Pressure Dependence of the Phase Transitions in Tetrathiafulvalene-Tetracyanoquinodimethane (TTF-TCNQ): Evidence for a Longitudinal Lockin at 20 kbar

R. H. Friend,[a] M. Miljak,[b] and D. Jérome
Laboratoire de Physique des Solides, Laboratoire associé au Centre National de la Recherche Scientifique, Université Paris-Sud, 91405 Orsay, France
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We report the pressure dependence of the three phase transitions in TTF-TCNQ as determined by resistivity measurements. There is only one transition above 15 kbar, and we find a 4-kbar regime centered at 20 kbar where the transition temperature peaks (the distortion temperature $T_d = 71$ K at 20 kbar), and the transition is first order. We suggest that there is a commensurate $\times 3$ superlattice in this pressure regime resulting from an increase in charge transfer to $\frac{2}{3}$.

Previous high-pressure conductivity measurements of TTF-TCNQ[1-3] were performed before structural information on the sequence of three phase transitions now observed became available, although some of the first evidence for more than one transition in this compound came from these experiments.[1,2] In the present work we have followed all three transitions in the pressure range up to 33 kbar by measurements of the stacking-axis resistivity. Our results are in broad agreement with the previous investigations, although we have been able to assemble a more detailed phase diagram.

X-ray and neutron diffraction experiments on the phase transitions at 53, 49, and 38 K are reviewed by Comès.[4] EPR,[5] C^{13} NMR,[6] and isotope-effect[7] experiments indicate that the TCNQ stacks distort at 53 K, and that the lower transitions are associated with the TTF stacks. The presence of $4k_F$ scattering has been taken as evidence for the importance of Coulomb correlations.[8-10] These are more important on the TTF stacks,[5] since the TTF bandwidth is appreciably smaller than that of the TCNQ.[11]

Both normal and N^{15}-substituted crystals were used, the latter because they have been found previously to show particularly sharp phase transitions.[7] Standard low-frequency ac resistivity and high-pressure techniques were employed,[12] using He gas as the pressure transmitting medium up to 8 kbar, and either isopentane or a mixture of isopentane and isoamyl alcohol above. Improvements in the cryogeny made possible much slower cooling and warming rates which effectively eliminated thermal lag between sample and temperature sensor (Cu-Constantan thermocouple inside the pressure cell in the range of the transitions). Samples showed σ(peak)/σ(300 K) of between 10 and 25, and "unnested" ratios[13] exceeded 20 at σ(peak). Figure 1 shows results at 1 bar and 4 kbar for a sample with peak ratio 25. The transitions at ~52 and ~38 K show up as maxima in $-d\ln R/dT$, and the ~49-K transition is seen most clearly as the temperature at which the thermal hysteresis recently reported by Ellenson *et al.*[14] begins. We note that at 1 bar below the ~52-K transition the resistivity only begins to rise again below the ~49-K transition, and that, in contrast, at 4 kbar the resistivity remains almost constant until close to the "38-K" transition, now depressed to 32 K. We conclude that the "49-K" transition is rapidly suppressed under pressure (helium gas at 4 kbar freezes at ~35 K, so that down to this temperature the sample was free from strain which affects this transition[14]).

The complete pressure-temperature phase diagram is shown in Fig. 2. All data points except those for the 49-K transition were defined by the

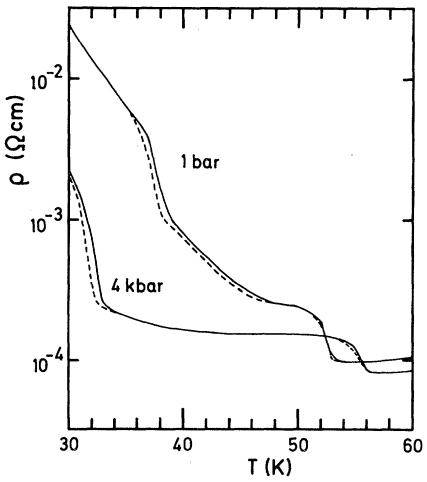

FIG. 1. Cooling (dashed) and warming (solid) resistivity curves for TTF-TCNQ at 1 bar and at 4 kbar [N^{15}-substituted sample, σ(300 K) normalized to 400 $(\Omega\ \mathrm{cm})^{-1}$, σ(peak)/σ(300 K) = 25 at 1 bar]. Data were recorded continuously on an X-Y recorder.

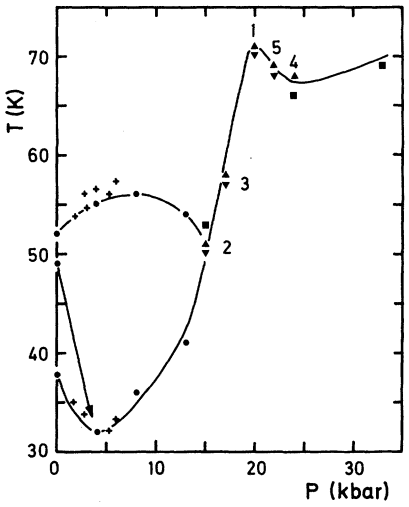

FIG. 2. Pressure dependence of the phase transitions in TTF-TCNQ as defined by maxima in $-d\ln R/dT$ (except for 49-K transition—see text). Plus signs are data points from Ref. 3, squares for a normal sample, and circles, triangles, and inverted triangles for N^{15}-substituted samples. Numbers indicate the order of runs for triangle sample.

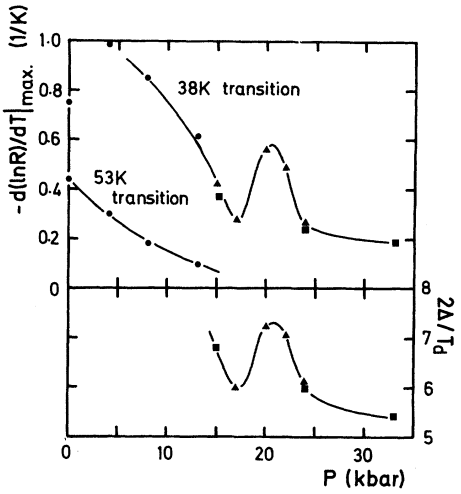

FIG. 3. Maxima in $-d\ln R/dT$ (the sharpness of the resistivity jump at a transition), and $2\Delta/T_d$ [Δ, defined by $\rho=\rho_{\min}\exp\{\Delta/kT\}$, determined from $\rho(T)$ below the transition] as a function of pressure. Symbols are same as for Fig. 2.

maxima in $-d\ln R/dT$. Above 15 kbar only one phase transition was observed, and except in the region around the maximum at 20 kbar, no temperature hysteresis was measured. However, at 20 kbar the transition was noticeably of first order, with temperature hysteresis of 1 K. Figure 3 shows the maxima in $-d\ln R/dT$ for the upper and lower transitions and $2\Delta/T_d$ [where Δ is defined by $\rho=\rho_{\min}\exp(\Delta/kT)$ below the transition,[15] and T_d, the distortion temperature, is defined by the maximum in $-d\ln R/dT$] plotted as a function of pressure. Both quantities show peaks at 20 kbar indicating the first-order character of the transition in this regime.

One of the puzzling features of this series of charge-transfer salts has been the presence of at least three transitions in TTF-TCNQ whereas the isostructural selenium analog tetraselenafulvalene (TSeF)-TCNQ shows only one.[15] Figure 2 establishes the relationship between these compounds, and we consider that for TTF-TCNQ above 15 kbar, and TSeF-TCNQ at ambient pressure, the intrinsic transition temperatures of the two types of stack are sufficiently close that interstack interactions are strong enough to couple the distortions together.

Two further features of the results we have shown warrant particular discussion.

(a) *The peak in T_d at 20 kbar.*—We consider that the sharp peak in T_d at 20 kbar, and the narrow pressure regime around this pressure where the transition is strongly first order, are evidence for a longitudinal lockin transition to a $3b$ commensurate superlattice, brought about by an increase in charge transfer from 0.59 to $\frac{2}{3}$ electron at 20 kbar. The temperature dependence of the $4k_F$ diffuse scattering ($0.55b^*$ at room temperature increasing to $59b^*$ at low temperature[4]) and the anomaly in the longitudinal sound velocity at the 53-K transition[16] have previously been interpreted as evidence for a dependence of charge transfer on lattice parameter[16]; an increase in parallel bandwidth for both stacks with a decrease in b-axis lattice parameter will increase the value of k at which the two bands cross and hence k_F. Both estimates, together with the pressure-dependent b-axis compressibility,[17] are consistent with $\frac{2}{3}$ transfer at 20 kbar.

This proposed longitudinal lockin transition is similar to transitions seen in the layer compounds,[18,19] for which a Landau theory has been developed by McMillan.[20] For the $3b$ superlattice proposed, the lockin energy is proportional to Δ^3, where Δ, the energy gap, is taken as the order parameter for the distortion.[21] It is this cubic term in the Landau free-energy expansion that makes the lockin transition first order. If $2k_F$ is not equal to $\frac{1}{3}b^*$ the lockin energy will be offset by an increase in electronic kinetic energy $\sim|\frac{1}{3}b^*-2k_F|\Delta$, and the system will remain metal-

lic, with holes above the gap on one stack and electrons below it on the other. Alternatively the degree of charge transfer may adjust to the commensurate value,[22] consistent with the strongly insulating behavior below the lockin transition (Fig. 3). There are two mechanisms for this change in charge transfer. Firstly, as for the increase in charge transfer with pressure, a change in donor and acceptor bandwidths coupled to a change in lattice parameter can adjust the value of k_F, with an increase in lattice energy $\sim |\frac{1}{3}b^* - 2k_F|^2$. Secondly, if the energy gaps opened up at $\pi/3b$ are sufficiently large, there will be inversion of the donor and acceptor bands near k_F and transfer of the $\frac{1}{3}\pi b \rightarrow k_F$ electrons. This condition is easily satisfied: For the limit of $\Delta k/k$ ($\sim 1\%$) for which the lockin is observed, the separation of the donor and acceptor bands at $\frac{1}{3}b^*$ is ~ 4 meV, appreciably less than the observed gap (Fig. 3). In either case, the change in charge transfer should be coupled to changes in the lattice parameters.

We note that for TSeF-TCNQ, charge transfer at 1 bar is 0.63,[23] and we expect a similar lockin at a lower pressure. In practice it is found that T_d increases rapidly at low pressures,[24] though no maximum in T_d was found. We discuss TSeF-TCNQ further in the following section. The narrow range of $2k_F$ for which a lockin is observed (half-width $\Delta k/k < 1\%$) in TTF-TCNQ contrasts with the large changes in the superlattice wave vector seen in the layer compounds towards the lockin transitions (2% for $2H$ polytypes,[19] up to 5% for $1T$ polytypes[18]). This reflects the nearly ideal Fermi-surface nesting in TTF-TCNQ ($t_\perp \lesssim kT_d$)[25] and the poorly defined peaks in χ_q calculated for the layer compounds.[26]

(b) *Coulomb correlations and charge-density-wave (CDW) formation.*—The evidence for, and the importance of, an on-site Coulomb repulsion of the same size as or larger than the parallel bandwidth has been stated by several authors.[8-10,25] It is our view that many of the features in Fig. 2 derive from the strongly correlated behavior of the electrons on the TTF stack. In particular, the rapid rise in the "38-K" transition from 32 K at 4 kbar to 71 K at 20 kbar can be naturally explained in terms of a pressure-broadened TTF stack bandwidth. The effect of electron-electron repulsion must always be to oppose CDW formation, which involves bringing the electrons closer together on average. The competition between electron-phonon and electron-electron couplings has yet to be calculated for a one-dimensional system, and we follow here the mean-field treatment of Chan and Heine.[27] The criterion for CDW formation has the form

$$2I^2/M\omega^2 - (2U - V) \geq 1/\chi_q.$$

The electron-phonon matrix element I is proportional to the bandwidth in tight binding,[28] and increases with pressure. The overall pressure dependence of the left-hand side may be considerably enhanced if the electron-phonon coupling and electron correlation terms are of similar size, as is likely on the TTF stacks. This effect, together with the possibility of a lockin transition, may explain the similar rapid rise in TSeF-TCNQ seen at low pressures[24]; the TSeF stack is less strongly correlated than TTF at 1 bar,[29] and the effects of correlation on T_d should disappear at lower pressures.

While the transverse lockin to $4a$ at 38 K has been satisfactorily modeled in the Landau free-energy expansion,[30] the physical driving force for this period remains unclear. Coulomb coupling between stacks with distortions at similar wave vectors will favor a transverse period of a,[22] and it is likely that the condensation of the $4k_F$ distortion is important in driving the period to $4a$. The fall in the 49-K transition, where the transverse period starts to move towards $4a$, reflects, therefore, the probable disappearance of the $4k_F$ distortion under pressure as correlation effects are reduced. (Note that no $4k_F$ reflections have been seen in TSeF-TCNQ.[23]) Thus we do not expect the low-temperature phase to show a transverse period of $4a$ above 4 kbar.

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[a] Permanent address: Cavendish Laboratory, Cambridge, United Kingdom.

[b] Permanent address: Institute of Physics of the University, P. O. Box 304, Zagreb, Yugoslavia.

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Mössbauer Spectroscopy of ^{57}Fe Impurities in Technetium

T. Takabatake, H. Mazaki, and T. Shinjo
Institute for Chemical Research, Kyoto University, Kyoto, Japan
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The Mössbauer effect of a dilute ^{57}Fe impurity in Tc was measured for the first time. The isomer shift and the quadrupole splitting at room temperature are -0.02 ± 0.01 and -0.13 ± 0.02 mm/s, respectively. Small induced magnetic fields, -4.5 ± 1 and -7.5 ± 1 kOe, were found in external magnetic fields of 30 and 45 kOe at 4.2 K. This indicates that the magnetic character of Fe impurities in Tc lies in the intermediate region between magnetic and nonmagnetic. The induced field may be attributed to local spin fluctuation.

Mössbauer-effect studies for ^{57}Fe as an impurity in transition metals have been done by many workers. For example, Qaim[1] investigated the isomer shift of ^{57}Fe embedded as a dilute impurity in 32 different metallic host lattices. The quadrupole splitting observed with the hexagonal transition metals[2,3] gave valuable information on the electric field gradient (EFG) in these metals. In addition, the Mössbauer effect is very useful to study the formation of the local magnetic mo-

