order exist. From Fig. 3, the reduced magnetization at 1.5 K in a field of 2.4 T is approximately 0.7. According to Fig. 5, this corresponds to $J \approx 1.6$ cm^{-1} leading to a Weiss field of 2.57 T, consistent with $H_w=2.4$ T. On the other hand, $J=2.1$ cm^{-1} leads to $H_w=3.3$ T at the nearest Gd sites, almost completely saturating the cluster magnetization at zero applied field and preventing the observation at 1.5 K of the effect of the spin-flop transition and the initial rise of Δ_{FC} (Fig. 4). Furthermore, the energy E_m necessary to promote the Gd cluster to a saturated ferromagnetic order is given approximately by $48S^2I = 59$ cm^{-1}; it is larger than the Δ_{FC} observed, therefore preventing relaxation in the ground states after the fluorescence. On the other hand, the smaller J value accounts for the effects arising from nonsaturation of the relaxed ground state.

The changes in the effective J may reflect the missing of higher-order terms in the Hamiltonian or a change in the interatomic distances around the Cr^{3+} in the $^4A_2$ state with magnetic field as there is observed a simultaneous change of the fluorescence lifetimes and intensities related to the magnitude of the low-symmetry components of the local crystal field.

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Systematic Trends in Short-Range Coulomb Effects among Nearly One-Dimensional Organic Conductors

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A resolution to the controversy over the magnitude of the effective short-range Coulomb interaction in molecular conductors is proposed by showing that it depends very strongly on band filling because of intermolecular correlations.

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The variety of electronic properties in nearly one-dimensional organic charge-transfer salts is remarkably rich. Structurally similar materials, consisting of chemically similar molecules, range from Mott insulators[1] through organic metals[2,3] and superconductors.[3] Although the systematics of this behavior have not been fully developed, there is little doubt that they depend heavily upon the effective short-range interactions among conduction electrons.[4] These interactions, however, remain poorly characterized. Intense controversy persists over whether they are large[5] or small[2,6] compared with the conduction bandwidth, and strong experimental evidence has appeared on each side.[2,5,6]

We seek here to resolve that controversy. We argue that the short-range interactions in these materials are not fixed, but are self-consistently screened through the long-range interactions. When intermolecular Coulomb correlations are included, this screening becomes extremely sensitive to the population of the conduction band. We demonstrate the effect by exact numerical calculations on finite chains, and show how the effective short-range interactions can be large for half-filled and also for quarter-filled bands, yet small for certain intermediate band fillings. In this light we reconsider the experimental evidence and show that the entire class of materials follows the pattern we predict.

Traditionally, short-range interactions in these materials have been discussed[5] in terms of the simple Hubbard Hamiltonian

$$H_0 = t\sum_{i,\sigma}(a_{i\sigma}^{\dagger}a_{i+1,\sigma} + a_{i+1,\sigma}a_{i\sigma}) + U_{\mathrm{eff}}\sum_i n_{i\alpha}n_{i\beta}, \qquad (1)$$

where the operator $a_{i\sigma}$ annihilates an electron of spin σ at site i. In this framework the relative strength of the interactions is measured by the ratio of U_{eff}, the effective repulsion between two electrons on the same site, to t, the tight-binding bandwidth parameter.

The Hamiltonian of Eq. (1) is incomplete. Importantly, it neglects all long-range Coulomb interactions, and with them the principal contributions to the cohesive energy,[7] high-frequency excitation spectrum,[8] and dielectric screening.[8,9] Especially in the metallic state, that screening acts to modify the intramolecular Coulomb repulsion, and must be considered even in the context of properties which depend primarily upon short-range interactions. To the extent that such properties can be described by Eq. (1), they will reflect an apparent U_{eff} which can be substantially smaller than the bare on-site interaction U, and which depends in general upon the density ρ of screening conduction electrons per molecule.

To demonstrate, recall that in the free constituent molecules, U (measured as the difference between the first and second ionization levels) is typically 4 eV. This corresponds to the repulsion between two electrons in a box of average radius 3.6 Å, consistent with actual molecular dimensions. That repulsion must be heavily screened in a metallic solid like TTF-TCNQ (tetrathiafulvalene-tetracyanoquinodimethane), where the nominal Thomas-Fermi screening length is but 1.2 Å. Indeed, a simple Thomas-Fermi calculation for a doubly charged impurity suggests that U is reduced fiftyfold. In the random-phase approximation[8] the reduction is less drastic, but still very substantial.

Such estimates are not self-consistent, and they neglect the effects of exchange and intermolecular correlations. To assess these we have developed elsewhere[9] a full calculation of the screening, which is, however, rapidly convergent only for a limited range of band fillings ρ. Our results do confirm that the screening is essentially complete, and the electronic pair correlation function is at its tight-binding Hartree limit, over distances larger than the nearest-neighbor intermolecular spacing. Hence it is sufficient to frame a discussion of correlation effects in terms of the first-neighbor extended Hubbard Hamiltonian,[10]

$$H = H_0 + V\sum_i n_i n_{i+1}, \qquad (2)$$

where V is the Coulomb repulsion between carriers on nearest-intrachain-neighbor molecules. More distant neighbors can quantitatively, but not qualitatively, affect our results. We take both U and V to have been renormalized by these effects and by the background high-frequency dielectric constant, and we defer until later a discussion of interchain screening.

To address the size of the short-range interactions we ask what value of U_{eff} is required in order that the low-frequency behavior of Eq. (1) best mimic that of Eq. (2). Representative of that behavior is the temperature-dependent static magnetic susceptibility $\chi(T)$, which will be enhanced over its Pauli value when U_{eff} is large. Using the method of Mazumdar and Soos,[11] we are able to calculate $\chi(T)$ exactly for finite chains. These cannot reproduce the low-temperature susceptibilities of the real materials, but for our purposes the high-temperature behavior will suffice.

As displayed in Fig. 1, our results depend strongly on ρ. For example, the position of the maximum in $\chi(T)$, nearly independent of ρ in the simple Hubbard model, decreases rapidly as $\rho \to 0.5$ in the more extended description. Consistent with this trend, we observe that the experimental $\chi(T)$ generally reach maxima near room temperature for materials with $\rho = 0.5$, but are still ascending at much higher temperatures for materials with larger ρ.

For a half-filled band ($\rho = 1$), the susceptibilities calculated from Eqs. (1) and (2) match closely when $U_{\mathrm{eff}} = U - V$, consistent with well-known results. Close to quarter-filling the susceptibility is still further enhanced, with U_{eff} approaching U itself. In contrast, for intermediate band fillings such as $\rho = 0.8$, the screening is far more

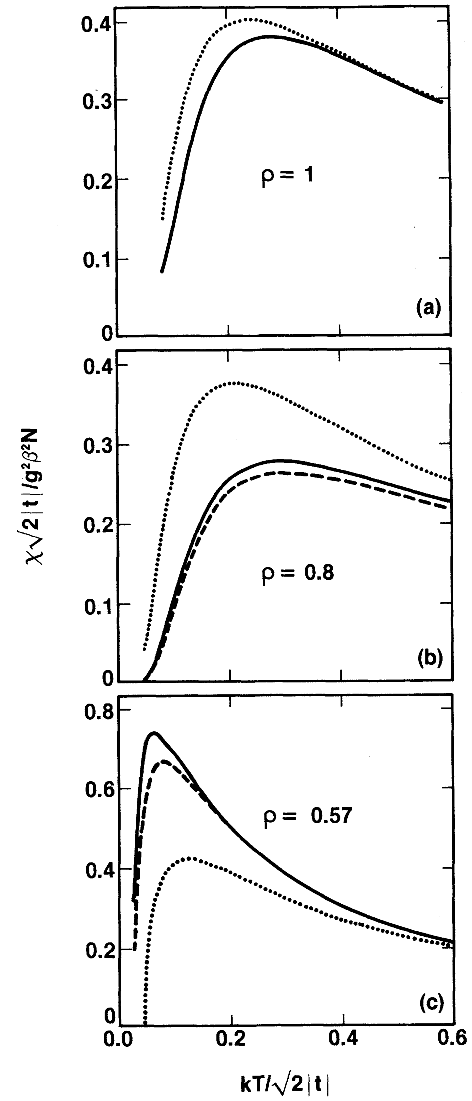

FIG. 1. Reduced magnetic susceptibilities vs reduced temperature for single chains of N molecules with $4|t| = 0.5$ eV, $U = 7\sqrt{2}\,|t|$, $V = 3\sqrt{2}\,|t|$, and $\rho = 4/N$. Solid line: Eq. (2). Dotted line: Eq. (1) with $U_{\rm eff} = U - V$. Dashed line: Eq. (1) with (b) $U_{\rm eff} = U - 1.6V$ and (c) $U_{\rm eff} = U$.

effective and $U_{\rm eff}$ is substantially *smaller* than $U - V$.

The correlation effects underlying this pattern are clearest in the limit $t \to 0$. Here the ground state of Eq. (2) is a Wigner crystal consisting of singly occupied and vacant sites, and $U_{\rm eff}$ is the difference in energy between this ground state and a weighted average of excited states containing exactly one doubly occupied site. For $\rho = 1$, all sites are singly occupied in the ground state, and the transfer of an electron from any site to a nearest neighbor requires an energy $U - V$. If, however, we eliminate the electron at site i, the energy of the special transfers $i \pm 2 \to i \pm 1$ is but $U - 2V$, and $U_{\rm eff}$ is slightly reduced by their contribution. With further depletion of the band the relative weight of such low-energy transfers increases until it reaches a maximum at $\rho = 0.75$, concomitant with a minimum in $U_{\rm eff}$. The contribution of these transfers then decreases rapidly until it vanishes at $\rho = 0.5$, where only second-neighbor sites are occupied in the ground state and $U_{\rm eff} = U$. When the same arguments are extended to include interchain correlations, the conclusions are unchanged for $\rho = 1$ and $\rho = 0.5$, but $U_{\rm eff}$ for intermediate ρ is further diminished.

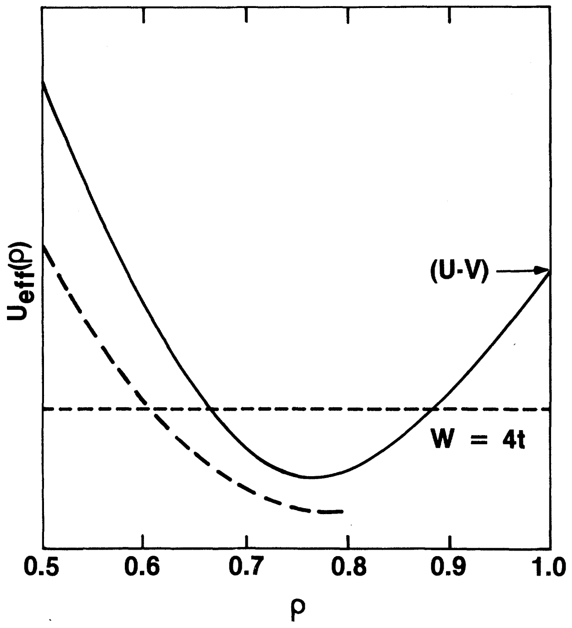

FIG. 2. Schematic behavior of $U_{\rm eff}$ vs ρ for single chain (solid line) and real nearly one-dimensional conductor (dashed line).

For finite t, the overall behavior of $U_{\rm eff}$ on a single chain is plotted as a function of ρ in Fig. 2. Also sketched is a schematic estimate of the effect in real organic conductors, where U and V are both substantially reduced (at low frequencies) by interchain metallic screening.[12] Materials with ρ in the neighborhood of 0.75 can behave as though $U_{\rm eff}$ is relatively small, while outside that region $U_{\rm eff}$ rises rapidly and can exceed the bandwidth $4t$. We have shown elsewhere[1a] that the metallic state is stable only below a critical value of ρ near 0.8, where a first-order transition occurs to a Mott insulator with $\rho = 1$. In such insulators the interchain screening is no longer metallic, and $U_{\rm eff} \sim U - V$.

TABLE I. Signatures of $U_{\rm eff}$ for organic charge-transfer salts in order of increasing band filling. The abbreviations in the materials column are, in part, as follows: MEM, methylethylmorpholinium; DEM, diethylmorpholinium; TCNQ, tetracyanoquinodimethane; Qn, quinolinium; TTF, tetrathiafulvalene; TSeF$_4$, tetraselenafulvalene; NMP, N-methylphenazine; Phen, phenazine. Some have prefixes DM, TM, or HM for dimethyl, tetramethyl, or hexamethyl, respectively.

Material	ρ	χ enhanced?	$4k_F$?
MEM(TCNQ)$_2$	0.5	yes[a]	yes[a]
DEM(TCNQ)$_2$	0.5	yes[b]	yes[b]
Qn(TCNQ)$_2$	0.5	yes[c]	yes[d]
TMTSeF-DMTCNQ	0.5	?	yes[d]
TMTTF-bromanil	0.5	yes[e]	?
TMTFF-chloranil	~0.54	yes[e]	?
TMTTF-TCNQ	~0.55	yes[f]	yes[e]
TMTSeF-TCNQ	0.57	yes[f]	no[d]
TTF-TCNQ	0.59	yes[f]	yes[g]
NMP$_x$(Phen)$_{1-x}$TCNQ			
$0.5 \leq x \leq 0.57$	0.5 – 0.57	yes[h]	yes[h]
$0.67 \leq x \leq 1$	0.57 – 0.67	no[h]	no[h]
TSeF-TCNQ	0.63	no[f]	no[g]
HMTTF-TCNQ	0.72	no[i]	no[g]
HMTSeF-TCNQ	0.74	no[f]	no[g]
TTF-Br$_{0.79}$	~0.79	no[j]	no[j]
HMTSeF-TCNQF$_4$	1.0	yes[k]	. . .
HMTTF-TCNQF$_4$	1.0	yes[l]	. . .

[a] Ref. 13.
[b] Ref. 14.
[c] Ref. 15.
[d] Ref. 19.
[e] Ref. 16.
[f] Ref. 2.
[g] Ref. 20.
[h] Ref. 21.
[i] Ref. 17.
[j] Ref. 18.
[k] Ref. 1a.
[l] Ref. 1b.

The commonly accepted signatures of large short-range Coulomb interactions in organic metals are enhanced magnetic susceptibilities[5] and the appearance[4] of diffuse x-ray scattering at wave vectors $4k_F$. We have surveyed the experimental literature[1,2,13-21] for such behavior, and in Table I we list representative findings in order of increasing ρ.

The results agree fully with the predictions of Fig. 2. Enhanced susceptibilities and $4k_F$ scattering always appear in the range $0.50 < \rho < 0.55$ and never appear in the range $0.63 < \rho < 0.8$. The intervening range $0.55 < \rho < 0.63$ forms a transition region: the symptoms appear at $\rho = 0.59$ in TTF-TCNQ, but do not appear at $\rho = 0.57$ in TMTSeF-TCNQ, with its considerably larger bandwidth. Compounds in the range $0.83 < \rho < 1.0$ are unknown,[22] and compounds with $\rho = 1$ are universally Mott insulators with $U_{\rm eff} \gg t$.

These patterns cannot reasonably rise from variations in bandwidth, crystal structure, or unscreened U. For example, the molecular U and the intrastack lattice constants and overlap patterns are nearly identical in the series TTF-TCNQ,[2] TMTTF-TCNQ,[2] HMTTF-TCNQ,[17] and the small-$U_{\rm eff}$ metal HMTSeF-TCNQ is isostructural[1a] with the large-$U_{\rm eff}$ Mott insulator HMTSeF-TCNQF$_4$. Especially persuasive are the systematic studies of NMP$_x$(Phen)$_{1-x}$TCNQ by Epstein *et al.*,[21] who were able to control ρ continuously in a single system. They observed an evolution from an enhanced susceptibility and pure $4k_F$ scattering at $\rho = 0.50$ to a Pauli susceptibility and pure $2k_F$ scattering, consistent with small $U_{\rm eff}$, at $\rho = 0.63$.

We expect corresponding ρ dependences in other quantities sensitive to correlation effects, such as thermoelectric power and spin-lattice relaxation rates. Reinterpretations of the data are in progress.

In summary, we find that "big-U"[5] and "small-U"[2,6] descriptions of organic metals are both correct, but in different domains of band filling ρ. It has become fashionable to construct phase diagrams for these materials in terms of separate coupling constants g_1 and g_2 for backward and forward scattering on the Fermi surface. Our work implies that the effective values of the g_i will also depend upon intersite Coulomb correlations, and hence upon ρ. The band filling thereby emerges as an important variable in the design of new organic conductors. Theoretical criteria for its chemical control will be discussed elsewhere.

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Theory for the Polarizability Function of an Electron Layer in the Presence of Collisional Broadening Effects and Its Experimental Implications

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The polarizability function of a two-dimensional electron layer submerged in a three-dimensional dielectric material and interacting with a random distribution of static charged impurity centers is calculated. Scattering and screening are treated self-consistently and each affects the other. The resultant scattering time is found to depend on the impurity density N_i through the $(aN_i + bN_i^2)^{-1}$ law which has been observed experimentally in silicon inversion layers. The theory is in good agreement with the experimental findings on the parameters a and b.

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The screening behavior of a two-dimensional electron gas has been a subject of great interest[1-5] in recent years. This interest is motivated to a considerable extent by the existence of electron systems which are dynamically two dimensional in their behavior.[6] Such systems are inversion and accumulation layers at semiconductor-insulator interfaces, and electrons trapped in the quantum wells of semiconductor heterostructures and superlattices. A good knowledge of the screening function is essential for our understanding of these systems. In particular, a theory of transport properties depends on the availability of an accurate static dielectric function. The dielectric function that has been commonly used[7] in the calculation of transport properties is the one obtained[1] within the random-phase approximation (RPA) in which one uses the polarizability of the noninteracting system in evaluating the dielectric function. One of the features of the RPA is that the corresponding level broadening or the scattering rate (including only the charged-impurity scattering effects), calculated within the Born approximation, is linearly proportional to the charged-impurity density N_i. This is a feature of the single-site approximation for impurity scattering, and the feature persists in the more sophisticated nonlinear screening formalism[4] of Vinter, which is based on the density functional theory of the inhomogeneous electron gas.