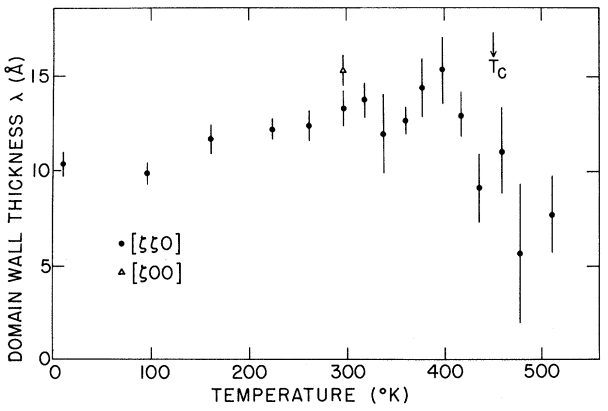

FIG. 4. The domain-wall thickness obtained from the fits shown in Fig. 3. The solid points are taken from measurements along [ζζ0] and the open points from measurements along [ζ00].

with that expected from the polarization reversal which occurs in randomly arranged domain walls. (4) The component of the quasielastic scattering intensity that peaks near T_c may possibly arise from the walls of dynamic domains or large clusters of polarization.

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Critical Behavior at the Metal-Nonmetal Transition in Tetrathiafulvalene-Tetracyanoquinodimethane (TTF-TCNQ)*

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We present the results of high-precision electrical resistivity measurements in the vicinity of the metal-nonmetal transition in TTF-TCNQ. We find a sharp negative divergence in the derivative of the resistivity, $R^{-1}dR/dT$, which suggests the existence of a second-order phase transition at about 53 K. A critical-exponent analysis of this divergence implies that the onset of long-range order occurs with a classical exponent (i.e., $\beta=\frac{1}{2}$) within a three-dimensional region which extends to approximately $|T-T_c|/T_c=t=10^{-1}$.

There has been considerable recent interest in the electrical properties of TTF-TCNQ and related highly anisotropic conductors.[1-5] Much of this interest has centered around the possibility of having an electronically driven structural transition, such as a Peierls distortion, or another intrinsically one-dimensional instability. In TTF-TCNQ specifically, recent diffuse x-ray studies[4] as well as elastic neutron scattering experiments[6] have shown that the metal-nonmetal transition is associated with a structural distortion arising from the condensation of a $2k_F$ phonon. On the other hand, there is as yet little specific experimental information about the actual character of the fluctuations associated with this distortion. In this Letter we present the first detailed exami-

nation of the fluctuation contributions to the resistivity near 53 K. Our results will be discussed in detail after the presentation of the data.

The samples for this study, single crystals of TTF-TCNQ, were obtained from and characterized by four different laboratories.[7] The resistivity measurements were made using a four-probe ac null technique (at 39 Hz) with a sensitivity of about 2×10^{-10} V and a precision of one part in 10^5. The data were taken at a drift rate of slower than 0.5 K/h while the sample temperature was continuously monitored with a carbon thermistor which had a relative sensitivity of better than 0.5 mK and an absolute calibration to about 0.2 K. Temperature derivatives were then calculated using the technique of sliding averages over regions about 120 mK wide. Typical results are shown in Fig. 1 where we plot the b-axis resistance R and its derivative $dR/d(T^{-1})$ versus temperature.

The sharp divergence in $dR/d(T^{-1})$ (or negative divergence in dR/dT) is rounded (presumably by impurities or structural disorder) by only about 150 mK and is similar in form to the resistive anomalies observed at antiferromagnetic transitions.[8] Furthermore, the peak in $dR/d(T^{-1})$ occurs at the same temperature as the observed peak in the specific heat.[9] These facts suggest the existence of a true three-dimensional second-order phase transition at about 53 K. With this motivation we made the following *Ansatz* which will be retained for the remainder of this Letter: *The feature in the conductivity at about 53 K is a three-dimensional second-order phase transition in which the order parameter (perhaps complex) is the lattice distortion generated by the condensation of a $k=2k_F$ phonon.*

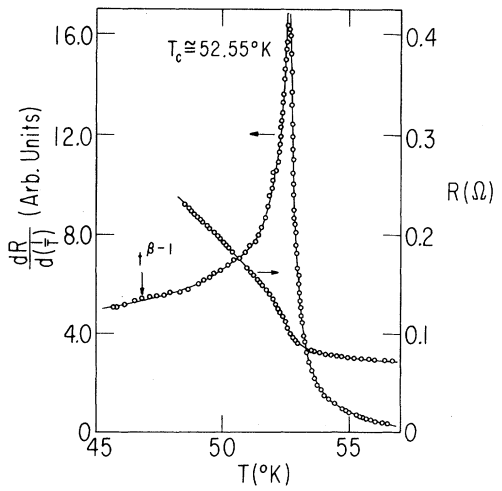

FIG. 1. Experimental values for the b-axis resistance R and the derivative $dR/d(1/T)$ versus temperature T.

As $T-T_c\to0+$, the negative divergence in dR/dT as well as the positive divergence in the noise power[10] implies that in the region $T_c\lesssim T\lesssim60$ K the fluctuations associated with the 54-K transition are resistive in nature.[9] Therefore, in the following discussion, we neglect the possibility of current-carrying fluctuations, which may be important at higher temperatures.[1,5]

With utilization of the large anisotropy in the electrical conduction,[3] the resistivity ρ can be estimated by treating the system as a collection of resistors in series. Then

$$\rho=\langle\rho[\Delta(x)]\rangle, \tag{1}$$

where $\rho[\Delta(x)]$ is the local resistivity and $\langle\rangle$ represents the usual statistical average over fluctuations in the order parameter $\Delta(x)$ with the probability distribution $\exp(-F/k_BT)$, with F the free-energy functional. Near T_c where the distance scale for fluctuations in $\Delta(x)$ becomes large, the local resistivity takes the form

$$1/\rho[\Delta]=\int\sigma(E)(-\partial f/\partial E)dE, \tag{2}$$

where $\sigma(E)$ is the energy-dependent conductivity and f is the Fermi distribution function. For F we choose a form characteristic of weakly couple one-dimensional chains.[11]

Near T_c the conductivity is dominated either by an increase in the scattering rate or by a decrease in the effective number of carriers arising from local fluctuations in $\Delta(x)$ for $T>T_c$ or from the onset of long-range order for $T<T_c$. We treat first $T<T_c$ by assuming that as observed in other materials, the dominant contribution to ρ (i.e., leading divergence in $d\rho/dT$) comes from the onset of long-range order.[12,13] Temporarily taking the scattering rate to be a constant, we can estimate $1/\rho[\Delta]$ from Eq. (2) by assuming a simple tight-binding band with $\sigma(E)=\sigma_0=$ const. In this limit one obtains the usual formula

$$1/\rho[\Delta]=\sigma_0/[1+\exp(\Delta/k_BT)]. \tag{3}$$

A more realistic form for $\sigma(E)$ will modify Eq. (3) slightly when $\Delta\ll k_BT$ but will not change the underlying physics. The total resistivity can now be trivially estimated by expanding the exponential in $\rho[\Delta]$ in semi-invariants. When $\langle\Delta\rangle\gg k_BT$ one obtains $\rho\simeq\rho_0\exp(\langle\Delta\rangle/k_BT)$. Thus $R^{-1}dR/dT\sim t^{\beta-1}$,[14] where β is the critical exponent for the onset of long-range order defined by $\langle\Delta\rangle\sim t^{\beta}$.

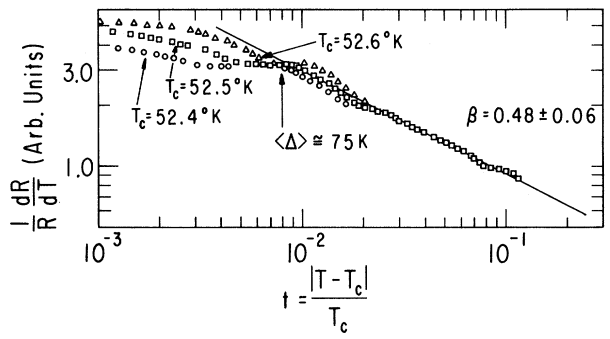

FIG. 2. $\ln(R^{-1}dR/dT)$ versus $\ln(|T_c-T|/T_c)$ for three different values of T_c.

The critical behavior of the experimental data for $T<T_c$ is shown in Fig. 2. T_c was determined from the peak in $R^{-1}dR/dT$ to be $T_c=52.55\pm0.1$ K. Note that for $\langle\Delta\rangle\gtrsim75$ K the resistivity has the form $R^{-1}dR/dT\sim t^{\beta-1}$ with $\beta=0.48\pm0.06$. The uncertainty in β reflects both the uncertainly in T_c and the scatter in the experimental data. For $\langle\Delta\rangle<75$ K the resistivity has a weaker divergence than would be predicted by Eq. (3). For $t\gtrsim10^{-1}$, $R^{-1}dR/dT\sim T^{-2}$ (data not shown) or $d\ln\rho/d(T^{-1})\simeq$ const. This implies that $\langle\Delta\rangle\simeq$ constant.[15] Therefore, the data below T_c can be summarized as follows: For $t\lesssim10^{-1}$, $\langle\Delta\rangle\simeq\Delta_0^{3D}t^{1/2}$, while for $t\gtrsim10^{-1}$, $\langle\Delta\rangle\simeq\Delta_0\simeq280$ K.[16] The value of Δ_0^{3D} can be estimated from the requirement that $\langle\Delta\rangle$ be continuous. We obtain $\Delta_0^{3D}=900\pm300$ K. The sharp saturation of $\langle\Delta\rangle$ is a characteristic of a system of weakly coupled chains which should contain a crossover from three-dimensional behavior near T_c to mean-field theory {i.e., $\langle\Delta\rangle=\langle\Delta\rangle^{MF}\equiv\Delta_0[(T_c^{MF}-T)/T_c^{MF}]^{1/2}$} as the temperature is lowered.[11,17] Here T_c^{MF} is the transition temperature of an isolated chain. If $T_c\ll T_c^{MF}$, $\langle\Delta\rangle^{MF}\simeq\Delta_0$ for all $T<T_c$. The crossover temperature between these two regions, t_{CR}, has been estimated by Scalapino, Imry, and Pincus[11] to be $t_{CR}\simeq T_c/T_c^{MF}$, which is crudely consistent with our data if $T_c^{MF}\simeq500$ K.[18,19] On the other hand, it is perhaps surprising[11] that within the three-dimensional region the exponent β has its classical value of $\beta=\frac{1}{2}$.

For $T>T_c$ where $\langle\Delta\rangle=0$ we treat first the contribution to ρ coming from local fluctuations in $\Delta(x)$. While Eq. (3) is not strictly valid in this region, we use it to illustrate the essential physics. The leading term in the cumulant expansion has the form $\exp[\langle|\Delta|^2\rangle/2(k_BT)^2]$. For $T\gg T_c$, $\langle|\Delta|^2\rangle$ is dominated by the weak temperature dependence of the longitudinal coherence length $\xi_\parallel\sim T_c^{MF}/T$.[18] As $T\to T_c$, $\xi_\perp(T)$ becomes larger than $1/2k_F$ (the inverse cutoff on the momentum integrals) and $\langle|\Delta|^2\rangle$ becomes dominated by the large-q correlation functions. In this region $\langle|\Delta|^2\rangle\sim t^{1-\alpha}$,[20] where α is the usual specific-heat exponent. Therefore, in the limit $T\to T_c$, fluctuations in the number of carriers lead to a specific-heat-like divergence in $R^{-1}dR/dT$.

The contribution to ρ from the scattering rate $1/\tau$ can be estimated by calculating $\sigma(E)$ in the Born approximation in analogy with treatments of the resistive anomalies observed for finite-k transitions in antiferromagnets. For an isotropic antiferromagnet at $T>T_c$ the dominant contribution to $1/\tau$ has been estimated by Suezaki and Mori[13] (SM) and leads to a resistive anomaly which has the form $R^{-1}dR/dT\sim t^{1-\alpha-\gamma}$. As $T\to T_c$, the approximations of the SM theory break down and a specific-heat-like divergence $R^{-1}dR/dT\sim t^{-\alpha}$ results.[21] In the present case, the SM theory becomes modified because of the one-dimensional nature of the electrical conduction. As $T\to T_c$, $\xi_\parallel/b$ (where b is the b-axis lattice spacing) becomes much greater than $(E_F/2k_BT)^{1/2}$ and the peak in $\chi(q)$ about $q=2k_F$ becomes so sharp that momentum conservation plays no role in the scattering integral. In this limit $dR/dT\sim d\xi/dT$, where, if the fluctuations are one-dimensional, $d\xi/dT\sim T_c^{MF}/T^2$, while in the three-dimensional limit $d\xi/dT\sim t^{-1-\nu}$. Therefore, in the limit $T\to T_c$, the derivative of the resistivity should be dominated by an increase in the scattering rate with the predicted behavior being $dR/dT\sim t^{-1-\nu}$.

Our experimental results for $T>T_c$ are shown in Fig. 3. The background value B of $R^{-1}dR/dT$ is difficult to determine since R is not linear in T for $T\gg T_c$. We have arbitrarily chosen this constant equal to $R^{-1}dR/dT|_{T=75K}$ but changes in B by more than a factor of 2 only have a small quanitative effect on the critical behavior. If one neglects crossover effects and fits the data with a straight line, a critical exponent for $R^{-1}dR/dT$ of 0.93 ± 0.13 is obtained.[22] This exponent is much too strong a divergence to represent either α or $\alpha+\gamma-1$ for any three-dimensional model. For comparison we have shown in Fig. 3 the value of $\alpha+\gamma-1$ for the three-dimensional X-Y model in which $\alpha+\gamma\simeq1.33$. Thus the strong divergence observed experimentally is characteristic of the one-dimensional nature of the conduction in TTF-TCNQ. On the other hand, the results are not consistent with the predicted $t^{-1-\nu}$ divergence.

It is interesting to speculate as to why the sim-

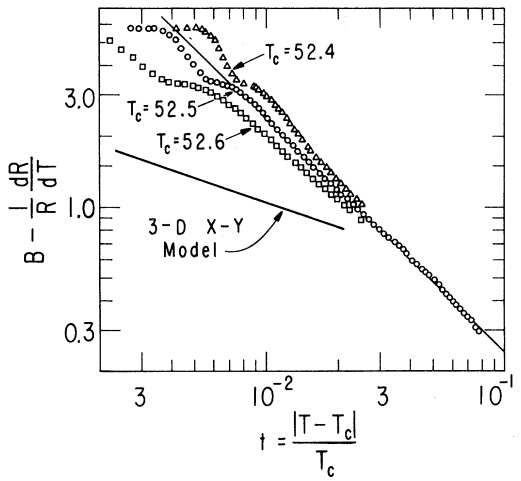

FIG. 3. $\ln(B - R^{-1}dR/dT)$ versus $\ln(|T - T_c|/T_c)$, where $B = R^{-1}dR/dT|_{T=75\,K} = 0.14$ in the arbitrary units used on the vertical scale. The slope of the bold solid line represents the divergence predicted by the Suezaki and Mori theory (Ref. 13) for an isotropic three-dimensional system with X-Y exponents.

ple SM-like theory fails to explain the observed experimental data. One possibility may be the inapplicability of the first Born approximation used in the estimate for τ. In isotropic materials, the bulk of experimental evidence suggests that the Born approximation represents a valid approach in calculating the critical scattering.[8] In the present case however, where the conduction is limited to one dimension, R itself is predicted to diverge and a static calculation based on the Born approximation must be invalid.

Finally, a word should be said about the sample dependence of our results. To the present we have examined the critical behavior of four different samples of TTF-TCNQ with conductivity peaks in the range $6 \leq \sigma(60\text{ K})/\sigma(300\text{ K}) \leq 18$. All of the samples studied had the same qualitative shape in dR/dT. Of these, three were compared quantitatively with the following results: (1) The rounding of the peak $R^{-1}dR/dT$ was sample dependent (ranging from about 120 to 250 mK). This suggests that the origin of the rounding of the derivative is an impurity effect and not intrinsic to the transition. (2) The value of $\beta \simeq \frac{1}{2}$ is quantitatively reproduced in all samples studied but the size of the three-dimensional region for $T < T_c$ varied slightly from sample to sample. (3) The critical behavior for $T > T_c$ was weakly sample dependent with all samples showing the same qualitative strong divergence.

Note added.—Recent preliminary measurements on the b-axis conductivity of tetraselenafulvalene-TCNQ have shown that for $T > T_c \simeq 29.0$ K, $dR/dT \sim t^{-1.49 \pm 0.18}$. This result is in essential agreement with the critical scattering model presented in the text which predicts $dR/dT \sim t^{-1-\nu}$. Detailed results will be presented elsewhere.[23]

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Anomalous Fluorescence Linewidth Behavior in Eu^{3+}-Doped Silicate Glass*

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We compare optical-homogeneous-linewidth measurements for the resonant $^5D_0 - {}^7F_0$ transition of Eu^{3+}-doped silicate glass and $YAlO_3$, using fluorescence line narrowing. The linewidth in the amorphous host is two orders of magnitude larger than in the crystal and exhibits an unusual temperature dependence. This behavior indicates an additional ion-lattice linewidth mechanism probably arising from an interaction between the Eu ions and "disorder modes" in the glass. Possible models are discussed.

Since the discovery of the anomalous low-temperature specific heat of amorphous materials by Zeller and Pohl in 1971,[1] there has been a renewed interest in the thermal and optical properties of these systems. Recent nuclear-spin-relaxation,[2] ultrasonic-attenuation,[3] Raman-scattering,[4] and infrared-absorption[5] experiments have all confirmed the existence of low-energy "disorder modes," consistent with the theory of Anderson, Halperin, and Varma[6] and Phillips.[7] These modes are associated with groups of atoms which can sit in either of two equilibrium positions, separated by potential barriers of varying heights.

In this Letter, we report on optical-linewidth measurements, using fluorescence line narrowing[8] (FLN) of the rare-earth ion Eu^{3+} doped into silicate glass at 2.6 mol%. Our results show an unusual temperature dependence for the homogeneous linewidth, never observed previously, and significantly different from that found in crystals. It indicates an additional ion-lattice linewidth mechanism which probably arises from an interaction between the Eu ions and the ensemble of two-level systems (TLS) comprising these "disorder modes."

It is well known that for an optically active impurity ion in a solid, homogeneous linewidths generally result from nonradiative relaxation processes, either longitudinal or transverse, mediated by lattice phonons. The ion-lattice coupling strength and the phonon density of states determine the magnitude of the linewidth; its temperature dependence reflects phonon occupation numbers and the type of process involved (direct, Raman, or Orbach).[9]