close to an $A \rightarrow C$ second-order transition. We observe the divergence of the corresponding Rayleigh intensity and the thermodynamic slowing down of the associated relaxation time from 350 mK to a few millikelvins near the transition. Both correspond to the same critical exponent $\gamma = 1.00 \pm 0.1_5$.[13] This result indicates a regular behavior of the associated viscosity and shows a better agreement with a mean-field model than with a heliumlike one in our temperature range. An improved apparatus can extend the measurements closer to T_{CA} and allow observation of an eventual "crossover" to a critical regime. The interferometric measurement of tilt angle by Galerne[6] is promising in that way. Note that our experiment is not sensitive to molecular rotations which would correspond to much higher frequencies; it thus cannot be conclusive on McMillan model[4] validity.

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Core Excitons in Tetrathiafulvalene-Tetracyanoquinodimethane (TTF-TCNQ)

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Inelastic electron scattering spectra of nitrogen, sulfur, and carbon core excitations in tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) are presented. The spectra exhibit sharp excitonic transitions to final states localized on separate TTF$^+$ or TCNQ$^-$ ions followed at higher energies by a continuum of transitions to free-electron states. In contrast to prior photoemission experiments, we find no evidence for neutral molecules in the bulk of TTF-TCNQ.

The well-known organic metal tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) is unique in that it contains two distince one-dimensional stacks of donor and acceptor molecules with conduction bands of comparable bandwidth due to similar intermolecular separations.[1] Techniques which probe low-energy excitations of this crystal are unable to distinguish between the two conducting chains. However, we have measured transitions from core states to low-lying final

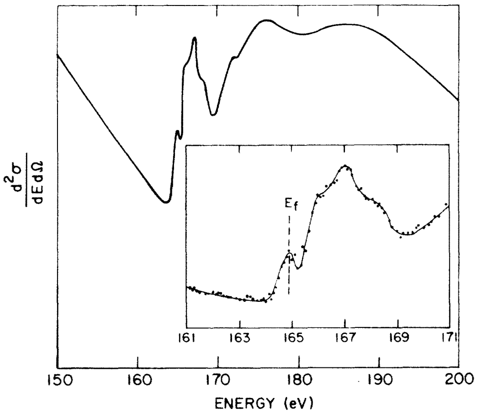

FIG. 1. Inelastic electron scattering spectra above the sulfur $L_{2,3}$ threshold.

states localized on each chain with inelastic electron scattering (IES) spectroscopy. Specifically, we masured excitations of sulfur $2p$ states (only in TTF) and nitrogen $1s$ states (only in TCNQ) as well as carbon $1s$ states. In all cases, the spectra consist of sharp excitonic transitions to molecular orbitals localized on TTF$^+$ and TCNQ$^-$ molecules followed by a continuum of transitions to three-dimensional free-electron states above the ionization threshold.

IES spectra, shown in Figs. 1–3, were obtained using 300-keV electrons transmitted through 1000-Å-thick self-supporting epitaxial films of TTF-TCNQ similar to those previously studied.[2] The energy resolution was 0.1 eV. Only scattering events near zero scattering angle were measured, so the spectra contain only electric dipole transitions. In this high-energy region, an IES spectrum is identical to an optical absorption spectrum and excellent agreement is obtained with recent synchrotron-radiation measurements[3] for the spectrum above the sulfur $L_{2,3}$ threshold.

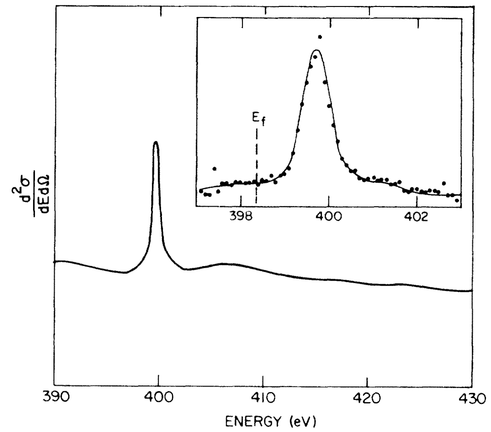

FIG. 2. Inelastic electron scattering spectra above the nitrogen K threshold.

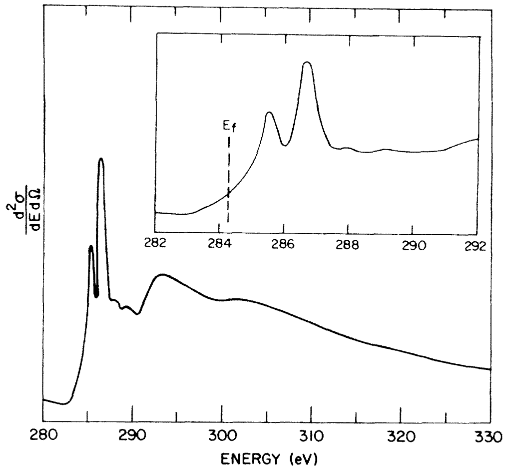

FIG. 3. Inelastic electron scattering spectra above the carbon K threshold.

Since the initial state is identified by the transition energy and is a well-known atomic core state, the measured spectrum gives us direct information about the accessible unoccupied states in the neighborhood of a specific atom. For sufficiently high final-state energy, we expect that the final-state wave function will approach a three-dimensional Coulomb wave or plane wave, depending on the strength of the screening, and that the spectrum in this region will resemble that of insulators or simple metals. The onset of this free-electron-like behavior will occur at about the ionization threshold, which was measured to be 5.0 eV above the highest occupied state.[4] Below this onset, we expect transitions to discrete molecular-orbital final states resulting in sharp excitonic absorption lines. In fact, as shown in Fig. 1, the broad continuum above the sulfur $2p$ threshold from 170 eV to above 200 eV has the same general shape as the absorption spectrum from the Na, Al, or Si $2p$ core levels previously observed.[5] The broad peaks at 176 and 186 eV resemble EXAFS (extended x-ray absorption fine structure); that is, they are likely due to the backscattering of the final-state wave function from neighboring atoms, resulting in constructive or destructive interference at the absorbing site. The most important backscattering comes from the molecules adjacent to the absorbing molecule in the molecular stack. Using the interplanar distance[6] of 3.47 Å for the parallel TTF molecules and a simple model for EXAFS,[5] we predict broad peaks at 175, 186, and 203 eV in the sulfur spectrum assuming the zero of kinetic energy in the final state to occur at 170 eV (the ionization threshold). As seen in Fig. 1, the agreement is quite reasonable. Similar modulation occurs in the free-electron continuum above the carbon K edge at about the same energy above the ionization threshold at 290 eV because of the similarity between interplanar spacings on the TTF and TCNQ stacks. Of course, the overall shape of the free-electron continuum for carbon has less of a delayed onset because of the lower centrifugal barrier for the s to p transitions. A similar but much weaker continuum is observed above the sharp peak in the nitrogen spectrum.

To describe the observed spectra completely we must identify the sharp peaks which occur below the ionization threshold. Their sharpness implies a local intramolecular nature. Despite the extreme surface sensitivity of x-ray photoemission spectroscopy demonstrated by varying the emission angle,[7] previous experiments[7,8] were interpreted as showing the presence of both neutral and charged molecules in the bulk material and the degree of charge transfer determined by their relative intensities. If such were the case, we would expect to see similar effects in IES spectra which measure energy losses throughout the bulk of the sample. However, as shown in Fig. 2 for TCNQ, only one peak at 399.75 eV [0.7 eV full width at half-maximum (FWHM)] is observed. To identify this transition as well as those in TTF, we calculated the core exciton spectra for the neutral and charged molecules, using a semiempirical version of the complete neglect of differential overlap (CNDO) method with a new parametrization which gives a good description of both the ground state energies and the absorption spectra for a variety of aromatic molecules,[9] including TCNQ.[10] An oscillator-strength calculation commensurate with the atomic selection rules of this problem was included. We find reasonable experimental agreement for the spectra of TTF^+ and $TCNQ^-$, but no agreement for the TTF^0 and $TCNQ^0$. More importantly, we can rule out the presence of both neutral and charged TCNQ, since the dominant peaks in the core exciton spectra of $TCNQ^0$ and $TCNQ^-$ are calculated to be separated by 5 eV as a result of the lower exciton binding energy in $TCNQ^-$. Positive identification of $TCNQ^-$ can be made using the clearly identified nitrogen 1s binding energy for $TCNQ^-$ in TTF-TCNQ.[7] If we neglect relaxation effects [which we assume to be identical in x-ray photoemission spectroscopy (XPS) and IES spectra], the XPS binding energy is the energy difference between the core state and the Fermi level, labeled E_F in the figures. In our calculation, E_F is the energy of the half-filled orbital on $TCNQ^-$. The dominant peak mentioned above is calculated to be a transition from nitrogen 1s to the close-lying empty molecular orbitals $b_{3u}(\sigma)$, $a_{1g}(\sigma)$, and $a_{1u}(\pi)$ and to occur about 1 eV above E_F in good agreement with experiment. The similar peak in $TCNQ^0$ would occur at ~394 eV. Our calculation also predicts a transition to the half-filled orbital $b_{2g}(\pi)$ of $TCNQ^-$; and its intensity is calculated to be about $\frac{1}{5}$ that the strong peak discussed above. Since no transition to the Fermi level is seen, its oscillator strength must be much weaker than the calculated value.

Transitions from the sulfur 2p core states to the conduction band on the TTF stack occur only to the extent that the $b_{1u}(\pi)$ orbitals which form this band have significant d character, since only atomic transitions from p to d are allowed (there is no s component in a π orbital). The fact that the peak at 164.9 eV (E_F) is quite strong indicates a large d component in this orbital. Berlinsky, Carolan, and Weiler[1] have shown that the inclusion of d orbitals leads to a bandwidth of 0.72 eV on the TTF stack as compared to 0.44 eV for the TCNQ stack. However, a total bandwidth for TTF-TCNQ of 0.5 eV is consistent with the plasmon spectrum in the random-phase approximation.[5] Moreover, from the line shape of the transition from the 2p core to the conduction-band orbital, we can in principle obtain a measure of the bandwidth of the empty states. As seen in Fig. 1, this peak is 0.8 eV wide (FWHM), but it is not significantly broader than other core exciton widths reported here, so additional broadening due to band formation is probably minimal and an empty bandwidth $\lesssim 0.4$ eV is not unreasonable.[1]

Atomic transitions from p to s in TTF^+ from the spin-orbit-split sulfur 2p states to σ orbitals of symmetry b_{3u}, b_{2u}, a_{1g}, and b_{1g} account for peaks at 166, 167, and 168 eV. The same transitions in TTF^0 would occur 4 eV higher; and since these are not seen, we can rule out TTF^0 in the bulk of TTF-TCNQ.

The core excitons seen in the carbon 1s spectrum (Fig. 3) are complicated by the presence of carbon in both TTF and TCNQ and will not be discussed here in detail. Nevertheless, using the separation between the core level and the Fermi level of 284.4 eV,[11] all excitons are seen to occur just above E_F. Peaks separated by ~ 10 eV would be expected from a mixture of neutral and charged molecules.

Further support for the lack of TCNQ^0 in TTF-TCNQ is based on the recently reported molecular monopole transition in TCNQ.[12] As momentum transfer is increased in an IES experiment, a sharp peak due to an optically forbidden transition in TCNQ^0 appears at 5.3 eV. We repeated the same experiment on TTF-TCNQ and found no such momentum-dependent peak, indicating the absence of TCNQ^0 in TTF-TCNQ.

We conclude that while x-ray diffraction experiments may be consistent with less than 100% charge transfer in TTF-TCNQ,[13] IES spectra from bulk samples show no such effects at small (5 eV) and large (400 eV) energy losses.

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Phason Instability in Tetrathiafulvalene-Tetracyanoquinodimethane (TTF-TCNQ)†

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The 49-K phase transition in tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) is interpreted in terms of a phason instability of the charge-density-wave ground state. The order parameter couples linearly to an external strain, and the phase transition can be suppressed by clamping the crystal. Recent neutron scattering experiments show indications of this effect. Renormalization-group calculations yield pure classical critical behavior at this phase transition, and *XY* exponents for the 54-K transition.

X-ray[1] and neutron-scattering[2] studies of tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) have shown evidence of structural phase transitions with a number of unusual features. At 54 K there is a Peierls-like distortion to an incommensurate structure with modulation wave vector $\vec{q} = (a^*/2, 0.295b^*, 0)$. At 38 K there is a first-order transition to a structure where the modulation vector in the a^* direction has decreased to $a^*/4$. Recently it was predicted that there should in fact be *three* transitions.[3] One set of chains orders at 54 K and the second set of chains orders at 47 K. The modulation wave vector in the a^* direction is $a^*/2$ between 54 and 47 K, and decreases as $a^*/2 - \lambda(47\ \mathrm{K} - T)^{1/2}$ between 47 and 38 K where it locks to a value of $a^*/4$. This behavior has been confirmed by a very recent experiment by Ellenson *et al.*[4] The new transition was found to occur at 49 K rather than 47 K. Knight-shift measurements[5] also indicate a phase transition near 49 K. In this paper, the properties of the 49-K transition will be analyzed from a theoretical point of view. We shall see that this transition is triggered by a soft "phason" mode. The phasons[6] are the elementary excitations of the charge-density-wave (CDW) ground state between 54 and 49 K.

Figure 1 indicates schematically the behavior of the CDW's on one type of chains (TCNQ) at the phase transitions (see Ref. 3). The high-tempera-