X-Ray Observation of Crossover of $2k_F$ to $4k_F$ Scattering in (N-Methylphenazinium)$_x$(Phenazine)$_{1-x}$(Tetracyanoquinodimethane) [(NMP)$_x$(Phen)$_{1-x}$(TCNQ)], $0.5 \leq x \leq 1.0$

A. J. Epstein
Xerox Webster Research Center, Webster, New York 14580

and

J. S. Miller
Occidental Research Corporation, Irvine, California 92713

and

J. P. Pouget and R. Comès
Laboratoire de Physique des Solides, Associé au Centre National de la Recherche Scientifique, Université Paris-Sud, 91405 Orsay, France

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We report the temperature-dependent x-ray diffuse scattering of (NMP)$_x$(Phen)$_{1-x}$-(TCNQ) as a function of conduction-electron density (x). With decreasing x three different unique electronic instability regimes are successively observed on the TCNQ chains: (i) the $2k_F$ instability for $\frac{2}{3} \leq x \leq 1$, (ii) both $2k_F$ and $4k_F$ instabilities for $0.57 \leq x \leq \frac{2}{3}$, and (iii) the $4k_F$ instability alone for x close to 0.5. These results provide direct evidence for the critical role of interchain screening in determining the magnitude of the effective Coulomb interaction.

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Considerable progress has been made in the understanding of one-dimensional (1D) metals in the past several years.[1] The occurrence of a Peierls transition in tetrathiafulvalene tetracyanoquinodimethane and related compounds, first deduced from the observation of low-temperature incommensurable modulated structures, was confirmed by the 1D character of the precursor $2k_F$ scattering[2] (twice the Fermi wave vector). Subsequent observation[3] of 1D x-ray diffuse scattering at the wave vector $4k_F$, in only a few materials,[4] led to a continuing controversy[5-7] concerning the detailed cause of this anomaly, although it had already been considered in early theoretical papers.[8] It has been proposed that the $4k_F$ scattering occurs when the on-site electron-electron Coulomb repulsion, U, is greater than the bandwidth, W. The factors which determine the relative magnitude of U and W have, until now, remained unresolved.[9] The $4k_F$ and $2k_F$ scatterings have often been associated with the independent behavior of the donor and acceptor stacks in two-chain materials such as tetrathiafulvalene tetracyanoquinodimethane, but it is conceivable that both anomalies arise on one chain. We have performed experiments to investigate the roles of the value of k_F and disorder in these systems and determine their effects on $4k_F$ scattering.

In this Letter we present the results of the x-ray diffuse scattering photographic investigation of the temperature-dependent dynamical properties of a series of isomorphous compounds of varying Fermi wave vector. Several unique features concerning the electronic instabilities of 1D conductors not observed in any of the previously studied systems are reported. As the conduction-electron density is reduced, a crossover from a two-chain conductor to a one-conducting-chain system is observed, accompanied by a crossover from a $2k_F$ to a $4k_F$ regime, with the coexistence in a narrow density range of both $2k_F$ and $4k_F$ anomalies. These results confirm the central role of interchain screening in determining the magnitude of U/W. The $4k_F$ anomaly is directly associated with $U/W > 1$ by comparison of properties of the systems exhibiting $4k_F$ with those of known large U/W systems and by comparison with other system properties, such as plasma frequency. As part of this detailed study, the degree of disorder on each chain was varied. The results demonstrate the weak effects of disorder on neighboring chains as compared with disorder on the conducting chain.

The systems studied are based upon (NMP)-(TCNQ), and are achieved by substituting neutral phenazine, phen^0, for up to 50% of the asymmetric NMP.[10] The phen^0 is of similar size, shape, and polarizability to NMP$^+$ but is neutral, closed shell, and symmetric. Detailed analysis has shown that the overall (NMP)(TCNQ) crystal structure[11] remains unchanged even with replacement of NMP by up to 50% phen^0.[10] Consequently, the number of conduction electrons per unit cell to be shared among the donors and TCNQ is equal to the fraction x of NMP in the alloy $(\mathrm{NMP})_x(\mathrm{Phen})_{1-x}(\mathrm{TCNQ})$.[10] Conductivity, σ, studies have shown these materials to have a $\sigma(T)$ similar to that of (NMP)(TCNQ) with a maximum in $\sigma(T)$ at a temperature lower than that of (NMP)(TCNQ).[12,13] The experimental setup for the photographic study of diffuse x-ray scattering was that previously used for other investigations.[3,14]

The two end points of the series, (NMP)(TCNQ) and $(\mathrm{NMP})_{0.5}(\mathrm{Phen})_{0.5}(\mathrm{TCNQ})$, have very different behavior. For $x = 1.0$, two types of temperature-dependent 1D scattering are observed[14]: A first 1D scattering is observed at room temperature at the wave vector $q_2 = 0.33a^*$; it couples three-dimensionally below 200 K. Further diffuse scattering is observed below 70 K at half the previous wave vector ($q_1 = 0.165a^*$). As expected for an intrinsically disordered system, no long-range 3D ordering is observed down to 20 K. A temperature-independent diffuse x-ray scattering was also observed[14] for $x = 1.0$, and assigned to the (short-range) orientational order of the asymmetric and polar NMP molecules. Substitution of the symmetrical phenazine molecule for the NMP molecule reduces the dipolar disorder at the expense of a substitutional disorder. For the alloys of lowest phenazine concentration ($x \geqslant 0.6$), the disorder keeps qualitatively the same correlations, although there is an increase in the correlation length of methyl groups along the chain with decreasing x. For $x \sim 0.50$, a 3D long-range order appears between NMP and phenazine molecules as shown in Figs. 1(a) and 1(b), for the donor plane.

Substitution of the phenazine for the NMP molecules also results in substantial changes in the temperature-dependent 1D x-ray diffuse scattering, removing ambiguities[14] in the q_1 and q_2 assignments. A typical x-ray pattern for the alloy $(\mathrm{NMP})_{0.786}(\mathrm{Phen})_{0.214}(\mathrm{TCNQ})$ at 25 K is shown in Fig. 2(a). It presents two interesting features: (a) The q_1 scattering is not observed and (b) the q_2 scattering is shifted towards the layers of main Bragg spots [$q_2 = (0.28 \pm 0.01)a^*$ for $x = 0.786$]. The vanishing of the q_1 scattering can be due to the additional disorder introduced on the donor stacks (their Fermi wave vector now is not defined). This assigns the q_1 scattering to the NMP chain, and consequently q_2 to the TCNQ chains. Taking into account the amount of available electrons, the assignment of q_2 to the TCNQ chains leaves but two possibilities[14]: $q_2 = 2k_\mathrm{F}$ or $q_2 = 1 - 4k_\mathrm{F}$. The shift of q_2 from $\frac{1}{3}a^*$ in pure

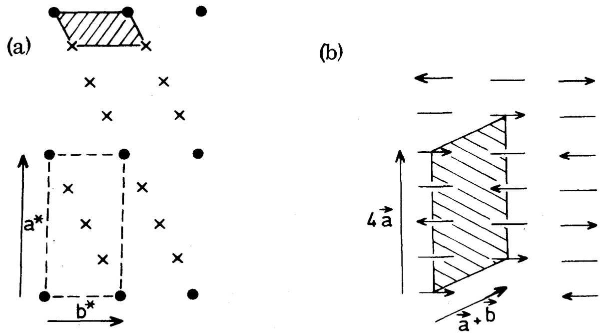

FIG. 1. (a) Position of the superstructure reflections (×) in $(\mathrm{NMP})_{0.5}(\mathrm{Phen})_{0.5}(\mathrm{TCNQ})$ with respect to the (NMP)(TCNQ) Bragg spots (dots). (b) Suggested NMP and Phen ordering in real space that would lead to (a).

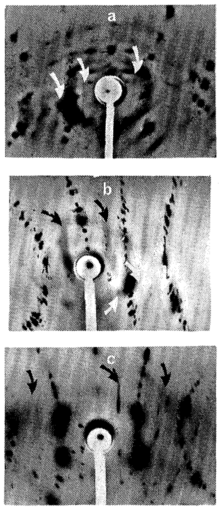

FIG. 2. X-ray diffuse scattering patterns of $(\mathrm{NMP})_x$-$(\mathrm{Phen})_{1-x}(\mathrm{TCNQ})$: (a) for $x = 0.786$ at 25 K and showing a quasi-1D scattering at $2k_\mathrm{F} = 0.28a^*$ (white arrows), (b) for $x = 0.59$ at 25 K and showing quasi-1D scattering at $2k_\mathrm{F} = 0.28a^*$ (white arrows) and $4k_\mathrm{F} = 0.56a^*$ (black arrows), and (c) for $x = 0.50$ at 200 K, and showing a temperature-dependent quasi-1D scattering at $4k_\mathrm{F} = 0.5a^*$ (black arrows). The a^* direction is horizontal on these patterns. The intensity distribution of the patterns taken at low temperature reveals an additional short-range 3D coupling as expected for a Peierls distorsion.

(NMP)(TCNQ) to a smaller value in the phenazine-doped material rules out the possibility $q_2 = 1 - 4k_F$ which implies an increase of q_2. Thus q_2 can be assigned to a $2k_F$ scattering from the TCNQ chain. This determines a charge transfer of $\frac{2}{3}$ electron per molecule in pure (NMP)(TCNQ), a value which has also been recently obtained from vibrational spectroscopy measurements.[15] Hence, the position of the q_2 scattering directly gives the charge transfer to the TCNQ chains ($\rho = 2q_2$) in the series of phenazine-doped samples, Fig. 3.

Figure 2(b) shows another typical x-ray pattern for $(NMP)_{0.59}(Phen)_{0.41}(TCNQ)$ at 25 K. In addition to the q_2 scattering which is still observed at $q_2 = (0.28 \pm 0.01)a^*$ (white arrows), another quasi-1D scattering can now be observed at a wave vector $q_3 = (0.56 \pm 0.01)a^*$ (black arrows), i.e., at $2q_2$ and therefore corresponding to $q_3 = 4k_F$. Figure 2(b) further shows that the intensity distributions in the two types of 1D scattering differ noticeably. Similarly, temperature-dependent q_3 ($4k_F$) scattering, although weaker, can be observed in addition to q_2 ($2k_F$) scattering in an alloy with $x = 0.64$; this last observation seems to set $x \simeq \frac{2}{3}$ as the upper limit for the observation of $4k_F$ scattering. With these results we have obtained a unique example in which both $2k_F$ and $4k_F$ instabilities are observed on the same kind of chains (TCNQ).

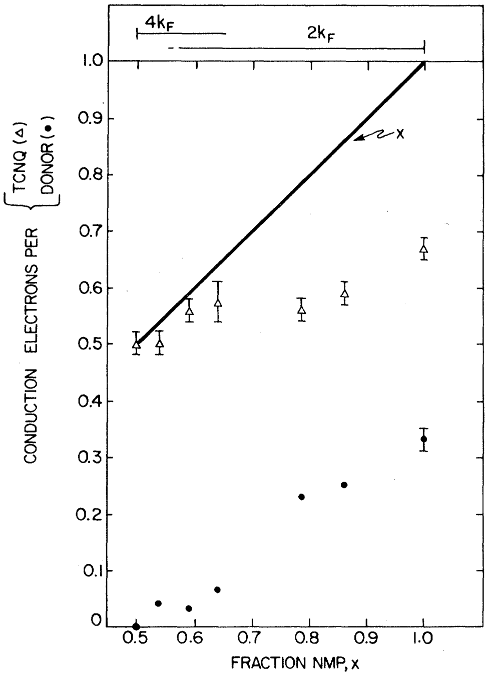

FIG. 3. Number of conduction electrons per TCNQ (triangles) and per donor molecule (dots) vs NMP concentration x. The solid line gives the total conduction-electron concentration available. The experimental determinations of the number of conduction electrons per TCNQ deduced from the value of the wave vector in chain direction of the $2k_F$ and/or $4k_F$ scattering are given with their error bars; the number of conduction electrons per donor, which is obtained by subtraction from the total available electrons x, is given without error bars. In the upper part of the figure the concentration ranges where $2k_F$ and/or $4k_F$ are observed is indicated.

For $(NMP)_{0.5}(Phen)_{0.5}(TCNQ)$ the temperature-dependent q_3 scattering has shifted to $q_3 = 0.5a^*$. In Fig. 2(c) (200 K) it corresponds to diffuse intensity lines (black arrows) which are superimposed on the superstructure satellites; at lower temperatures the intensity of the q_3 scattering increases with coalescing into broad discrete spots (3D coupling). The other 1D scattering q_2 assigned to $2k_F$ for the lower phenazine concentrations is no longer observable. A diffuse scattering at $0.5a^*$ implies one conduction electron per repeat unit if it is associated with $2k_F$ or 0.5 conduction electron per repeat unit if it is associated with $4k_F$. From the chemical requirement that there is a maximum total of 0.5 conduction electron for both stacks together, q_3 must be associated with $4k_F$, corresponding to a full charge transfer (Fig. 3).

In summary the x-ray diffuse scattering investigation of $(NMP)_x(Phen)_{1-x}(TCNQ)$ has revealed several unique features concerning the electronic instabilities in 1D conductors which were not observed in any of the previously studied systems: (a) In pure (NMP)(TCNQ) the donor and acceptor stacks have distinct $2k_F$ instabilities at, respectively, $q_1 = \frac{1}{6}a^*$ and $q_2 = \frac{1}{3}a^*$, with $\frac{2}{3}$ electron transferred to the TCNQ molecule. (b) The disorder introduced on the donor NMP stacks by the substitutional phenazine leads to a poorly defined Fermi wave vector, and consequently to the suppression of the corresponding $2k_F$ scattering (q_1). (c) The progressive decrease of electron density for increasing phenazine concentrations induces in the first stage, $\frac{2}{3} < x < 1$, a simple shift of the corresponding $2k_F$ wave vector from the acceptor TCNQ stack (decrease of q_2). (d) For lower electron densities, $0.57 \lesssim x \lesssim \frac{2}{3}$, $2k_F$ and $4k_F$ scattering from instabilities occurring on the same TCNQ stacks can be observed. (e) At 50% phenazine concentration ($x = 0.5$) full charge transfer is found and the $4k_F$ instability alone is observed on the TCNQ chains. In addition, the diffuse x-ray scattering from the TCNQ stacks seems quite insensitive to the detailed order on the donor stacks.

The simultaneous appearance of $4k_F$ scattering together with a nearly complete charge transfer occurs at about the same phenazine concentration as the anomalous red shift of the plasma frequency reported by Weinstein *et al.*[16] On this basis as well as magnetic susceptibility[17] and electron-spin-resonance results,[18] they proposed that as x decreases below $\sim\frac{2}{3}$ there is an emptying of the conduction band on the donor stack and a simultaneous shift from small U/W to large U/W behavior.[19] As the bandwidth increases[10] slightly in going from $x = 1.0$ to $x = 0.5$, the increase in U/W must be due to an increase in U. This increase in U coincides with the emptying of the planes of donor molecules of mobile conduction electrons; these results directly demonstrate for the first time the critical role of interchain screening in determining the effective Coulomb repulsion and that the Coulomb repulsion is not determined solely by on-site interaction.[20]

It has been earlier noted[19] that the $(NMP)_{0.5}(Phen)_{0.5}(TCNQ)$ is nearly indistinguishable in its transport and magnetic behavior from other one-quarter-filled-band TCNQ compounds such as $(quinolinium)(TCNQ)_2$. The behavior of these systems has been interpreted[21] in terms of $U/W > 1$, although this assignment has been called into question.[22] The direct observation of $4k_F$ scattering in the $x = 0.5$ system, as well as strong $4k_F$ scattering and weak $2k_F$ scattering in $(quinolinium)(TCNQ)_2$,[23] now confirms that $U > W$. It has also been proposed that disorder-induced localization is of paramount importance in the one-quarter-filled-band systems.[24] The presence of indistinguishable transport and magnetic properties for the crystallographically ordered $(NMP)_{0.5}(Phen)_{0.5}(TCNQ)$ indicates the secondary role of off-chain disorder in inducing electron localization in these systems.

Part of this work was performed by one of us (A.J.E.) as visiting scientist at Université Paris-Sud.

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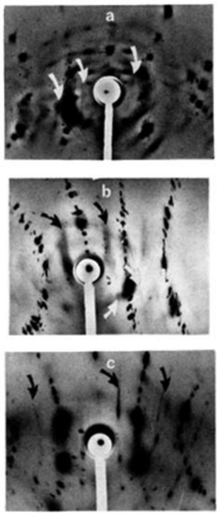

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