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LETTER TO THE EDITOR

Pauli susceptibility at a Peierls transition

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Abstract. Using general arguments borrowed from magnetism, we show that it is short-range order parameter fluctuations close to T_c that lead to the observed behaviour of χ at a Peierls transition; in the quasi-static approximation $d\chi/dT$ should vary as the lattice specific heat. The addition of impurities produces rounding of the $d\chi/dT$ cusp when the true phase transition is destroyed by disorder. The theory compares favourably with experiment.

The observation of a sharp cusp in the temperature derivative of the static magnetic susceptibility $d\chi/dT$ is often interpreted as a clear signature of a continuous structural phase transition. Such behaviour is particularly prominent in low-dimensional compounds undergoing a Peierls transition, where there is a large change in the density of states. Despite the fact that this $d\chi/dT$ measurement is a standard experimental method for determining T_c for charge density wave compounds, the behaviour of the static magnetic susceptibility is not well understood theoretically, particularly close to T_c [1]. In the simplest model the electrons are treated as a non-interacting electron gas, and then χ is simply proportional to the density of states at the Fermi energy. Charge conservation arguments imply that ionic density fluctuations close to T_c lead to variation in the electronic density of states, and it is therefore these effects which we would like to calculate.

Historically the Peierls transition has been treated using a soft-phonon picture; however, because of the large anharmonicities present for $T \simeq T_c$, diagrammatic calculations with phonon basis states become very complicated. An alternative view is to consider the formation of a pseudo-gap above T_c due to the presence of large critical fluctuations. This approach is certainly not new, and was used in the study of magnetic materials by De Gennes and Friedel [2], and by Fisher and Langer (FL) [3]. More recently it has been applied to the Peierls transition by Lee, Rice and Anderson (LRA) [4]. Using critical slowing-down arguments we can treat the fluctuations as quasi-static, and can therefore consider electron–ion scattering in the elastic limit near T_c. Strictly speaking only electron–ion energy transfers of the order of the gap will significantly alter our results, and so the elastic scattering assumption seems acceptable on physical grounds.

The problem of interest has therefore been reduced to that of an electron scattering from a single-body static potential $V(r)$ that fluctuates in momentum space which, for $T > T_c$, satisfies

$$\langle V_q \rangle = 0 \tag{1a}$$

$$\langle V_q V_{q'} \rangle = S(q) \langle V_q^2 \rangle \delta_{q,-q'} \tag{1b}$$

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where V_q is the Fourier transform of $V(r)$ and $S(q)$, the structure factor, is strongly peaked at $q = 0$ ($Q = k_F$). For $T < T_c$ the order parameter $\langle V_Q \rangle$ is finite, and there is an additional delta-function contribution to (1*b*). Because the Peierls transition has a small critical region, (e.g. $t_G \sim (\Delta e_F)^4 \sim 10^{-6}$ for quasi-one-dimensional blue bronze) [1, 5] we shall model $S(q)$ by a Lorentzian centred at the nesting vector. The correct normalisation for $S(q)$ is important so as to ensure that the integrated structure factor has a smooth temperature dependence. We use the Fisher–Langer argument, borrowed from magnetism, to contend that the electronic mean free path l will provide a lower cut-off to the width of the structure factor. More physically, the electrons will never sample ionic fluctuations with wavelengths longer than their own mean free path, and therefore electronic properties near T_c will be dominated by short-length-scale ionic behaviour. We then expect χ to have an energy-like appearance, and in particular $d\chi/dT$ should be proportional to the lattice specific heat [6]†.

For a non-interacting electron gas scattering from a static potential the spin susceptibility is simply proportional to the thermally averaged density of states $D(\omega)$. We solve for $D(\omega)$ using a standard self-consistent Born approximation, and calculate the full Green function using Dyson's equation. Symmetry-breaking self-energy diagrams must be calculated to all orders to produce a gap at the transition. Studies of disordered systems indicate that crossed diagram contributions do not significantly affect the density of states, and therefore these terms are neglected in this calculation. Such diagrams would, however, be important for the study of transport properties.

If we only retain coupling to nearby degenerate states and use the self-consistent Born approximation described above, Dyson's equation becomes

$$G^{-1}(\boldsymbol{k}, \omega) = \omega - \varepsilon(\boldsymbol{k}) - \int \frac{d\boldsymbol{Q}\, S(\boldsymbol{Q}) \langle V_Q^2 \rangle}{\omega - \varepsilon(\boldsymbol{Q}) + i/\tau} \tag{2}$$

for $T > T_c$ where $\varepsilon(k) \sim \varepsilon(k - Q)$ and $1/\tau = v_F/l$ in the standard relaxation time approximation. Below T_c both order parameter fluctuations and growth contribute to χ and we calculate G in (2) making the simple transformation

$$S(\boldsymbol{Q}) \langle V_Q^2 \rangle \Rightarrow S(\boldsymbol{Q}) \langle V_Q^2 - \langle V_Q \rangle^2 \rangle + \delta(\boldsymbol{Q} = 2\boldsymbol{k}_F) \langle V_Q \rangle^2. \tag{3}$$

Here we take $S(Q)$ to be a normalised Ornstein–Zernike distribution centred at $Q \sim 2k_F$ with width κ where κ is the inverse correlation length ξ. This choice of structure factor is inherent to a Gaussian model; in short, here we treat thermal fluctuations in the harmonic approximation.

For the highly anisotropic systems of interest we perform our calculation with a model Fermi surface of cylindrical symmetry. This Peierls gap will occur in the perfectly nested regions of this surface where there are planes parallel in momentum space. We model the ionic structure factor $S(q)$ by a normalised Ornstein–Zernike function

$$S(\boldsymbol{q}) \sim N/(q_\parallel^2 + \alpha^2 q_\perp^2 + \kappa^2) \tag{4}$$

where $\parallel$ and $\perp$ refer to the cylindrical axes, κ is the inverse correlation length, α is a dimensionless anisotropic parameter, N is a normalisation constant and $q = 0$ corresponds to a nesting vector $Q = 2k_F$. A cut-off q_0 reflects the degree of Fermi surface nesting and will be of order the inverse lattice spacing where details vary according to band structure. Because the Lorentzian structure factor is only valid for long-wavelength fluctuations, an additional cut-off q_c must be introduced to ensure its proper normalisation. If we define $q^* = \min(q_c, q_0)$ then if $\alpha q^*/\boldsymbol{\kappa} \ll 1$ the electronic system will be

† $d\chi/dT \sim c_v$ has been conjectured in TTF–TCNQ for somewhat different reasons in [6]. The authors of [6] do not support this statement with a detailed calculation, and in particular do not discuss mean-free-path effects which play a central role, via the Fisher–Langer argument, in our present treatment.

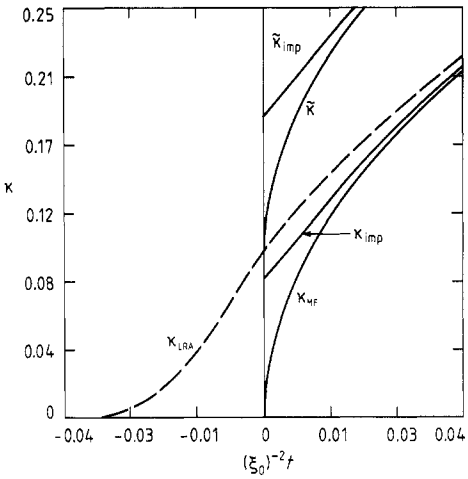

Figure 1. Inverse correlation lengths as defined in the text.

quasi-one dimensional.

If the anisotropy is very large, as in the case of the quasi-1D Peierls system $K_{0.3}MoO_3$ ($\alpha q^* \sim 10^{-5}$) [7], then unless we are very close to the transition we may assume a one-dimensional electronic band structure. In this case the integral over Q in (2) for $T > T_c$ leads to

$$G^{-1}(k, \omega) = G_0^{-1}(k, \omega) - \langle V_Q^2 \rangle [G_0^{-1}(k - 2k_F, \omega) + i v_F \xi^{-1}] \tag{5}$$

where

$$\xi^{-1}(t) = \xi^{-1}(t) + l^{-1} \tag{6}$$

Equation (6) embodies the crucial fact that the electronic mean free path l, which remains fixed through the Peierls transition, provides a lower cut-off to the wavelength of density fluctuations that scatter electrons; this argument was first pointed out by Fisher and Langer in the context of transport properties at a magnetic critical point. The density of states, and thus χ, is then calculated from G in (5) by the standard method.

Figure 1 shows the temperature dependence of the inverse correlation lengths used in [4] and the present theory. LRA consider a one-dimensional system with finite correlation length for $T > 0$, where $\xi(T)$ is determined using transfer matrix techniques. In figure 2 we make a comparison between the LRA approach and the present theory, and experimental results on blue bronze ($K_{0.3}MoO_3$). Though LRA describe several features of χ near a Peierls transition—in particular its smooth form through T_c and the effect of the density of states gap—they only treat one-dimensional non-critical fluctuations. Close to T_c this is not adequate, and therefore in our theory we include Gaussian critical fluctuations in all three dimensions through our structure factor $S(q)$. In all our theoretical curves presented here $\chi_{t<0}$ and $\chi_{t>0}$ are matched at $t = 0$ ($T = T_c$); this is reasonable since, by the Fisher–Langer argument, χ is proportional to the lattice energy and therefore must be a smooth function of temperature. In figure 2 we use $\xi_{0_{eff}}/\xi_0 = 2.1$ and $\xi_{0_{eff}}/l = 1$ where $\xi_{0_{eff}} \sim \hbar v_F/\Delta_{eff}$ and $\xi_0 \sim \hbar v_F/\Delta$ (where $\Delta_{eff} \sim \sqrt{\langle V_Q^2 \rangle}$ and $\Delta \sim \langle V_Q \rangle^2$); this is in good agreement with the experimental values $\Delta(0) = 565$ K [1], $\Delta_{eff} = 282$ K [1] and $\tau = 6.8 \times 10^{-15}$ s [7]. We note that for $l \gg \xi_{0_{eff}}$ the calculated χ will assume a form similar to that of LRA.

We can also extend the present theory to describe χ near T_c for higher-dimensional

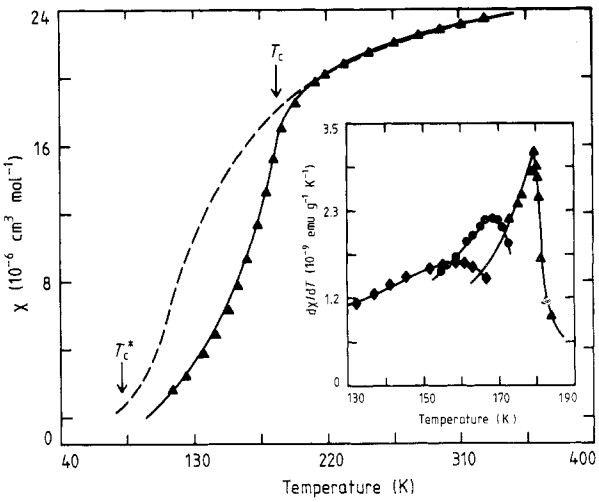

Figure 2. χ for $K_{0.30}MoO_3$: theory versus experiment. LRA and experimental points are taken from [1]; here T_c^* is the three-dimensional LRA ordering temperature and T_c is the transition of the present theory. Full curve: present theory; broken curve: LRA theory. Inset: $d\chi/dT$ for $K_{0.30}Mo_{1-x}W_xO_3$. Data points are taken from [7]. ▲, $x = 0$; ●, $x = 0.004$; ◆, $x = 0.01$.

Peierls compounds. Structure factor normalisation is necessary to prevent divergence of the electronic self-energy Σ integrals. The density of states integrals must be performed numerically, though we can determine leading-order behaviour analytically as $T \rightarrow T_c$ by considering the limits $\alpha q^*/\kappa \gg 1$ and $\kappa \rightarrow 0$. We find that for dimensions $d = 1$, 2 and 3

$$d\chi/dt \sim (-\operatorname{sgn} t)|t|^{1/2} \qquad t \rightarrow 0 \tag{7}$$

where t is the reduced temperature. Equation (7) indicates that for this particular Fermi surface geometry it is only coherence length and mean-free-path factors that affect $d\chi/dT$ near T_c as a function of dimension. According to the Fisher–Langer argument, $d\chi/dT$ should be proportional to c_v; this is indeed the case in (7) for the Gaussian model ($\alpha = 0.5$). Theoretical curves, obtained numerically, for $d\chi/dT$ in 1, 2 and 3 dimensions are shown in figure 3. Here we assume that l and $\xi_{0\,\mathrm{eff}}$ will be constant as a function of dimension. In the inset of figure 3 we also compare our theoretical results to χ-measurements on $K_{0.03}MoO_3$ (1D) [5], $K_3Cu_8S_6$ (2D) [8] and CuV_2S_4 (3D) [9] with good agreement.

We observe that (7) implies a diverging $d\chi/dT$, ever-present lattice imperfections in realistic systems will provide a cut-off to the ionic correlation length leading to a non-diverging specific heat and thus to a cusp in $d\chi/dT$. The effects of disorder can be included explicitly in our calculations. It is well known that impurities destroy long-range order in Peierls systems of physical interest [10]; the correlation length will remain finite and will saturate to a value determined by the impurity concentration and potential. For low impurity levels there will be a crossover temperature T^* corresponding to the formation of 'local' gaps [11]; in order to determine χ near T^* in a 'dirty' Peierls system we have modelled κ_{imp}, the inverse ionic correlation length in the presence of impurities, by an expression (shown in figure 1) motivated by McMillan's leading-order treatment of impurity fluctuations [11]

$$\kappa_{\mathrm{imp}} \sim (1/\xi_0)\{(-t) + [(-t)^2 + N^4]^{1/2}\}^{1/2} \tag{8}$$

where $N = \Lambda x^{1/d}$, $t = (T - T^*)/T^*$, d is the system dimension, x is the impurity concentration and Λ is an input length scale determined by the impurity potential. We can

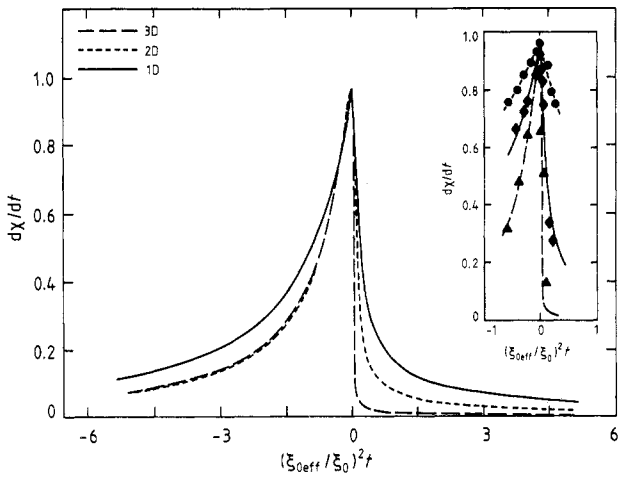

Figure 3. Theoretical curves for $d\chi/dt$ with $1.35(\xi_0)_{1D} = (\xi_0)_{2D} = (\xi_0)_{3D}$ and $\xi_{0_{eff}}/l = 1$. Inset: Comparison of theory and experiment for 1, 2 and 3 dimensions. ◆, $K_{0.3}MoO_3$ (1D; $\xi_{0_{eff}}/l \sim 1.2$, $\xi_{0_{eff}}/\xi_0 = 2.1$); ●, $K_3Cu_8S_6$ (2D; $\xi_{0_{eff}}/l \sim 1.4$, $\xi_{0_{eff}}/\xi_0 = 2.4$); ▲, CuV_2S_4 (3D; $\xi_{0_{eff}}/l \sim 1.0$, $\xi_{0_{eff}}/\xi_0 = 6.4$).

incorporate (8) into our calculation of χ, and in the inset of figure 2 we show $d\chi/dT$ versus T for $K_{0.30}MoO_3$, both theory and experiment [5], for varying impurity concentrations. Here we take Λ to be roughly a lattice spacing ($\Lambda \sim 4.5$ Å); this corresponds to a weak impurity potential. We assume that $\xi_{0_{eff}}/l = 1.2$ remains constant for low levels; we then find that the coherence length ξ_0 decreases with increasing impurity concentration, as expected ($x = 0$, $\xi_{0_{eff}}/\xi_0 \sim 2.1$; $x = 0.004$, $\xi_{0_{eff}}/\xi_0 \sim 2.4$; $x = 0.01$, $\xi_{0_{eff}}/\xi_0 \sim 2.6$).

In conclusion we have presented a theory for the DC magnetic susceptibility at a Peierls transition that includes Gaussian critical fluctuations in all three dimensions. We have incorporated the Fisher–Langer argument, borrowed from magnetism, into our calculation and show that the short-range order parameter fluctuations and growth provide the dominant contribution to χ near T_c. In particular $d\chi/dT$ will be proportional to the lattice specific heat and therefore will have a cusp for physically realistic systems at $T \sim T_c$. Similar reasoning can be applied to the nuclear spin relaxation rate $1/T_1$ and the thermoelectric power Q. Comparison with experimental results from quasi-one-dimensional blue bronze, with varying impurity concentrations, yields favourable agreement. Good agreement with experiment is also found for $K_3Cu_8S_6$ (2D) [8] and CuV_2S_4 (3D) [9]. We would like to encourage more accurate measurements of $d\chi/dT$ and c_v on the same Peierls systems; this would provide a good test for the theory.

Naturally there remain many open questions. Future projects include a study of resistivity where backscattering effects must be included. Though the present theory does extend to several higher-dimensional compounds, the dichalcogenide 2H-$TaSe_2$ certainly provides a mystery—its χ near T_c has a pronounced discontinuity [12] and thus does not have an energy-like appearance. It has been suggested that this anomalous behaviour in χ near the transition may be due to specific band-structure features and/or electron–electron interactions [13], neither of which has been addressed here. Finally, it would be interesting to investigate the dynamics of these Peierls systems a little bit further from T_c, and in particular to learn how the quasi-static fluctuations become phonons at higher temperatures.

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