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Fluctuation effects on the Pauli susceptibility at a Peierls transition

P Chandra

Corporate Research Science Laboratories, Exxon Research and Engineering Company, Annandale, NJ 08801, USA

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Abstract. The observation of a sharp cusp in the temperature derivative of the magnetic susceptibility $d\chi/dT$ is often used as a signature of a second-order 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. 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; 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.

1. Introduction

Sharp structure in the temperature derivative of the static magnetic susceptibility ($\chi(T)$) has often been interpreted as a signature of a continuous structural phase transition. For example, ter Haar *et al* [1] used this method to determine the transition temperature (T_c) of $K_3Cu_8S_6$; similar measurements have been performed on $TaSe_3$ [2], $K_{0.3}MoO_3$ (blue bronze) [3, 4] and 2H-$TaSe_2$ [5]. A variation in the susceptibility at a structural phase transition is not surprising, as the latter is accompanied by changes in the density of states. These changes will be greatest at metal–insulator transitions, particularly in the case of quasi-one-dimensional materials undergoing a Peierls transition [6]. Here, the driving force for a periodic structural distortion at wavevector Q is the strong nesting of the Fermi surface at $Q = 2k_F$. In quasi-one-dimensional materials this will lead to the opening of a gap in the density of states at temperatures $T < T_c$.

Theoretically the behaviour of the magnetic susceptibility at a Peierls transition is not well understood in detail, particularly close to T_c [3]. Here we will follow the notation of [3] and Δ_{eff} is the so-called pseudo-gap. In this paper we shall study this question in the context of quasi-one-dimensional systems. The simplest model of χ at a Peierls transition treats the electrons as a non-interacting free electron gas, and χ is then proportional to $g(e_F)$, the density of states at the Fermi energy. By charge conservation arguments, ionic density fluctuations close to T_c lead to variation in $g(e_F)$ and it is these effects which we would like to calculate.

Historically the Peierls transition has been treated using a soft-phonon picture; here one phonon frequency $\omega(Q)$ vanishes leading to the formation of a condensate at finite wavevector Q that reflects the new periodic order in the low-temperature phase. Because large anharmonicities are present for $T \sim T_c$ the single-phonon approximation

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of Migdal's theorem [7] is not valid, and diagrammatic calculations with phonon basis states become very complicated [8].

An alternative view to the soft-phonon picture is to consider the formation of a pseudogap above T_c due to the presence of large critical fluctuations. Lee, Rice and Anderson (LRA) [9] have shown that in one dimension this approach leads to significant changes in χ above the transition temperature. Here, the critical fluctuations are treated as quasi-static; this elastic scattering assumption near T_c is easily justified using time scale arguments. In particular we need to show that the conduction electron passes through the spatially restricted region of a critical fluctuation in a time short compared to the fluctuation lifetime τ_{fl}. In the language of dynamical scaling [10],

$$\tau(k)_{fl} \sim \Gamma_{fl}(\xi/a)^z f(k\xi) \tag{1.1}$$

where ξ is the correlation length, z is the dynamical exponent, a is the lattice spacing, and $f(k\xi)$ is a scaling function of O(1) near $T \sim T_c$ ($k \to 0$, $\xi \to \infty$). Γ_{fl} is a microscopic fluctuation rate; most likely it will be determined by the dominant phonon frequency $\omega \sim k_B T_c/\hbar$. Here we follow LRA and assume that it is the low-momentum, long-wavelength ($k \to 0$) fluctuations that determine the electronic behaviour. Because the critical region at a structural transition is small, e.g. [11], we may use mean field results for a theory with a non-conserved order parameter; here $z = 2$. Therefore for ballistic motion the elastic assumption is valid if

$$\xi/v_F < \Gamma_{fl}(\xi/a)^2 \tag{1.2}$$

where v_F is the Fermi velocity. Equation (1.2) is easily satisfied in the neighbourhood of a second-order transition, and is a statement of the 'thermodynamic slowing down' of long-wavelength critical fluctuations near T_c.

The problem of interest therefore becomes that of an electron scattering from a single-body static, fluctuating potential $V(r)$ which, for $T > T_c$, satisfies

$$\langle V_q \rangle = 0 \qquad \langle V_q V_{q'} \rangle = S(q)\langle V_q^2 \rangle \delta_{q,-q'} \tag{1.3}$$

where V_q is the Fourier transform of $V(r)$. The structure factor $S(q)$ is strongly peaked at $q = 0$ ($Q = 2k_F$). Below T_c the order parameter $< V_q >$ is finite. We shall model $S(q)$ by a normalised Ornstein–Zernike function [12]; this is appropriate because the critical region is small (e.g., $t_G \sim (\Delta/e_F)^4 \sim 10^{-6}$ for quasi-one-dimensional blue bronze) [3, 4]. The correct normalisation for $S(q)$ is important so as to ensure that the integrated structure factor has a smooth temperature dependance. This was pointed out by Kasuya and Kondo [13] in the context of a study of resistivity close to a magnetic critical point. In fact it has been noted elsewhere [14] that electronic fluctuations at a Peierls transition are strongly reminiscent of transport properties at a magnetic critical point, and we will pursue this analogy here. In both phenomena 'critical slowing down' arguments indicate that the electron gas samples the static and not the dynamic properties of critical fluctuations near the transition. In the magnetic case Fisher and Langer [15] contend that the electron scattering will be dominated by short-range fluctuations due to the finite nature of the mean free path; this then leads to the elimination of spurious divergences in transport properties. We will incorporate this argument into our expression for χ; it results in an infinite temperature derivative [16] (the present paper is an elaboration and extension of this Letter) in the density of states at $T \sim T_c$, a feature that is observed experimentally but does not emerge

from the LRA calculation. This singular behaviour of $d\chi/dT$ near T_c is strongly reminiscent of the antiferromagnetic case [17]. However, it is also important to stress the distinctions between the magnetic and the Peierls transitions. In antiferromagnetic materials the magnetic moments that scatter the electrons are intrinsic to the rare earth structure, and therefore one may adequately treat the problem using a first-order Born approximation. The situation is somewhat more complicated at a Peierls transition. Here multiple scattering events lead to the formation of a gap, and therefore one must calculate the Born approximation in a self-consistent fashion.

We must now return to our earlier justification of the quasi-static assumption; it depended on the low-momentum ($\boldsymbol{q}$) nature of the critical fluctuations. However, we have just argued that it is in fact the short-range, high-$\boldsymbol{q}$ ionic fluctuations that will determine the electronic behaviour; as $\xi \to \infty$, τ_{fl} must remain constant for all momenta [10] so that the quasi-static approximation is still valid. Strictly speaking, only electron–ion energy transfers of the order of the electronic gap $\Delta(T = 0)$ will significantly alter our results so that the elastic scattering assumption near T_c seems acceptable on physical grounds. Experimental justification for this approximation comes from inelastic neutron scattering; we require that $\delta\omega/\Delta(0) \ll 1$ for $T \sim T_c$ where $\delta\omega$ is the width of the structure factor $S(q = 2k_F, \omega \sim 0)$. For blue bronze ($K_{0.3}MoO_3$), the specific material of interest here, experiments [18] indicate that $\delta\omega/\Delta(0) \sim 10^{-2}$, so there is no significant inelastic scattering near the transition.

It is important to note that we are not presenting a theory for the Peierls instability itself, but instead are interested in its effects on the electronic properties of the system. The mechanism of the transition appears in our calculations only through the structure factor; since the critical region is small we assume a Ginzburg–Landau free energy and hence an Ornstein–Zernike $S(q)$; an alternative structure factor could easily be incorporated into our calculations, e.g. see [19]. At present there is no microscopic theory for the Peierls T_c, since the standard calculation based on the Fröhlich Hamiltonian neglects phonon entropy effects [20]; therefore we must take T_c from experiment. However, we do argue [16] that the static magnetic susceptibility, χ, will be dominated by short-range ionic fluctuations at temperatures $T \sim T_c$ and that in particular $d\chi/dT$ will be proportional to the lattice specific heat c_V close to the Peierls transition [21]†. These ideas can be applied to electronic systems of one, two and three dimensions, and to quasi-one-dimensional systems with impurities.

Before we continue, let us briefly summarise the main assumptions (see figure 1) and results of this paper. Using 'critical slowing down' arguments, we treat the ionic fluctuations near the Peierls transition as quasi-static and can therefore consider electron–ion scattering in the elastic limit near T_c. Because the electrons will never sample ionic fluctuations with wavelengths longer than their own mean free path l, electronic properties near T_c will be dominated by short lengthscale ionic behaviour. On dimensional grounds, we then expect χ to have an energy-like appearance, and in particular $d\chi/dT$ should be proportional to the lattice specific heat [16]. It is important to note that here we are implicitly assuming a hierarchy of lengthscales; in particular we assume that the electron samples *local* not *global* ionic fluctuations, i.e. $\xi_0 < l < \xi_0 t^{1/2}$ where ξ_0 is the coherence length ($\xi_0 \sim v_F/\Delta$) and t is the reduced temperature. Detailed calculations of the Pauli susceptibility in one, two and three

† $d\chi/dt \sim c_V$ has been conjectured in TTF-TCNQ for somewhat different reasons in [21]. The authors 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.

dimensions for a model cylindrical Fermi surface yield the following expression:

$$d\chi/dt \sim (-\operatorname{sgn} t)|t|^{-1/2} \qquad t \to 0 \tag{1.4}$$

where t is the reduced temperature. We emphasise that these Peierls systems are inherently three dimensional due to their finite transition temperatures; here we refer to the dimension d of Fermi surface nesting. Equation (1.4) indicates that for this particular Fermi surface geometry it is only coherence length and mean free path factors that affect χ as a function of dimensionality. It is crucial to note that (1.4) is only valid for temperatures $|t| > t_G$, where t_G is the Ginzburg temperature. In any case, because t_G is so small the critical region is irrelevant for comparision to experiment. Equation (1.4) 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 $d\chi/dT$. Impurity effects are explicitly included in our calculations, and we see that they produce a rounding of the $d\chi/dT$ cusp when the true phase transition is destroyed.

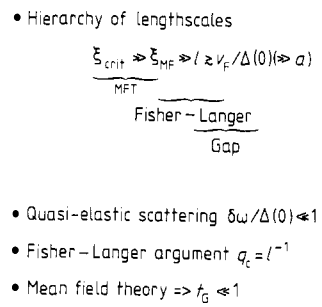

Figure 1. A summary of the main assumptions used in this paper.

The layout of this paper is as follows. In § 2 we perform a calculation for a quasi-one-dimensional material similar to that of LRA but we include a finite electronic mean free path and focus on the behaviour near a finite T_c. We then extend our ideas to higher-dimensional compounds, with good agreement with experiment. Most systems are strongly affected by disorder, and this is particularly evident in quasi-one-dimensional systems. The impurity effect on the Peierls transition is analogous to the random field on a continuous spin model [22, 23]. The correlation length remains finite at the smeared transition, and in § 3 this feature is incorporated into our susceptibility calculation. Comparison is then made to experiment with favourable results. We end with a summary, and also discuss suggestions for future work.

2. The susceptibility calculation

Because we are interested in the temperature dependence of the static susceptiblity near a Peierls transition, we now calculate the Pauli contribution to χ near T_c. The spin susceptibility for a non-interacting electron gas scattering from a static potential is

$$\chi = \frac{(g\mu_B)^2}{2} \int \frac{d\omega}{2\pi} \left(\frac{-\partial f}{\partial \omega}\right) D(\omega) \tag{2.1}$$

where $D(\omega)$ is the electronic density of states, $f(\omega)$ is the Fermi–Dirac function, and μ_B and g refer to the Bohr magneton and the Landé g-factor respectively. Physically, the static potential preserves the phase coherence of the electronic wavefunctions so that the scattered states are linear combinations of eigenstates of the system. All response functions can therefore be calculated using a single-particle Green function (this is simply an extension of Anderson's dirty superconductor theorem [24]). In order to determine the density of states $D(\omega)$ in (2.1) we must solve Dyson's equation for the full Green function of the system. As a result of the 'critical slowing down' arguments given in the Introduction we have reduced our problem to that of solving a Schrödinger equation with a static potential that fluctuates in momentum space. We use a standard self-consistent Born approximation; symmetry-breaking self-energy diagrams, shown in figure 2, must be calculated to all orders to produce a gap at the transition. It is crucial to note that this approach is very different to that in the localisation problem; here we have a self-energy with strong momentum dependence which will, in particular, affect the density of states. Because crossed diagram self-energy contributions are of order (Δ/e_F) they will be neglected in this calculation. Such diagrams would, however, be important for the determination of resistivity and other transport properties, e.g. [25], and this question will be addressed in a future paper.

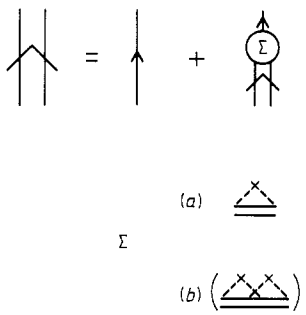

Figure 2. Dyson's equation for the full Green functions with self-energy contributions that are (*a*) included and (*b*) neglected in the present calculation.

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

$$G^{-1}(\boldsymbol{k},\omega) = \omega - \epsilon(\boldsymbol{k}) + \frac{\mathrm{i}}{\tau} - \int \frac{\mathrm{d}\boldsymbol{Q}\, S(\boldsymbol{Q})\, \langle V_Q^2 \rangle}{\omega - \epsilon(\boldsymbol{k}-\boldsymbol{Q}) + \Sigma(\boldsymbol{k},\omega)} \tag{2.2}$$

for temperatures $T > T_c$ where $\epsilon(k) \sim \epsilon(k-Q)$, $S(Q)$ is the structure factor defined by (1.3) and $\langle V_Q V_{Q'} \rangle = \Delta_{\mathrm{eff}}$ is the effective gap due to the presence of large thermal fluctuations. Because we are in a wide band regime Re Σ is negligible and Im Σ can be approximated by a constant $1/\tau$; in the standard relaxation time approximation $1/\tau = v_F/l$ where v_F and l refer to the Fermi velocity and the electronic mean free path respectively. Here we take $S(Q)$ to be a normalised Ornstein–Zernike distribution [12] 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 do our calculation with a model Fermi surface, shown in figure 3, with cylindrical symmetry. The Peierls gap will

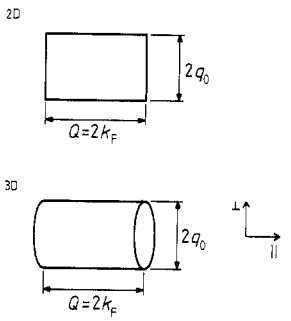

Figure 3. Model cylindrical Fermi surface used in the present theory with parameters as defined in the text.

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

$$S(\boldsymbol{q}) \sim N/(q_{\parallel}^2 + \alpha^2 q_{\perp}^2 + \kappa^2) \tag{2.3}$$

where $\parallel$ and $\perp$ refer to the axes shown in figure 3, κ is the inverse correlation length, α is a dimensional anisotropic parameter, N is a normalisation factor, and $q = 0$ corresponds to a nesting vector $Q = 2k_F$. A cut-off q_0, shown in figure 3, reflects the degree of Fermi surface nesting and will be of the order of the inverse lattice spacing where details vary according to band structure. Because the Lorenzian structure factor is only valid for long-wavelength fluctuations, an additional cut-off q_c must be introduced to ensure its proper normalisation; then

$$2\pi \int_0^{q_c} q_{\perp}\, \mathrm{d}q_{\perp} \int_{-\infty}^{+\infty} \mathrm{d}q_{\parallel}\, S(q_{\parallel}, q_{\perp}) = 1. \tag{2.4}$$

If we define $q^* = \min(q_c, q_0)$ then the system will be electronically quasi-one dimensional for $\alpha q^*/\kappa \ll 1$.

If the anisotropy is very large, as in the case of the quasi-one-dimensional Peierls system $K_{0.3}MoO_3$ ($\alpha \sim 10^{-4}$, $q^* \sim 10^{-1}$) [26–29], then unless we are very close to the transition we may assume a one-dimensional band structure. In this case the integral over Q in (2.2) for $T > T_c$ leads to

$$G^{-1}(k, \omega) = G_0^{-1}(k, \omega) - \langle V_Q^2 \rangle \left(G_0^{-1}(k - 2k_F, \omega) + \mathrm{i} v_F \tilde{\xi}^{-1} \right) \tag{2.5}$$

and

$$\tilde{\xi}^{-1}(t) = \xi^{-1}(t) + l^{-1} \tag{2.6}$$

where the bands have been linearised near the Fermi surface in the standard fashion. Equation (2.6) embodies the *crucial fact* that the electronic mean free path l, which remains fixed through the Peierls transition, provides a cut-off to the wavelength of density fluctuations that scatter electrons; this argument was first pointed out by Fisher and Langer [15] in the context of transport properties at a magnetic critical point, and was used to explain why no divergences were observed in the resistivity of magnetic metals.

The electronic density of states is found by integrating Im $G_k(w-i\delta)$ over wavevector

$$\frac{D(\tilde{\omega})}{D_0} = \mathrm{Re}\,\frac{\tilde{\omega} - \frac{1}{2}i\tilde{\gamma}}{[(\tilde{\omega} - \frac{1}{2}i\tilde{\gamma})^2 - 1]^{1/2}} \tag{2.7a}$$

where

$$\tilde{\omega} = \frac{\omega}{(\langle V_Q^2\rangle)^{1/2}} \qquad \text{and} \qquad \tilde{\gamma} = \frac{v_F}{(\langle V_Q^2\rangle)^{1/2}}\,(\tilde{\xi}^{-1} + l^{-1}). \tag{2.7b}$$

It is important to note that the mean free path l enters the calculation through G_0, the bare electron propagator, and therefore enters twice into the $D(\omega)$ calculations; this accounts for the term $2l^{-1}$ in $\tilde{\gamma}$ above. In the limit $l \to \infty$ we recover the LRA expression [9]; we will discuss this theory further when we make comparison to experiment. As $T \to T_c^+$, $\kappa \to 0$ so that close to the transition we may expand the denominator of (2.7*a*) in the standard fashion. Because experimentally $2\Delta(0)/kT_c \sim 6$ (here $\Delta(0) \sim \langle V_Q\rangle$ and $\Delta_{\mathrm{eff}} \sim (\langle V_Q^2\rangle)^{1/2}$) [3] thermal averaging effects in χ will not be appreciable and χ is essentially proportional to $D(\omega \sim 0)/D_0$; therefore

$$\mathrm{d}\chi/\mathrm{d}t \sim -\mathrm{d}\kappa/\mathrm{d}t \sim -t^{-1/2} \qquad t \to 0^+ \tag{2.8}$$

where t is the reduced temperature and κ is the inverse correlation length; here we have used the Gaussian exponent for κ [12]. According to the Fisher–Langer argument, $\mathrm{d}\chi/\mathrm{d}T$ should be proportional to c_V; this is indeed the case in (2.8) for the Gaussian model ($\alpha = 0.5$).

We now turn to temperatures $T < T_c$; an obvious extension of the method already described is to calculate the full Green function G in (2.2) making the simple transformation

$$S(\boldsymbol{Q})\langle V_Q^2\rangle \Rightarrow S(\boldsymbol{Q})\langle V_Q^2 - \langle V_Q\rangle^2\rangle + \delta(\boldsymbol{Q} = 2\boldsymbol{k}_F)\langle V_Q\rangle^2 \tag{2.9}$$

which leads to

$$\mathrm{d}\chi/\mathrm{d}t \sim (-t)^{-1/2} \qquad t \to 0^-. \tag{2.10}$$

We note that in (2.10) $\mathrm{d}\chi/\mathrm{d}T$ has the form of a Gaussian specific heat, as expected.

Before comparing our results with experiment, let us briefly contrast our approach with that of an earlier theory developed by Lee, Rice and Anderson (LRA) [9]. Here we calculate the magnetic susceptibility of a non-interacting *one-dimensional* electron gas in the presence of a *three-dimensional* ionic field near a Peierls instability. We take advantage of our proximity to a second-order phase transition and model the ionic degrees of freedom by a classical, static, momentum-dependent potential; its Fourier transform yields a structure factor $S(q)$ that is strongly peaked at $q = 0$ ($Q = 2k_F$). LRA have also used this pseudo-gap approach in their calculation, and it is important that we emphasise how the two approaches differ. LRA consider a completely one-dimensional sytem with finite correlation length $\xi(T)$ for $T > 0$. Using transfer matrix techniques [30], LRA determine $\xi(T)$ and interpret the three-dimensional ordering temperature T_c^* as the temperature where $\xi(T)$ starts to increase exponentially. Though the LRA theory describes 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—it only treats one-dimensional, non-critical fluctuations. Close to T_c this is not adequate [3]; specifically the predicted

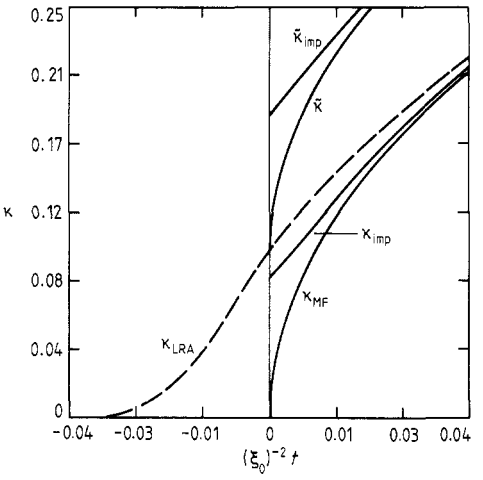

Figure 4. Inverse correlation lengths as defined in text with $\kappa \sim \xi_0 t^{\nu}$ and mean field values for all exponents. ξ_{LRA}^{-1} is taken from [9] and $\tilde{\kappa}_{imp} = \kappa_{imp} + l^{-1}$ where l is the electronic mean free path (here $\kappa_{sat}\xi_0 \sim 0.08$, $l^{-1} = 0.01$).

position of T_c^* on the $\chi(T)$ curve *does not* match well with experiment, and furthermore $d\chi/dT$ *does not* have a sharp cusp as observed. In our calculation we include Gaussian fluctuations in all three dimensions through our structure factor $S(q)$. Moreover we argue that the electronic mean free path l provides a natural cut-off to the width of $S(q)$; the electrons can never sample ionic correlations on lengthscales longer than l.

Figure 4 shows the temperature dependence of the correlation lengths used in the LRA and in the present theory. $\tilde{\xi}$ is the effective correlation length that incorporates the Fisher–Langer argument, as discussed above.

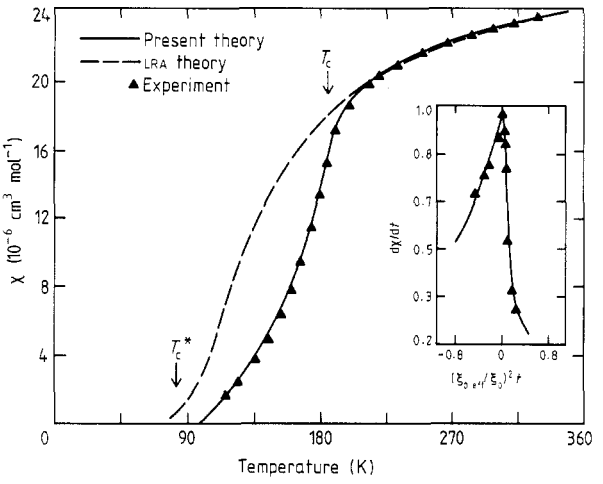

Figure 5. χ for $K_{0.30}MoO_3$: theory versus experiment. LRA and experimental points are taken from [3]; here T_c^* is the three-dimensional LRA ordering temperature and T_c is the transition temperature of the present theory. Inset: $d\chi/dt$ for $K_{0.30}MoO_3$: theory versus experiment ([4]).

In figure 5 we make a comparision between the LRA and the present theories, and experimental results on quasi-one-dimensional blue bronze ($K_{0.3}MoO_3$) [3]. In our theoretical fit we use the values $\xi_{0\,\mathrm{eff}}/\xi_0 = 2.1$ and $\xi_{0\,\mathrm{eff}}/l = 1.2$, both taken from experiment [3, 4]. We note that in all the curves 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. We observe that the Fisher–Langer argument plays an important role in determining the slope of χ near T_c; this is best seen in the temperature derivative of the susceptibility, as shown in the inset of figure 5. There is good agreement between theory and experiment for $|(\xi_{\mathrm{eff}}/\xi_0)^2 t| < 1$ ($\xi_{\mathrm{eff}} \sim 1/\Delta_{\mathrm{eff}}$); since $l \sim \xi_{0\,\mathrm{eff}}$ this suggests that the condition

$$l/\xi < 1 \tag{2.11}$$

where ξ is the ionic correlation length may be crucial to the validity of the quasi-static approximation (for ballistic motion). In general, our theory should be appropriate for all quasi-one-dimensional Peierls systems where Coulomb interactions are negligible; examples other than $K_{0.30}MoO_3$ include TTF–TCNQ, $(TaSe_4)I$ and o-$TaSe_3$. We note that for $l \gg \xi_{0\,\mathrm{eff}}$,where l is the electronic mean free path and $\xi_{0\,\mathrm{eff}} \sim \hbar v_F/\Delta_{\mathrm{eff}}$ is the 'effective' zero-temperature coherence length ($\Delta_{\mathrm{eff}} \sim (\langle V_Q^2 \rangle)^{1/2}$), the calculated χ will assume a form similar to that of LRA [9].

We would also like to extend the present theory to describe χ near T_c for higher-dimensional Peierls compounds. As discussed earlier, structure factor normalisation is necessary in order to prevent divergence of the electronic self-energy Σ integrals; for the model cylindrical Fermi surface these normalisation terms ensure that all d-dimensional self energies Σ_d are well behaved as $T \to T_c(\kappa \to 0)$. For $d = 2$ and 3 we calculate Σ_d analytically and check that $\lim_{\alpha q^*/\kappa \to 0} \Sigma_d = \Sigma_1$ and that Σ_d is finite as $\alpha q^*/\kappa \to \infty$. The density of states integrals must be performed numerically, though we can determine leading order behaviour analytically as $T \to T_c$ by considering the limits $\alpha q^*/\kappa \gg 1$ and $\kappa \to 0$. We find that for dimensions $d = 1, 2$ and 3

$$\mathrm{d}\chi/\mathrm{d}t \sim (-\mathrm{sgn}\, t)|t|^{-1/2} \qquad t \to 0. \tag{2.12}$$

Equation (2.12) implies that for this particular Fermi surface geometry it is only coherence length and mean free path factors that change $\mathrm{d}\chi/\mathrm{d}t$ near T_c as a function of dimension; theoretical curves for $\mathrm{d}\chi/\mathrm{d}t$ in $d = 1, 2$ and 3 dimensions are shown in figure 6.

Here we assume that l and $\xi_{0\,\mathrm{eff}}$ will be constant as a function of dimensionality; then we note that ξ_0 will be the shortest in 1D, in agreement with x-ray measurements [31], and that $\xi_{0\,2D} = \xi_{0\,3D}$ due to the symmetry of our model Fermi surface. Because, to our knowledge, there is no detailed information of Δ_{eff} in either $K_3Cu_8S_6$ or in CuV_2S_4, we must simply do theoretical fits for $\xi_{0\,\mathrm{eff}}/\xi_0$. The resulting numbers ($\xi_{0\,\mathrm{eff}}/\xi_0 \sim 2.4$ and 6.4 for $K_3Cu_8S_6$ and CuV_2S_4 respectively) are certainly within the physical parameter range suggested by measurements on blue bronze. Experiments [1, 32] indicate that the electronic mean free paths are within a constant of O(1) of that of blue bronze; our theoretical fits are in agreeement with this ($\xi_{0\,\mathrm{eff}}/l \sim 1.4$ and 1 for $K_3Cu_8S_6$ and CuV_2S_4 respectively). In the inset of figure 6 we compare our theoretical results to susceptibility measurements on $K_{0.3}MoO_3$ (1D) [4], $K_3Cu_8S_6$ (2D) [1, 33] and CuV_2S_4 (3D) [32, 34] with good agreement. We note that these materials have different mean free paths; therefore their behaviour close to T_c will be slightly different. Again we see that we have good agreement between theory and experiment for $|(\xi_{\mathrm{eff}}/\xi_0)^2 t| < 1$ or identically for $l < \xi$, as discussed earlier in this section. It would be interesting to specifically test the predicted exponents (2.13) with experiment.

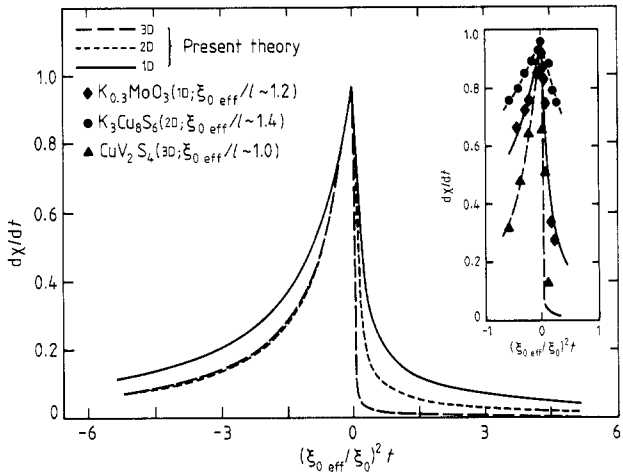

Figure 6. Theoretical curves for $d\chi/dt$ versus t in 1, 2 and 3 dimensions. Here $1.35(\xi_0)_{1D} = (\xi_0)_{3D} = (\xi_0)_{2D}$ with $\alpha = 1$ ($d = 2, 3$) and $\xi_{eff}/l = 1$ (see text). Inset: comparison of theory and experiment for one, two and three dimensions.

3. Impurity effects on χ

The effect of impurities on a Peierls system is a subject of great interest; here we address the question in the context of the Pauli susceptibility. The impurity potential couples linearly to the charge density wave (CDW) distortion [35], and long-range order cannot be maintained for dimensions $d < 4$ [22, 23]. In a Ginzburg–Landau free energy the linear coupling to the impurity potential will result in a renormalisation of the transition temperature ($T_c^{imp} = T_c^{pure} - \Delta T$); fluctuation calculations beyond the mean field treatment show that the impurity concentration is relevant for $d < 4$ so that we call T^* ($T^* = T_c^{imp}$) the 'crossover' temperature. In general impurities play an important role in charge density wave transport; for example Ong *et al* have shown that the threshold field increases with increasing concentration [36, 37] as predicted by Lee and Rice [38]. At the normal–incommensurate 'smeared' transition of the 'dirty' system the crossover temperature T^* will be depressed from the T_c of the pure material; also, at some $T < T^*$ the correlation length will saturate to a value determined by the impurity concentration and the strength of the impurity potential [39]. Recently Schneemayer *et al* [4] have studied the Pauli susceptibility as a function of impurity concentration in $K_{0.3}MoO_3$; here we try to model this χ behaviour at the smeared transition and compare with their experimental results.

As we discussed in the Introduction, the impurity effect on the Peierls transition is analogous to the random field on a continuous spin model. We follow the Fukuyama–Lee argument [40], analogous to that of Imry–Ma [23] and of Harris [41], to determine the relevance of the impurity concentration. Physically the incommensurate wave is flexible, and the characteristic linear dimension of the 'domain' L_0 will result from competition between the energies due to the random potential and to domain formation. Strictly speaking there can be no domain formation in a system with continuous symmetry; instead there exists a slow continuous variation of the phase on a characteristic lengthscale ξ, the correlation length. Nonetheless the term 'domain' is used widely in this context, and we shall do so here. At low temperatures amplitude variations are negligible, and thus only elastic energy costs due to phase fluctuations

are considered. If we assume that the CDW phase ϕ varies over a lengthscale L, then by the central limit theorem, the impurity potential in each cell has fluctuations of order $L^{d/2}$. The charge density wave can therefore lower its energy by this amount upon adjusting its phase. Because we have continuous symmetry the characteristic energy associated with phase fluctuations is $O(L^{d-2})$; therefore the system will be unstable to domain formation if

$$d - 2 \leq d/2. \tag{3.1}$$

Equation (3.1) may also be derived from a direct calculation of the susceptibility in d dimensions [22]. Therefore we see that for $d < 4$ it is energetically favourable for the system to form domains, and there will be no long-range order but only a 'smeared' transition. For the sake of completeness, we should mention that this type of argument has been criticised in the closely related random-field Ising model, e.g. [42]; in particular it neglects domain entropy considerations and implicitly assumes that all configurations within a 'typical' domain are ordered. In the broadest sense, (3.1) presents a lower bound for d_c, the lower critical dimensionality; therefore for Peierls systems of physical interest the impurity concentration will always be a relevant variable. As an aside, it is important to note that impurities in a CDW system do not play the same role as do magnetic impurities in a conventional BCS superconductor. The analogy between these two phenomena is a common mistake is the literature and is worthy of comment. Though the mathematical structure of the Peierls theory closely follow that of BCS superconductivity the physics of these two systems is quite different. In particular, magnetic impurities depress but do not immediately destroy a superconducting transition, whereas the impurity concentration is always relevant in a Peierls system for dimensions less than four.

Though impurities destroy long-range order in Peierls systems of physical interest, they do lead to local CDW deformations [39] on a lengthscale L, the linear domain size. According to the Fisher–Langer argument the electrons will probe spatially restricted lattice regions of order the mean free path l; therefore if $l < L$ the electrons will simply 'see' a distortion that is non-vanishing as $T \sim T^*$ and there will be a resulting gap in the electronic energy spectrum. As L becomes shorter with increasing impurity concentration the electrons will scatter into this local gap and the density of states will eventually become constant. L, the saturation value of the correlation length ξ as $T \sim T^*$, will be roughly determined by the average inter-impurity distance and will also depend on the strength of the impurity potential [39]. In the absence of a phase transition the free energy and its derivatives must have no singularities or discontinuities at any temperature; therefore for low impurity levels there may be temperature variation but not sharp structure in $d\chi/dT$.

In order to determine χ near T^* in a 'dirty' Peierls system, we must use an expression for ξ that smoothly saturates to a finite value L for $T < T^*$. Here we have modelled κ_{imp}, the inverse ionic correlation length in the presence of impurities, by an expression that is motivated by McMillan's leading order treatment of impurity fluctuations [39]

$$\kappa_{imp} \sim \xi_0^{-1}\{(-t) + [(-t)^2 + N^4]^{1/2}\}^{1/2} \tag{3.2a}$$

with

$$N = \Lambda x^{1/d} \tag{3.2b}$$

and

$$t = (T - T^*)/T^* \tag{3.2c}$$

where d refers to the system dimension, x is the impurity concentration and Λ is an input lengthscale determined by the impurity potential. The form (3.2*a*), shown in figure 4, is similar to that of McMillan [39], though we use an intuitive expression for $\kappa_{sat} = L^{-1} = N/\xi_0$ near T^* as described above†. We note that (3.2*b*) is also different from the inverse Fukuyama–Lee domain length L_0 [40], which was calculated for low temperatures where amplitude fluctuations are negligible.

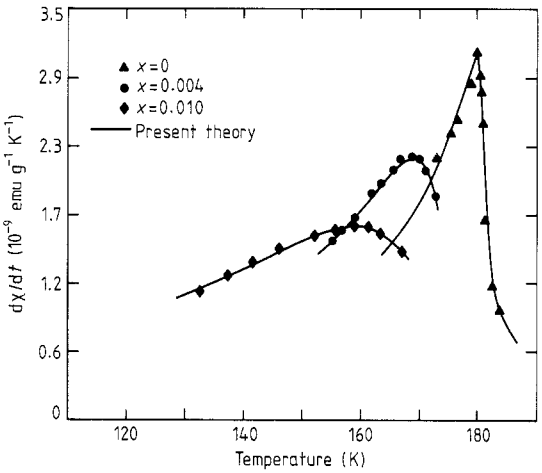

Figure 7. $d\chi/dt$ for $K_{0.30}Mo_{1-x}W_xO_3$. Data points are taken from [4].

In figure 7 we show $d\chi/dT$ versus T for $K_{0.30}MoO_3$, from both theory and experiment, for varying impurity concentrations. Here T^* must be taken from experiment, as there is no existing theory linking McMillan's Ginzburg–Landau free energy to microscopic system parameters. We assume that l and $\xi_{0\,\mathrm{eff}}$ remain constant for low impurity levels, and use the experimental values $\xi_{0\,\mathrm{eff}}/l = 1.2$ as before. Using the volume cell dimensions of blue bronze ($V = 1359.6$ Å^3) [28] we determine the concentration of impurities for a given doping level x. We take Λ (equation (3.2*b*)), an input lengthscale determined by the impurity potential to be roughly a lattice spacing ($\Lambda \sim 4.5$ Å) [28]; this corresponds to a weak impurity potential. It is important to note that the 'rounded peak' in the 'dirty' $d\chi/dT$ occurs at some temperature $T < T^*$; this is due to the presence of non-vanishing local lattice distortions as $T \sim T^*$. As expected, $d\chi/dT$ loses its temperature variation with increasing impurity concentration; it would be interesting to verify if it flattens out at $l \sim L$.

4. Discussion

In conclusion, we have presented a theory for the DC magnetic susceptibility at a Peierls transition. Using a pseudo-gap approach we incorporate the Fisher–Langer argument, borrowed from magnetism, into our calculation and show that the short-range ionic fluctuations provide the dominant contribution to χ near T_c. In particular

† For the present purposes (3.2*a*) is adequate as $T \to T^{*-}$ since $\Delta_{local} \sim \kappa_{imp}$ (in mean field theory) will reach a finite value yielding a 'rounded peak' in $d\chi/dt \sim d/dt(\Delta_{local})$. However, (3.2*a*) will not yield a smooth form for χ through T^* as required; for this purpose a higher-order calculation in the impurity fluctuations is necessary.

the temperature derivative of the static susceptibility, $d\chi/dT$, will be proportional to the lattice specific heat and will therefore have a cusp at $T \sim T_c$. Similar reasoning can be applied to the nuclear spin relaxation $1/T_1$ and the thermoelectric power Q. Comparison with experimental results from blue bronze, a quasi-one-dimensional material, yield favourable agreement. We can also extend our treatment of χ near T_c to higher dimensions; here we consider a model cylindrical Fermi surface, and must be careful about structure factor normalisation. Good agreement with experiment is found for $K_3Cu_8S_6$ (2D) [1] and CuV_2S_4 (3D) [32]. In the last section we treat the quasi-one-dimensional system with impurities; now long-range order is destroyed, though local lattice distortions may still be present depending on the impurity strength and potential. Because $d\chi/dT$ is proportional to the lattice specific heat it cannot show discontinuous behaviour in the absence of a phase transition; this is in agreement with experimental observation. It is important to note that all theoretical input parameters are in good agreement with physical values. 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 this theory.

Naturally there remain many open questions. Future projects include a study of resistivity near the Peierls transition where back-scattering effects cannot be neglected, e.g. [43]. Though the present theory does extend to several higher-dimensional compounds the dichalcogenide 2H-$TaSe_2$ certainly provides a mystery; its susceptibility has a discontinuity near T_c [5], and thus does not have an energy-like appearance. Rice and Scott [44] have suggested that saddle points in the band structure may be responsible for this anomalous behaviour near the transition. Features of such a star-shaped Fermi surface have certainly not been included in our simple cylindrical model. It has also been argued that strong electron–ion coupling effects might lead to such discontinuities in χ [8, 45]; then the electrons could be 'trapped' in the ionic fluctuations and electron–electron interactions could not be neglected. χ for 2H-$TaSe_2$ bears a striking ressemblance to that of TTF $CuS_4C_4(CF_3)_4$ a known spin–Peierls system, e.g. [46], and this comparison should be pursued. Finally, it would also be interesting to investigate the dynamics of these Peierls systems a little bit further from the transition, and in particular to learn about how the quasi-static fluctuations become phonons at higher temperatures.

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