with a turn angle corresponding to $\vec{q}_0 \cong (0.1\ \text{Å}^{-1})\hat{z}$. I suspect that in the critical region, $\Gamma^{xx}(\vec{q}_0, T) \sim (T - T_c)^{-\gamma}$ and $C_H \sim (T - T_c)^{-\alpha}$ with γ and α given by the $d = 3$ value of the xy model. These speculations may be tested experimentally. (2) Unless $\bar{A}_3$ could be adjusted experimentally, I am unable to make any quantitative prediction about the crossover behavior of materials which possess Dzialoshinski-Moriya interaction. The crossover exponents, in particular $\varphi^{(2)}$, may, however, be tested numerically.

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Fluctuation Effects at a Peierls Transition

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The effects of fluctuations on the Peierls transition in one dimension are calculated by taking a functional average over variations in the order parameter. It is found that the transition is suppressed to a temperature of approximately one quarter of the mean-field transition but remains fairly sharp. The coherence length and density of states are calculated as a function of temperature, and brief comparison is made to experimental systems.

It has long been known that a one-dimensional metal is inherently unstable with respect to charge or spin-density waves.[1-3] In recent years a wide range of both inorganic and organic compounds which have characteristic one-dimensional metallic behavior have been discovered and extensively studied.[4-6] Theoretical calculations to date have been carried out only within a mean-field-theory description, although it is well known that fluctuation effects are very important in one-dimensional systems. In this Letter we report theoretical calculations incorporating fluctuation effects on the Peierls transition in a one-dimensional metal.

We consider a model with noninteracting electrons in a linear chain coupled to phonons:

$$H = \sum_{p\sigma} \epsilon_p c_{p\sigma}^{\dagger} c_{p\sigma} + \sum_q \omega_q b_q^{\dagger} b_q + (\sqrt{L})^{-1} \sum_{p,\sigma} \sum_q g(q) c_{p+q\sigma}^{\dagger} c_{p\sigma} (b_q + b_{-q}^{\dagger}), \quad (1)$$

where $c_{p\sigma}^{\dagger}$ and $b_q^{\dagger}$ are creation operators for a Bloch state and longitudinal phonon, respectively, with energies ϵ_p and ω_p, respectively. Because a Fermi surface in one dimension is a point, it is, of necessity, a perfect nesting Fermi surface causing an instability in the lattice with wave vector $2k_F$, where k_F $(= \pi N/2L)$ is the Fermi wave vector. A description of this instability within mean-field theory for the case where k_F is incommensurate with the underlying lattice periodicity (π/a) has been given by Fröhich,[2] Kuper,[7] and Rice and Strassler.[8] The mathematical structure of the theory closely parallels that of the BCS theory of superconductivity. The effects of fluctuations on phase transitions in one dimension have been studied by many authors. It is possible to treat the problem accurately by performing a functional integral over all possible fluctuations described by a Landau expansion of the free energy. Recently Scalapino, Sears, and

Ferrell[9] have performed extensive calculations based on this method, and we shall make use of their results. In the problem at hand the Landau expansion of the free energy F per atom is

$$F[\Psi_Q] = a(T, 2k_F)|\Psi_Q|^2 + b(T, 2k_F)|\Psi_Q|^4 + c(T, 2k_F)(Q - 2k_F)^2|\Psi_Q|^2, \quad (2)$$

where the order parameter Ψ_Q is proportional to the lattice displacement: $\Psi_Q = 2g_Q\langle b_Q\rangle$. The coefficients a, b, and c are determined by a mean-field-theory calculation as

$$\begin{aligned} a &= D_0(T - T_c)/T_c; \\ T_c &= 1.14W\exp(-\omega_{2k_F}/g^2D_0), \\ b &= D_0[b_0 + (b_1 - b_0)T/T_c], \\ c &= D_0 + \xi_0^2(T), \end{aligned} \quad (3)$$

where $\xi_0^2(T) = 7\zeta(3)v_F^2/16\pi^2k^2T^2$, $b_0 = 0.5/(1.76)^2$, and $b_1 = 7\zeta(3)/16\pi^2$, and we have chosen a band of width $2W$ with a constant density of states $D_0 = \frac{1}{2}W$.[10] The coefficients b and c are chosen to be temperature dependent so as to allow the calculations to be carried out for temperatures well below T_c.[11] The form chosen for b is a linear interpolation between its value near T_c and the value necessary to reproduce the mean-field value for $\langle\Psi_{2k_F}\rangle_{T=0}$. The coefficient c was obtained by examining the extra free energy required to open up a Peierls gap at $Q/2$ slightly away from k_F.[12] We have not allowed the electronic density to adjust to the changing wave vector and create fluctuations in the average charge along the chain. Such possibilities would further increase fluctuation effects.

These considerations, strictly speaking, apply only to values of $2k_F$ incommensurate with the lattice periodicity. We have found, however, that the commensurability energy falls off as $g(g/E_F)^{M-2}$, where M is the order of commensurability, and so is negligible for large M. For a half-filled band, however, the Landau expansion breaks down, and there is a leading term $\sim|Q - 2k_F|$ at $T < T_c$. Our calculations do not apply to this case.

In one dimension the correlations fall off exponentially with distance,

$$\langle\Psi(x)\Psi(x')\rangle = \langle\Psi^2\rangle\exp[-|x - x'|\,\xi^{-1}(T)]\times\cos[2k_F(x - x')]. \quad (4)$$

The temperature-dependent correlation length $\xi(T)$ may be calculated using the results of Scalapino, Sears, and Ferrell.[9] The results are

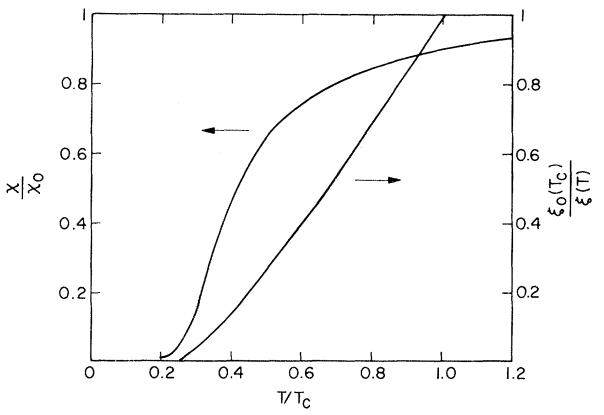

FIG. 1. The correlation length $\xi(T)$ and the Pauli spin susceptibility normalized to the susceptibility in the metallic state, plotted versus T/T_c. The length $\xi_0(T_c)$ is defined after Eq. (3).

shown in Fig. 1. The ratio $\xi(T)/\xi_0(T_c)$ increases approximately linearly at first. For $T < \frac{1}{4}T_c$, however, $\xi(T)$ becomes very large, increasing exponentially with temperature. This dependence is characteristic of a real order parameter. When $\xi(T)/\xi_0(T_c)$ becomes very large, one expects three-dimensional (3D) ordering to occur. The critical temperature for such ordering is $T_c^{(3D)} \approx \frac{1}{4}T_c$.

From a knowledge of the coherence length and the potential it is possible to calculate the electronic properties. By truncating the equations of motion for the one-particle Green's function $G(k, \omega)$ and keeping only the coupling to the nearly degenerate states, we arrive at the result[13]

$$G^{-1}(k, \omega) = \omega - \epsilon(k) - \int dQ\, S(Q)\langle\Psi^2\rangle \times[\omega - \epsilon(k \pm Q) + i\delta]^{-1}, \quad (5)$$

where the plus or minus is chosen according to the condition $\epsilon(k \pm Q) \approx \epsilon(k)$, and the structure factor $S(Q)$ is a Lorentzian centered at $Q = 2k_F$ of width $\xi^{-1}(T)$. The potential $\langle\Psi^2\rangle$ is given by Eq. (4), and its value is also obtained from Scalapino, Sears, and Ferrell.[9] In our approach the lattice displacements with wave vector near $2k_F$ are singled out and treated accurately. Additional scattering mechanisms, e.g., impurities, long-wavelength phonons, disorder, will introduce additional smearing of the structure in the density of states. However, in one dimension long-wavelength phonon scattering is reduced by $(s/v_F)^2$, where s is the velocity of sound and is not expected to be significant.

The integral over Q in Eq. (5) can be performed

at once leading to the result

$$G^{-1}(k,\omega)=\omega-\epsilon(k)-\langle\Psi^2\rangle \times[\omega-v_F(|k|-k_F)+iv_F\xi^{-1}(T)]^{-1}. \quad (6)$$

The density of states $D(\omega)$ can be obtained by integrating the imaginary part of G with the result

$$\frac{D(\tilde{\omega})}{D_0}=\frac{\alpha[2(y+x)]^{1/2}}{[2(y+x)-\alpha^2]y}, \quad (7)$$

where

$$\tilde{\omega}=\omega/\langle\Psi^2\rangle^{1/2}, \quad \alpha=v_F\xi^{-1}(T)/\langle\Psi^2\rangle^{1/2}, \quad x=1+\tfrac{1}{4}\alpha^2-\tilde{\omega}^2, \text{ and } y=(x^2+\tilde{\omega}^2\alpha^2)^{1/2}. \quad (8)$$

In Fig. 2 the results are plotted for a series of temperatures. Again we see that only when $T \leq 0.5T_c$ is a reduction of more than 50% in the density of states at the Fermi energy obtained. Indeed if we compute the thermal average,

$$D_T=\int D(\omega)(\partial f/\partial\omega)\,d\omega, \quad (9)$$

where f is the Fermi function, we find it is not changed appreciably for $T>0.5T_c$. In Fig. 1 we have plotted the temperature dependence of D_T which is directly proportional to the Pauli spin susceptibility $\chi(T)$.

Recently a Peierls distortion has been observed in a class of Pt compounds, particularly $K_2Pt(CN)_4Br_{0.3}\cdot 3H_2O$, by x-ray scattering techniques.[14] In these compounds the d_z^2 sub-band of the Pt has 0.3 holes per Pt. The total sub-band width is approximately 1 eV. Three-dimensional ordering is observed around 100 K. This indicates that T_c is approximately 400 K. From Fig. 1 we expect the main change in susceptibility to occur in the interval 100–200 K. This is confirmed by recent NMR results of Niedoba and Launois.[15] The ratio ξ_0/a $[\approx W\sin(0.15\pi)/\pi kT_c]$ is about 5, where a is Pt-Pt spacing ($a=2.88$ Å). We estimate $\xi(T=300\text{ K})/a\approx 7$. However, this value is considerably less than that reported by Comes *et al.*[14] $[\xi(T=300\text{ K})/a>140]$. While a recent neutron scattering experiment[16] does not have sufficient resolution in q space to determine $\xi(T=300\text{ K})$, the phonon spectrum at room temperature is found to show a dip at $Q=0.3\pi/a$. In this paper we have found large effects from the fluctuations on the static properties, and it is reasonable to expect similar modification of the dynamics. Thus we would expect the phonon frequency at $Q=2k_F$ to go to zero, or develop a central mode only at a temperature somewhat below mean field T_c.

A Peierls distortion has also been proposed for

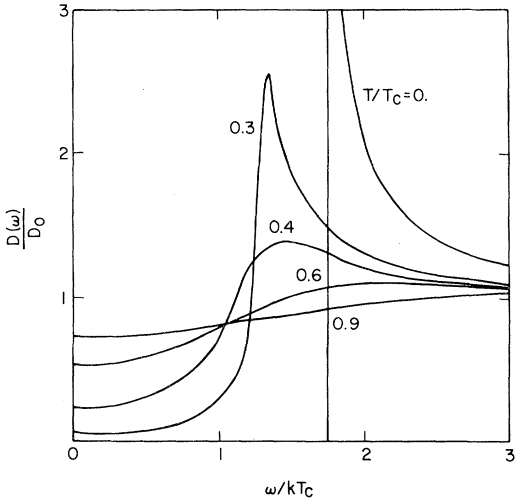

FIG. 2. The electronic density of state as given by Eq. (7) normalized to the metallic density of state, plotted versus ω/kT_c for various temperatures. The $T/T_c=0$ curve is the mean-field result. For large ω, $D(\omega)/D_0-1$ goes like $1/\omega^2$, and it can be shown explicitly to be properly normalized.

tetrathiofulvalinium-tetracyanoquinodimethan (TTF-TCNQ).[17] A decrease of approximately 50% has been observed in the magnetic susceptibility between 300 and 100 K.[18] At lower temperatures a transition occurs, probably to a three-dimensionally ordered Peierls distortion on both TTF and TCNQ chains. Our results for the susceptibility would indicate that $T_c \gtrsim 250$ K for at least one of the chains. A similar conclusion was reached by Anderson, Lee, and Saitoh[19] on different grounds. In this paper we have discussed fluctuation effects that are common to one-dimensional compounds showing a Peierls distortion. Such considerations are clearly important also for an understanding of the giant conductivity observed in a few samples of TTF-TCNQ. These and related questions we hope to discuss in a separate publication.

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[12]The form for $\xi_0(T)$ is obtained in a small-$|\Psi_Q|/kT$ expansion. Numerical computations show that this form works reasonably well even for $|\Psi_Q| \gtrsim kT$.

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