magnitude of χ above that predicted for noninteracting electrons. This enhancement results from the fact that Coulomb interactions tend to make states with paired spins (on the same molecule) energetically unfavorable, thus increasing the fraction of magnetic states.

As an outline of this paper, we start in Sec. II by making a simple comparison of the observed χ with our calculations for a tight-binding band of noninteracting electrons. A more general test of the assumption of noninteracting electrons is presented in the Appendix, where we examine the product of $T\chi$. In Sec. III, the observed χ is compared to calculations for a simple Hubbard model, in both the weak and strong Coulomb coupling limits. It is concluded that the observed χ is enhanced by Coulomb correlations. Additional evidence for and against the presence of Coulomb interactions is summarized in Sec. IV.

The experimental susceptibility χ of TTF-TCNQ has been measured by a number of different groups,[5,14-19] with very similar results. In Fig. 1

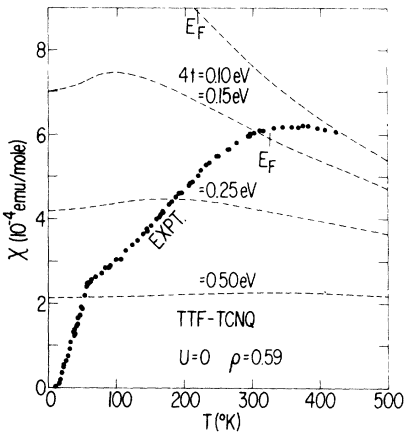

FIG. 1. Comparison of experimental magnetic susceptibility (solid points) with that calculated using a tight-binding model of noninteracting electrons.

we show the combined data points of Refs. 15 and 16. From the temperature dependence of $\chi(T)$, we can readily distinguish three distinct temperature regions: (i) below 53 K, where the temperature dependence of χ is dominated[5,16,18,19] by the energy gaps associated with the phase transitions; (ii) between 60 and ~280 K, where the change in $\chi(T)$ with T has been attributed to fluctuations associated with the phase transition[9,16,20-22] or to interactions between the TTF and TCNQ stacks (i.e., hybridization)[23-25]; and (iii) above ~280 K, where $\chi(T)$ is relatively independent of temperature. In this paper we shall concentrate on the latter region, above ~280 K, since at these high temperatures, kT is large compared to the gaps due to hybridization, Peierls, etc., and hence $\chi(T)$ should be governed by the largest interactions, which are what we want to examine. In principle, the observed χ contains contributions from both the TTF and TCNQ stacks. The fact that the observed[15,26] EPR g value between 70 and 300 K is found to be very close to the average of the TTF and TCNQ values strongly suggests[26] that, in this range, χ on the TTF stack is not very different from that on the TCNQ stack. For this reason and for simplicity, we shall assume that the TTF and TCNQ stacks behave the same magnetically. Our results may be readily generalized to the more specific case where the bandwidths, for example, are somewhat different on different stacks.

II. χ FOR A TIGHT-BINDING BAND

As a starting point, we will compare the experimental data of Fig. 1 with the predictions of a theoretical model of *noninteracting* electrons. The simplest and most reasonable such model for TTF-TCNQ is a one-electron tight-binding band with a bandwidth $4t$, where t is the transfer (or resonance) integral. The number of electrons ρ per molecule is 0.59, as inferred from measurements[27-30] of the Peierls wave vector (see Appendix A). For simplicity and for the reasons given in Sec. I, we concentrate on the region above 280 K and assume that the bandwidths are the same for the TTF and TCNQ stacks. The calculated $\chi(T)$ is now a function of only one parameter—the bandwidth $4t$. At zero temperature, χ for one kind of stack is given[31] by the simple Pauli susceptibility

$$\chi_P(0) = \frac{N_0\mu_B^2}{\pi t \sin(\frac{1}{2}\pi\rho)}, \quad U = 0, \tag{1}$$

where N_0 is Avogadro's number and μ_B is the Bohr magneton. For the bandwidth in units of eV, χ in units of emu/mole, and $\rho = 0.59$, Eq. (1) is equivalent to $\chi_P(0) = 0.511 \times 10^{-4}/4t$ for each kind of stack.

For narrow bands, however, χ becomes strongly temperature dependent (as we shall see) and it is not at all sufficient to use the simple low-temperature expression, Eq. (1). For this reason, we have calculated the temperature-dependent susceptibility for a one-dimensional tight-binding band. This has been done by calculating[32] the eigenvalues and then χ for a finite stack of 200 molecules in length. For temperatures such that the thermal energy kT is large compared with the splittings between adjacent levels (due to the finite length of the stack), such a calculation just simulates the results for a tight-binding stack of infinite length.

The temperature-dependent $\chi(T)$ calculated in this way is shown in Fig. 1 for values of $4t = 0.10$, 0.15, 0.25, and 0.50 eV.[33] At this stage, we are not concerned with the discrepancy between the observed and calculated temperature dependence of $\chi(T)$, since including additional (weaker) interactions in the calculation, e.g., fluctuations or hybridization, would decrease the calculated χ at lower temperature and improve the qualitative agreement with experiment. In fact, χ is clearly decreased by the phase transition near 60 K. The most important feature, however, which is what we want to focus on, is the magnitude of the high temperature χ, which is large.[4] This point has also been recognized by Walsh *et al.*,[26] who noted that the magnitude of χ at 300 K is ~40% of the Curie susceptibility (see Appendix B). For a simple tight-binding band of noninteracting electrons, this large magnitude of χ can only be accounted for by relatively small values of the bandwidth (~0.12 eV), as seen in Fig. 1. For such narrow bands, the associated Fermi energies E_F are also low (~260 K)[34] and hence the calculated $\chi(T)$ near 300 K is strongly temperature dependent (Fig. 1).

Are such low values of $E_F \sim 260$ K and $4t \sim 0.12$ eV consistent with values obtained from other measurements (interpreted using the same model of noninteracting electrons)? The value of $4t \sim 0.12$ eV may be readily compared with the following estimates of the bandwidth: (a) $4t = 0.45$ and 0.61 eV, as indicated[35] from measurements[36,37] of the plasma frequency; (b) $4t \sim 0.2$ to 0.7 eV for the TTF and ~0.5 eV for the TCNQ stack, from extended Hückel[38] and $X\alpha$-molecular-orbital[39] calculations.[40] Even larger values are obtained using[41] CNDO-2 (complete neglect of differential overlap, version 2) and MINDO-2 (modified intermediate neglect of differential overlap, version 2); (c) $4t \sim 0.4$ eV from the observed[42,43] optical conductivity, which is large up to 0.6 eV (and which cannot extend much beyond $4t$); and (d) $4t \sim 0.5$ eV, indicated by early thermoelectric power measurements.[44]

The effect of the Peierls instability in TTF-TCNQ is to open up an energy gap at E_F in an otherwise metallic conductor. The gap thus opened up at low temperatures should be significantly smaller than E_F. (Otherwise, the electron-phonon interaction could not be treated as a perturbation, and would have to be incorporated in the theory in zeroth order, as in the small polaron problem.) Nevertheless, the values of the measured gaps appear large or comparable with $E_F \sim 300$ K: (a) an infrared gap[43] of 1200 K; (b) a Peierls gap of ~1100 K, from an analysis[20] of the temperature dependence of χ between 280 and 60 K; and (c) activation energies[5,18,19,45-48] for σ and $T\chi$ ranging between ~100 and 400 K, i.e., energy gaps ~200–800 K. From the above estimates of $4t$ and E_F, the calculated χ would be considerably less than that observed at high temperatures (Fig. 1).

The above analysis is based on the assumption that the noninteracting electrons form simple tight-binding cosine bands, with equal widths on the TTF and TCNQ stacks. For the more general case of noncosine bands, the above discussion could have been carried out in terms of the density of states. In that case, the magnitude of χ at high temperatures indicates a very high density of states. The apparent inconsistency with the plasma frequency, for example, still remains, since the latter (in one dimension) is a measure of the reciprocal of the density of states at E_F. Large differences in χ on the TTF and TCNQ stack, due to large differences in density of states, for example, are not possible, since these would be inconsistent with the measured g value.[15,26] Nevertheless, it is difficult to extend the type of discussion above to the case of an anomalous, unknown band structure. For this reason it is useful to have a more general analysis, which we have given in Appendix B. There we examine the product $T\chi$ and conclude that at high temperatures the magnitude of $T\chi$ is quite large, indicating that the width of states contributing to χ is ~300 K. This conclusion is similar to that obtained above, but is very general since it is based on only two assumptions: (i) Fermi-Dirac statistics; and (ii) the assumption of noninteracting electrons.

Thus, *at high temperatures the magnitude of* χ *is large*, compared to what we would have expected for noninteracting electrons. If the electrons in TTF-TCNQ were noninteracting, a number of related conclusions could be drawn on the basis of the discussion in this section and in Appendix B: (a) *The relatively flat* $\chi(T)$ observed between ~280 and 415 K *is not simply the temperature-independent Pauli susceptibility* of a large metallic density of states. Compared to the calculated magnitude of χ, the measured χ is too high to be flat at these temperatures. Thus, one cannot simply use Eq. (1) to relate the magnitude of χ in this region to the bandwidth or the density of states; (b) since the inferred value of E_F (~260 K) would not be much less than kT at 300 K, *TTF-TCNQ would be an extremely nondegenerate metal at room temperature*. This fact is dramatically evidenced by the large value of $T\chi$ at 300 K compared to the infinite temperature limit, as seen in Appendix B. Thus, a large fraction of the electrons would be excited above the Fermi level and the Fermi surface would not be sharp. This conclusion is in direct conflict with the well defined Fermi surface indicated by the recent discovery[29,30] of diffuse x-ray scattering at "$4k_F$" observed even at 300 K; (c) from the (large) magnitude of χ at 300 K, we would infer *values of* E_F *and* $4t$, *which are relatively low and not readily consistent* with values inferred from other measurements; and (d) electron-phonon interactions (either Peierls- or BCS-like) tend to pair electron spins, open up a gap at E_F, and thus decrease[21,22] χ. Since the calculated χ is already very low (see this section and Appendix B), these *electron-phonon interactions at* 300 K *cannot be strong* enough to appreciably decrease χ. In fact, the experiments which were first interpreted[22] as evidence for strong electron-phonon (Peierls-Fröhlich) interactions at 300 K have recently been given different interpretations: the neutron inelastic scattering[49] (first identified as a giant Kohn anomaly) has been attributed[6,9] to the excitation of spin waves; and the "Peierls gap" in the infrared[43] might be an electron–optical-phonon interference (or Fano) effect,[50] or the onset of electron-electron umklapp scattering.[51]

Thus, it is very difficult, if not impossible, to reasonably account for the large magnitude of χ at high temperatures with a model of noninteracting electrons. For this reason, we conclude that χ is enhanced and in Sec. III we remove the restrictive assumption that $U = 0$ and consider the possibility of an enhanced χ caused by on-site Coulomb correlations.

III. χ OF A HUBBARD MODEL

In this section, we consider the simplest model which includes the effects of Coulomb correlations: the Hubbard model.[52] In this model, one includes only the repulsive Coulomb energy U between two electrons when they are on the same molecule, i.e., longer-range interactions are neglected.[53] At $T = 0$, $\chi(0)$ has been calculated for the Hubbard model in one dimension by Shiba[31] for arbitrary values of U, ρ, and $4t$. Unfortunately, the full temperature dependence of χ has been examined only in the two extreme limits: (a) $U \ll 4t$; and (b) $U \gg 4t$.

In the limit of $U \ll 4t$, the magnetic susceptibility can be written[54] in terms of the Pauli ($U=0$) susceptibility $\chi_P(t,T)$, calculated in Sec. II, as

$$\chi(T) = \frac{\chi_P(t,T)}{1 - U/4\pi t}, \quad U \ll 4t. \tag{2}$$

Thus, the effect of Coulomb interactions in this limit is to enhance χ_P by the enhancement[55,56] factor in Eq. (2). Exact calculations of this enhanced $\chi(T)$ for the one-dimensional Hubbard model are contained in the very recent work of Lee, Rice, and Klemm,[13] who use renormalization-group methods. While their results agree with Eq. (2) at low T, the enhancement of χ at higher temperatures is somewhat stronger than that given by Eq. (2). They apply their results to TTF-TCNQ and also conclude that χ is enhanced.

It should be emphasized that Eq. (2) is an approximation to the exact Hubbard model calculations[54] of Shiba[31] in the limit $U \ll 4t$. Care must be taken *not* to use the mean-field result[55] or to use Eq. (2) for values of $U/4t$ which are so large that Eq. (2) is no longer valid.

Using Eq. (2) for $4t = 0.25$ eV, the calculated $\chi(T)$ is shown in Fig. 2, for a series of values of U. It is clear that the large magnitude of χ observed at high temperatures can be readily accounted for with this enhancement. Thus, including Coulomb interactions eliminates the inconsistencies and difficulties encountered in Sec. II by the restriction $U=0$.

In the second limit, $U \gg 4t$, the calculation of $\chi(T)$ for arbitrary ρ is much more difficult, even in one dimension. Recently, Klein and Seitz[57] have found that in this limit the spin-dependent part of the Hubbard Hamiltonian can be written as a Heisenberg interaction, with an effective exchange

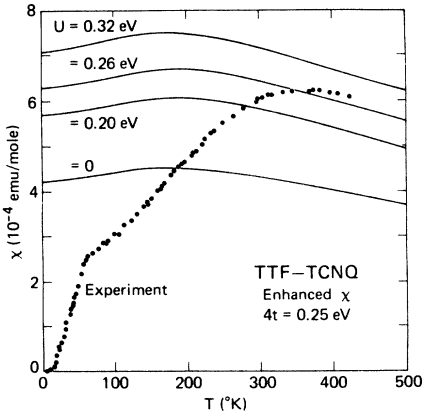

FIG. 2. Comparison of experimental magnetic susceptibility (solid points) with that calculated using a Pauli susceptibility enhanced by the presence of Coulomb interactions, using Eq. (2).

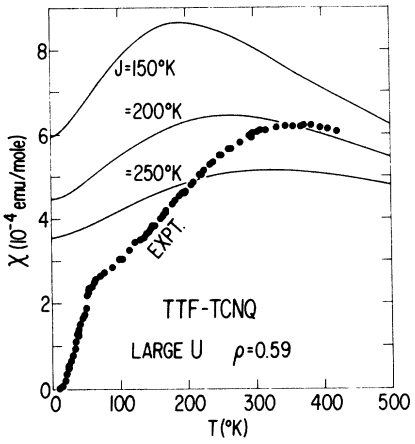

FIG. 3. Comparison of experimental magnetic susceptibility (solid points) with that calculated for a Hubbard model with strong Coulomb interactions.

interaction J (antiferromagnetic) which is given by[57,58]

$$J = (2t^2/U)\rho(1 - \sin 2\pi\rho/2\pi\rho), \quad U \gg 4t. \tag{3}$$

(In the case that U is not $\gg 4t$, J becomes weakly temperature dependent.[57]) Thus, the magnetic part of the Hubbard model can be described[57] by a Heisenberg linear chain of ρN_0 spins and hence the magnetic susceptibility is given by the familiar Bonner-Fisher result.[59] At $T=0$, χ for one kind of stack is then given by

$$\chi(0) = (2N_0\mu_B^2/\pi^2 J)\rho, \quad U \gg 4t. \tag{4}$$

Both Eqs. (3) and (4) agree with the $T=0$ calculations of Shiba.[31] For the special case of $\rho=1$ (half-filled band, Mott insulator), the electronic spins are known[52] to form a linear Heisenberg stack with $J = 2t^2/U$, in agreement with Eq. (3). For $\rho = 0.59$, as in TTF-TCNQ, Eq. (3) gives $J = 1.35t^2/U$.

In this limit, $\chi(T)$ is determined by one parameter J. Using values of $J = 150$, 200, and 250 K, we compare the calculated[60] values of $\chi(T)$ with experiment in Fig. 3 (assuming the same value of J for each kind of stack). As discussed earlier in connection with previous comparisons, we are not concerned with the agreement of the temperature dependence of χ. Rather, we want to concentrate on comparing the magnitudes, calculated and observed. It is clear from Fig. 3 that the large magnitude of χ near 300–400 K can be accounted for by a Hubbard model with a value of $J \sim 150$–200 K. Further agreement can be seen in the high-temperature behavior of the data, as discussed in Appendix B, where the data are shown to appear to have an asymptotic behavior more similar to the large U calculations than to that of the $U=0$ calculations.

A direct consequence of this description of $\chi(T)$ in terms of Coulomb interactions in the Hubbard model is the prediction that spin waves should be present in TTF-TCNQ. If $U \gg 4t$, their energy is given by the calculations of Coll[58]

$$E(q) = \pi J \sin(qb/\rho), \tag{5}$$

where J is given by Eq. (3) and b is the lattice constant along the stacking direction. Very recently, this prediction has been applied[6,9] to inelastic neutron-scattering measurements in TTF-TCNQ, in which some of the scattering is interpreted as due to the direct excitation of spin waves, with $J \sim 150$ K. Spin waves would also be predicted, presumably, for intermediate values of $U/4t$, but we have no calculations to help interpret the data in this difficult regime.

What are the values of $4t$ and U inferred from fitting χ with a Hubbard model in Figs. 2 and 3? Are these values consistent with the limit of $U \ll 4t$ or $U \gg 4t$ in which they are calculated? First we must recognize that the magnitude of the high temperature χ is a *single* number, from which we cannot extract values of *both* $4t$ and U. Nevertheless, we can use χ to determine a relation between $4t$ and U in both limits; so that, given an independent estimate of $4t$, for example, we can obtain the corresponding value of U as inferred from the magnitude of the experimental χ. As we shall see, it turns out to be more convenient to determine the relation between $U/4t$ and a given value of $4t$. In the large-U limit, for example, we have from Fig. 3 near 400 K and Eq. (3): $J = 200\ \text{K} = 1.35t^2/U$. From this we obtain the linear relation between $U/4t$ and $4t$ shown in Fig. 4. Similarly, one can use the experimental

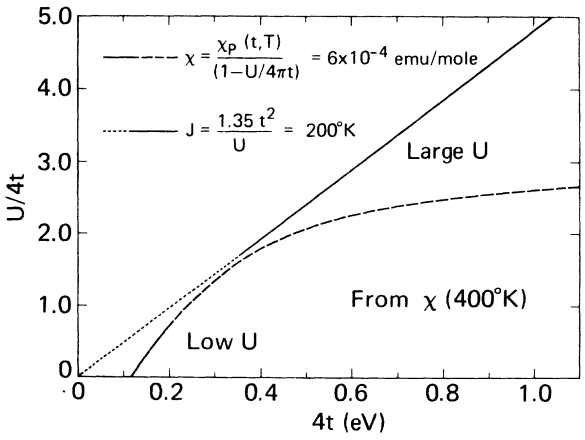

FIG. 4. Relationship between the quantity of $U/4t$ and the bandwidth ($4t$) for the observed magnitude of χ (400 K).

$\chi(400\ \text{K}) = 6 \times 10^{-4}$ emu/mole, Eq. (2), and the results of Fig. 1 to obtain the second curve in Fig. 4. This curve is shown as a dashed line for large and intermediate values of $U/4t$, since in this region the approximations used to obtain it are invalid. Similarly, the large U result is shown as a short dashed line at low and intermediate $U/4t$.

It is noteworthy that the result at low U can be connected with the result at large U by a reasonably smooth curve, which presumably would represent the result for arbitrary U. We can thus conclude that the behavior of χ for intermediate U is not unusual, but is simply intermediate between the behavior calculated for low and large U. This curve can be used to tabulate the values of $U/4t$ and U inferred from a series of values of $4t$ as in Table I.

Care must be taken not to attribute too much significance to the result in Fig. 4. It is valid only[53] for the Hubbard model, which is at best an approximate model for TTF-TCNQ. Within this context, if we had an independent estimate for $4t$, we can use Fig. 4 or Table I to infer a value of $U/4t$ and hence an approximate value for U. In Sec. II, we quoted estimates of $4t$ from a variety of sources. In addition, a value of $U \sim 1$ eV (at near infrared frequencies) has been inferred from optical measurements by Torrance, Scott, and Kaufman.[1] Using Table I, these estimates suggest that the *strength of the Coulomb interaction is at least comparable with the bandwidth* and quite possibly larger.

A similar comparison between the calculations of a tight-binding band ($U = 0$) and a large-U Hubbard model has been given[61,62] in connection with the magnetic susceptibility of some other TCNQ salts. It was concluded that the calculated values for the product $T\chi$ (at the temperature where χ has its maximum value) is essentially the same for both models, and hence it is not possible to

TABLE I. Values of U and $U/4t$ obtained for representative values of the bandwidth ($4t$) using the magnitude of the experimental χ (400 K) (see Fig. 4)

$4t$ (eV)	U (eV)	$U/4t$
0.1	0.0	0
0.15	0.05	0.3
0.2	0.16	0.8
0.3	0.4	1.4
0.4	0.8	1.9
0.5	1.2	2.4
0.6	1.8	2.9
0.7	2.4	3.4
1.0	4.7	4.7

use the observed data for the magnitude of χ to determine whether U is large or small. This conclusion is incorrect, however, since it is based on an expression for the susceptibility of a tight-binding stack that involves an erroneous multiplicative factor g^2. The values of χ thus calculated in the previous work are four times larger than the correct values.

We concluded in Sec. II that the magnitude of χ in TTF-TCNQ is enhanced at high temperatures. In this section, we demonstrated that this enhancement can be readily and reasonably accounted for by the Coulomb correlations of a Hubbard model.

IV. COULOMB INTERACTIONS IN TTF-TCNQ

The full Coulomb interaction e^2/r between any two electrons is certainly present in every solid, including TTF-TCNQ. The important question is how much this interaction is reduced or screened by the other degrees of freedom in the solid, e.g., the conductivity of other electrons, the acoustic phonons, excitons, optical phonons, etc. The effective Coulomb interaction at low frequencies which remains after this screening is the "Coulomb interaction" we have been discussing in this paper. In three-dimensional metals with strong metal-metal overlap, such as Na and Ag, it is well known that the Coulomb interactions are completely screened, for all practical purposes, by the conduction electrons. In many TCNQ salts other than TTF-TCNQ, on the other hand, it is generally accepted[1,12,52,55,62-64] that Coulomb interactions play a significant, if not dominant, role in their electronic and magnetic properties. For TTF-TCNQ, however, these interactions have been previously neglected by the majority of workers in the field. As justification, four pieces of evidence have been given[16,20,22,65] that Coulomb correlations play only a minor role in the properties of TTF-TCNQ: (i) the magnetic susceptibility is not enhanced; (ii) the ground state at $T=0$ is nonmagnetic; (iii) the NMR relaxation rate, using a Korringa relation, is not enhanced; and (iv) the activation energies below the phase transitions associated with χ and σ are the same.

The first argument is simply incorrect, as has been demonstrated in this paper. For the second point, one need only recall that the $T=0$ ground state of a magnetic system is nonmagnetic ($\chi=0$) if there is a distortion with wave vector $q=\frac{1}{2}\rho b^*=2k_F$ (see Appendix A). For example, a linear Heisenberg chain with one electron per site ($\rho=1$) has a nonmagnetic ground state at $T=0$ if the chain is dimerized.[66] In TTF-TCNQ, a distortion has been observed[27-30] at $q=0.295b^*=\frac{1}{2}\rho b^*$, and hence its ground state will be nonmagnetic, independent of whether $U=0$ or U is large. As for the third piece of evidence[20,65] (the lack of enhancement of T_1^{-1}), new measurements of the field dependence of T_1^{-1} have lead Jerome *et al.*[11] to conclude that T_1^{-1} is, in fact, enhanced and that Coulomb interactions must be included.

The fourth piece of evidence,[16] i.e., the equality of activation energies for σ and χ, is not correct, as first demonstrated by Tomkiewicz, Taranko, and Torrance.[5] As they discuss, the quantities which should be compared are the conductivity σ and the product $T^{1/2}\chi$, for the same stack. In Fig. 5 we plot $\ln(T^{1/2}\chi)$ (for the TTF stack) with $\ln\sigma$, which is believed[5,18,45,67] to be dominated by the TTF stack below ~50 K. Clearly, these quantities do *not* have the same temperature dependence as would have been expected for noninteracting electrons; in fact, the apparent activation energy of $T^{1/2}\chi$ is a factor of $\sim 2\frac{1}{2}$ smaller than that for σ. This fact is thus evidence *for* the presence of significant Coulomb interactions.

On the other hand, there are a growing number of indications[9] that Coulomb interactions play an important, if not dominant, role in the properties of TTF-TCNQ:

a. Optical properties. The infrared-visible absorption spectrum of TTF-TCNQ shows[1,43,68] an absorption peak near 1.3 eV, which has been interpreted by Torrance, Scott, and Kaufman[1] as due to an electronic charge transfer (intermolecular) excitation at an energy $\sim U$. In this way, similar values of $U\sim 1$ eV are obtained for other TCNQ salts.[1,12,63,64] This was the first indication that Coulomb interactions were strong (at least at near infrared frequencies) in TTF-TCNQ.

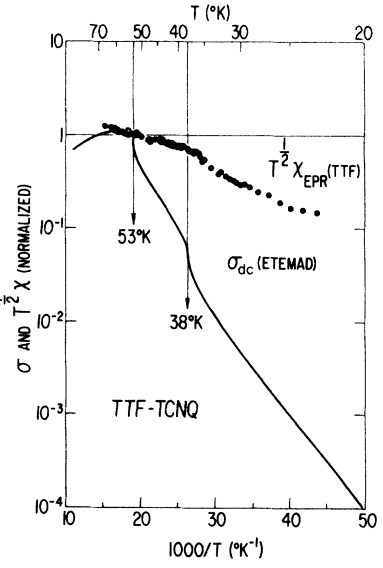

FIG. 5. Comparison between the conductivity and magnetic susceptibility at low temperatures showing that their activation energies are not the same.

b. Madelung energy calculations. Calculations of the crystal binding energy of TTF-TCNQ indicate[2,3,69,70] that the classical electrostatic Coulomb (or Madelung) energy is a very important energy. Furthermore, the observation[27-30] that the charge transfer from TTF to TCNQ is incomplete is most reasonably understood[3,71] by including strong electron correlation along the stacks.

c. The inequality of the activation energies for $T^{1/2}\chi$ *and* σ. While the difference in their behavior evident in Fig. 5 might be caused[5] by an activated mobility gap, it could well be caused[5] by the presence of Coulomb correlations. These interactions tend to separate the spin excitations from the charge excitations. Thus, in the presence of a distortion, the gap for the spin excitations would be expected to be different from that of the charge excitations, as observed experimentally (Fig. 5).

d. Enhancement of χ, at high temperatures, indicates[4] the presence of Coulomb interactions, which are at least comparable to the bandwidth, as discussed in Sec. III.

e. Spin waves. Recently, inelastic neutron scattering near $q = 0.295b^*$ has been interpreted[6,9] as being due to the excitation of spin waves, which would indicate at least intermediate strength Coulomb interactions, with a value of J comparable with that inferred from χ.

f. Scattering at "$4k_F$*."* New diffuse x-ray scattering has been recently discovered by Pouget *et al.*[29] and by Kagoshima *et al.*[30] at the wave vector $0.59b^*$, which is twice the wave vector $0.295b^*$ initially observed.[27,28] There have been two interpretations given (by Torrance[6] and by Emery[7]), both of which attribute this new scattering to Coulomb interactions of at least intermediate strength. The charge density wave associated with this scattering at "$4k_F$" is closely related[6,9] to the strong electron correlations of the Wigner crystal predicted in Refs. 2 and 3.

g. Enhancement of T_1^{-1}. Both the measurements and interpretation of the NMR relaxation rate in TTF-TCNQ have been extended by Jerome, Soda, Weger, and co-workers.[11,72] They conclude that Coulomb interactions play a significant role in the observed T_1^{-1} behavior.

In addition, it has been suggested[73] that the resistivity above 60 K in TTF-TCNQ is dominated by electron-electron scattering, presumably via Coulomb interactions. Coulomb interactions between charge density waves on different stacks are also included in most descriptions of the phase transition.[74] The fact that the observed ground state in TTF-TCNQ is not superconducting is also consistent with repulsive electron-electron interactions.[75]

It would be important to compare the magnitude of these Coulomb interactions with that of the electron-phonon interactions. While some of the interpretations[22] involving electron-phonon interactions remain controversial, recent x-ray and elastic-neutron measurements[27-30] have demonstrated that these interactions play a crucial role in TTF-TCNQ at low temperatures. The problem is how to quantitatively compare the strength of the electron-phonon interaction to that of the Coulomb interaction. One way is to recognize that the electron-phonon interaction gives rise to an attractive electron-electron interaction, which can be compared with the repulsive Coulomb interaction between electrons. Thus, the gap[76] induced by the electron-phonon interaction can be compared to the magnitude of U estimated in Sec. III. The maximum estimate of this gap, and hence the attractive electron-electron interaction, is ~ 0.12 eV (from the infrared "gap"). Since this magnitude is considerably smaller than the most conservative estimate of U (Table I), we would conclude that Coulomb interactions cannot be neglected from any discussion involving electron-phonon interactions. In fact, an improved approach would be to start with a model of strong-to-intermediate Coulomb interactions and add the electron-phonon interaction as a perturbation.

The evidence then, at this stage, indicates that the Coulomb interactions in TTF-TCNQ are comparable with the bandwidth, and probably larger, for at least one stack. The preceding evidence is also reasonable and consistent with the probable case that the interactions are comparable on both stacks. It is thus important that further work on TTF-TCNQ include the effects of Coulomb interactions. While much of the physics of these interactions is contained in the Hubbard model, new theoretical results are needed for the effects of the longer range parts of the Coulomb interaction, i.e., not only the on-site interaction, as well as for the Hubbard model with intermediate coupling.

Note added in proof. Very recently, Ehrenfreund and Heeger (unpublished) have examined the possible importance of Coulomb interactions on T_1^{-1} and χ. They conclude that these measurements are consistent with a value of $U/4\pi t \sim \frac{1}{3}$, or $U/4t \sim 1$ [being careful to use Eq. (2) and *not* mean-field theory[55]].

APPENDIX A: CHARGE- AND SPIN-DENSITY WAVE—DETERMINATION OF ρ

In order to quantiatively examine the magnetic susceptibility in Secs. II and III, it was necessary to know the average number ρ of electrons per molecule in TTF-TCNQ. The value of $\rho = 0.59$ was obtained from the magnitude of (the b-axis compo-

nent of) the wave vector q of the quasi-one-dimensional Peierls-like distortion observed at low temperatures. In this Appendix we discuss how q is related to ρ and how this relationship can be complicated by the presence of Coulomb interactions. In the case of noninteracting electrons ($U=0$), the wave vector of the Peierls distortion is equal to twice the Fermi wave vector $k_F = \rho(\pi/2b)$, so that

$$q_{CDW} = 2k_F = \tfrac{1}{2}\rho b^*, \quad U=0, \tag{6}$$

where b^* is the reciprocal-lattice vector along the stack. This is the wave vector [Eq. (6)] of the Peierls CDW (charge-density wave). Since the primary distortion observed[27-30] at low temperatures in TTF-TCNQ is at $q=0.295b^*$, Eq. (6) directly implies that $\rho=0.59$ (if the electrons are noninteracting) as shown schematically in Fig. 6(a). It was, therefore, this value of ρ which was used in the $U=0$ calculations of Fig. 1.

In the presence of significant Coulomb interactions, the situation is more complicated.[9] For example, it is not *a priori* clear[77] that such a system will have a well defined one-electron Fermi wave vector or that there will be a divergent response at any specific q. In the extreme limit that $U\to\infty$, the Hubbard model Hamiltonian for ρN_0 electrons in one dimension can be rigorously transformed[78] to one of $|1-\rho|N_0$ spinless noninteracting fermions. These fermions are like the $U=0$ fermions, but have a different value of k_F, such that the q of the distortion is twice as large as that given by Eq. (6), as shown by Bernasconi *et al.*[79] This is shown in Fig. 6(b) for the CDW distortions, which for $q>0.5b^*$ are folded back about the zone boundary $q=0.5b^*$. For large, but finite, values of U, the calculations of Coll[58] indicate an electronic (CDW) degeneracy in the electron-hole excitation spectrum at the same value of q [Fig. 6(b)]. These calculations[58] also reveal another complication associated with the presence of Coulomb interactions: in addition to the CDW degeneracy, there is a SDW (spin-density-wave) degeneracy, which has a different q from that of

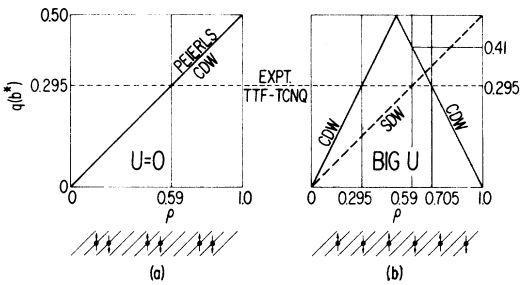

FIG. 6. Relationship between the wavevector of a CDW and SDW and the number (ρ) of electrons per molecule for $U=0$ and large U.

the CDW. In fact q_{SDW}, shown by the dashed line in Fig. 6(b), is also given by Eq. (6). In the limit of large U and $\rho=1$, this degeneracy at q_{SDW} has been shown[80] to be unstable to a "spin-Peierls distortion." Presumably for $\rho<1$, such an instability is also present, with a wave vector given by Eq. (6).

Some insight into the physical origin of the difference between the q of the CDW distortion in the case of $U=0$ compared to that in the large U case can be gained by examining the schematic view of a stack with $\rho=0.5$ at the bottom of Figs. 6(a) and 6(b). For $U=0$, the CDW (and SDW) corresponds to a pairing of electrons with period $4b$ (for $\rho=0.5$), as shown in the bottom of Fig. 6(a). In the case of strong repulsive interactions between electrons, on the other hand, the electrons stay away from each other and the period of the CDW is $2b$ along the stacks. In the limit of strong long-range Coulomb interactions, this CDW is the Wigner crystal.[2,3] Due to antiferromagnetic correlations, there is a SDW, whose period ($4b$) is twice that of the CDW, as seen in the bottom of Fig. 6(b).

There is another way of viewing the differences in Fig. 6. In a band with $U=0$, a given ρ, and $T=0$, ρN_0 electrons occupy $\frac{1}{2}\rho N_0$ states up to E_F, since each state can contain two electrons. In the presence of a strong U, however, ρN_0 electrons occupy ρN_0, or twice as many states, because the states with two electrons are increased in energy by $\sim U$. The magnitude of k_F is accordingly doubled, compared to the value calculated assuming $U=0$. In contrast, the effect of an attractive U (or electron-phonon interactions) is to open up a gap at E_F. This gap affects the energy of the states near E_F, but leaves the magnitude of $2k_F$ unaltered. Thus, Eq. (6) and Fig. 6(a) are valid for $U<0$ and in the presence of electron-phonon interactions.

The case of intermediate, repulsive $U\sim 4t$ would be expected to be somehow in between the two extreme limits of Figs. 6(a) and 6(b). According to Emery,[7,8] the case of weak U contains two CDW instabilities, one at the $U=0$ value, Eq. (6), and one at the large-U value.

In the presence of strong Coulomb interactions, Fig. 6(b), the magnitude of the observed wave vector $q=0.295b^*$ of the distortion alone does not uniquely determine the value of ρ. In fact, three values of ρ could give a distortion at the wave vector observed in TTF-TCNQ: $\rho=0.295$, 0.59, and 0.705. This ambiguity was removed by the very recent discovery[29,30] of additional diffuse x-ray scattering at $q=0.41b^*$. From Fig. 6(b), this scattering would be predicted only for the value of $\rho=0.59$ and therefore this value has been used

in Sec. II. Thus, in TTF-TCNQ, the observed distortions are interpreted to give the same value of $\rho = 0.59$ using the $U = 0$ or large U model.

This new scattering at $q = 0.41b^*$ is equivalent to $q = 0.59b^*$, which is twice the wave vector, $0.295b^*$, initially identified as $2k_F$. For this reason, the new scattering has been called "$4k_F$." The above discussion would suggest that it should be called $2k_F$, and that the scattering at $0.295b^*$ should be called "k_F" scattering. We note that this additional scattering is not readily understood by a $U = 0$ model, Fig. 6(a). Using a large-U model, on the other hand, such scattering was, in fact, predicted[81] for TTF-TCNQ. The observed wave vector is interpreted[6,9] as being associated with the Coulombically driven CDW described above. In the extreme large-U limit, this is the wave vector of the Wigner crystal, predicted in Refs. 2 and 3. This new scattering has been independently described by Emery[7,8] from a different point of view. He recognized that in the presence of weak Coulomb interactions, there is an instability of otherwise noninteracting electrons at $4k_F$. This is more rigorously described as a correlated state of a number of ($U = 0$) CDW's. In order to account for the dominant intensity of the "$4k_F$" scattering at 300 K, Emery extended this description to intermediate, and even strong, Coulomb interactions. While this interpretation at first appears quite different from ours, it is possible that the same physical effect is being described from two different limits: Emery's from the low-U limit, and ours from the strong-coupling limit. The important point, at this stage, is that both interpretations involve strong, or at least intermediate, Coulomb correlations and both determine the same value of $\rho = 0.59$.

APPENDIX B: PRODUCT $T\chi$

In Secs. II and III the experimental magnetic susceptibility χ was compared to the predictions of three simple models for the case of magnetically equivalent TTF and TCNQ stacks. It was found in Sec. II that a simple Pauli susceptibility of noninteracting electrons could fit the observed χ only with the parameters of E_F and $4t$ which appeared inconsistent with those inferred from other experiments. It is not clear if this inconsistency will remain when we consider the effects of unequal bandwidths on the two stacks, noncosine bands, interstack coupling, and other complications. Since we cannot consider each of these effects, with all possible parameters, explicitly in this paper, we need a general way to examine χ which is independent of the details of a particular model. For this reason, we consider the product $T\chi$, which can be viewed as proportional to the effective number of unpaired spins. This is a useful quantity because for $kT \gg E_F$ it approaches a limiting, saturation value which is determined *only* by (i) Fermi-Dirac statistics; and (ii) the assumption that the electrons are noninteracting. For $\rho = 0.59$, this limit is

$$T\chi_{T\to\infty} = \frac{\rho(2-\rho)}{2}\frac{N_0\mu_B^2}{k} = 0.416\frac{N_0\mu_B^2}{k}, \quad U = 0 \qquad (7)$$

for each kind of stack. Note that this limit is independent of the bandwidth, anomalies in the density of states, different behavior on different stacks, interstack coupling, and other details. This limit is shown in Fig. 7, along with the calculated values (short dashed lines) of $T\chi$ for a simple tight-binding band with $4t = 0.10$ and 0.15 eV (Sec. II, Fig. 1). At high temperatures, both curves approach the limit of $0.832N_0\mu_B^2/k$ (for two stacks) in accord with Eq. (7).

In the case of strong Coulomb interactions with $J \ll kT \ll U$, the spins are no longer correlated by J and

$$T\chi_{T\to\infty} = \rho\frac{N_0\mu_B^2}{k} = 0.59\frac{N_0\mu_B^2}{k}, \quad \text{big } U \qquad (8)$$

for each kind of stack. The difference between this large limiting value for big U and that of Eq.

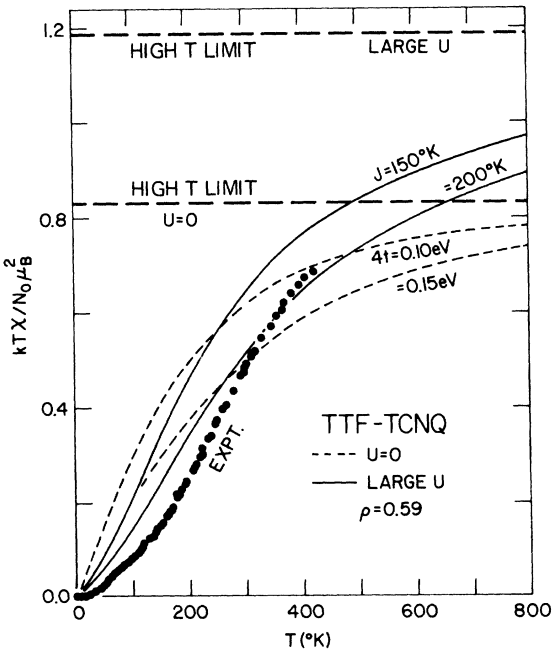

FIG. 7. Comparison of the experimental value of the product $T\chi$ (solid points) to the limiting value at infinite temperature. Also shown are the theoretical curves for $T\chi$ for a tight-binding band (dashed lines) and a large-U Hubbard model (solid line).

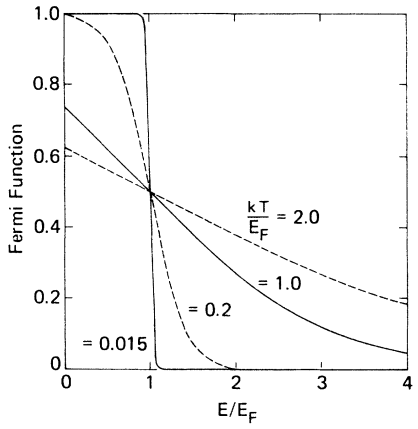

FIG. 8. Fermi function as a function of temperature, showing how quickly the sharpness of the Fermi surface washes out for large values of kT/E_F.

(7) for $U=0$ is due to the doubly occupied states (with paired spins) which are allowed if $U=0$, but excluded in the case of large Coulomb interactions. Thus, a larger fraction of the states are magnetic in the presence of a large U. The calculated values of $T\chi$ in the limit of large U (Sec. III) are also shown in Fig. 7 (solid lines) for $J=150$ and 200 K along with the limiting value, Eq. (8). The solid points in Fig. 7 are the experimental data, which are taken[15] only up to 415 K because of irreversible changes in the data occurring above this temperature. Thus, one can only speculate whether the data at higher temperatures would suddenly begin to saturate toward the limiting value for noninteracting electrons ($U=0$) or whether they would continue beyond this limit toward the big-U limit.

Nevertheless, we can explore the significance of the fact that $T\chi$ at 300–415 K is already very close to the $T=\infty$ limit (assuming $U=0$). First let us discuss the physical meaning of $T\chi$, the effective number of unpaired spins, with the aid of Fig. 8 which shows the Fermi distribution function for different values of kT/E_F. For a density of states of noninteracting electrons at zero temperature, each of the states below E_F is occupied by two electrons, whose spins are paired antiparallel, while the states above E_F are unoccupied; hence, the number of unpaired spins, $\sim T\chi$, is zero. At finite temperatures, electrons from states with energy $\sim kT$ below E_F are excited above E_F, giving rise to unpaired spins and hence a finite value of $T\chi$. As long as $kT/E_F \ll 1$ (for example, $kT/E_F \sim 0.01$ for metallic Cu and Na), only a small number of electrons near E_F will be affected and the vast majority of the spins will remain paired. The metal will be "degenerate," with a sharp Fermi surface (Fig. 8). As a measure of this, the product $T\chi$ will remain a small fraction of the $T\to\infty$ limiting value, Eq. (7). If the temperature was increased so that kT/E_F is no longer small, many more electrons will be excited, the Fermi surface will broaden, and $T\chi$ will increase, as seen in Figs. 8 and 7. For a cosine band with the values of $kT/E_F=0.015$, 0.2, 1.0, and 2.0 shown in Fig. 8, the product $T\chi$ (Fig. 7) is, respectively, 1%, 15%, 63%, and 85% of the $T\to\infty$ limit.

How does TTF-TCNQ fit into this physical picture? In Fig. 7, the value of $T\chi$ for TTF-TCNQ at 300 K is ~65% of the $T\to\infty$ limit, and it increases to ~85% at 415 K. This fact indicates most generally that *TTF-TCNQ is extremely nondegenerate at 300 K*, assuming only that $U=0$ and Fermi-Dirac statistics apply. The fact that $T\chi$ is ~85% of its $T\to\infty$ value at 415 K indicates that if we assume $U=0$ on both stacks, both stacks are extremely nondegenerate. In fact, in order for 85% of the limit of $T\chi$ to be reached at 400 K, the energy of a large majority of the paired states must be less than ~400 K. Thus, we can estimate that the total energy width of the large majority of the states is ~300 K wide ($E_F \sim 300$ K), assuming $U=0$. (Similar estimates were made for the specific case of a cosine band in Sec. II.)

This extreme nondegeneracy is completely inconsistent with the recent discovery[29,30] at 300 K of diffuse x-ray scattering at $0.59b^*$, the so-called "$4k_F$" scattering. In order for any scattering to be observable at such an incommensurate wave vector, a relatively sharp Fermi surface is necessary, at least on one stack. The possibility of markedly different χ on different stacks is excluded by the g-value[15,26] results. Hence, it appears most likely that Coulomb correlations are significant on both stacks.

In the case of large U, the infinite temperature limit corresponds to the electronic spins being paramagnetic. The fact that the observed magnitude of $T\chi$ at 415 K is large indicates that the spins in TTF-TCNQ are paramagnetic at these high temperatures. This observation is consistent with the fact that kT (= 415 K) is large compared with the estimated interaction energy between spins, i.e., $J=150$–200 K. In any model the data plotted in Fig. 7 indicate that the *spins* are paramagnetic. It is only in a large U model, however, that the *charges* can be sufficiently ordered that there is a well defined CDW or Fermi surface.

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$$4t = (0.255/\sin\tfrac{1}{2}\pi\rho)(\hbar\omega_p)^2 ,$$

where $4t$ and $\hbar\omega_p$ are in units of eV. Values quoted are for $\rho = 0.59$.

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Shiba (Ref. 31) for the case of $\rho = 1$. For $\rho = 0.6$, Shiba's numerical calculations are better fit with a factor $\sim 1.1U/4\pi t$ in the denominator of Eq. (2). The small difference is neglected and Eq. (2) is used for the enhancement factor.

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