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Fluctuations and Thermodynamics of the Charge-Density-Wave Phase Transition

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We present results on the resistivity ρ, specific heat C_p, and susceptibility χ of $K_{0.3}MoO_3$ near the Peierls transition T_p at 180 K. Our resistivity measurements demonstrate that fluctuations intrinsic to the material persist over a temperature interval that is at least 30 K wide. Associated with the large fluctuations is an enhanced specific-heat anomaly that we analyze in terms of the short coherence lengths characteristic of many Peierls systems. We find a scaling relation between the spin susceptibility and the specific heat that covers the intrinsic fluctuation regime.

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In spite of continued interest in various aspects of the collective mode called the charge-density wave[1] (CDW), some fundamental aspects of the phase transition have not been clarified in model compounds such as the trichalcogenides $NbSe_3$ and TaS_3, or the potassium blue bronze $K_{0.3}MoO_3$. Many investigations of macroscopic properties[2] have revealed substantial differences between compounds as to the importance of fluctuations to the phase transition. Although these differences are thought to be quantitative only, the effect of fluctuations associated with the Peierls transition on various physical properties, and how they are related, is not well established. The issue is further complicated by a smearing of the phase transition by impurities, thus destroying the divergences that are expected from fluctuations.

Here we present a study of the resistivity ρ, specific heat C_p, and magnetic susceptibility χ of the model CDW system $K_{0.3}MoO_3$ near the Peierls transition $T_p = 180$ K, undertaken to gain a more complete understanding of the relationship between thermodynamic properties in a system that has such pronounced effects from fluctuations. We first show that the broadening of the transition (which contrasted with the mean-field theory) is not due to impurities, but is the result of intrinsic fluctuations. We also find that the entropy associated with the specific-heat anomaly is much larger than what is predicted using the mean-field theory to describe the transition. The enhancement is a result of a large contribution from the lattice degrees of freedom associated with the Kohn anomaly in the phonon spectrum. Further, it is observed that the derivative of the spin susceptibility $d(\chi T)/dT$ is proportional to the specific heat C_p, thus confirming recent theoretical predictions that they are equivalent thermodynamic measurements.[3] The scaling relation between $d\chi/dT$ and the electronic contribution to C_p in Peierls systems was first conjectured, for reasons similar to that for antiferromagnets,[4] by Horn, Herman, and Salamon[5] who observed that $d\chi/dT \sim |T - T_p|^{-1/2}$ at the 53-K transition in tetrathiafulvalene tetracyanoquinodimethane (TTF-TCNQ). Here, however, the fluctuation component of C_p is enhanced because of short coherence lengths and electron-phonon coupling. The results give direct experimental evidence from macroscopic thermodynamic quantities that the spin entropy scales with the lattice entropy. As far as we know, it is the first observation and direct comparison of this type of scaling at a Peierls transition.

The samples were prepared by the standard electrolytic method at both UCLA and Los Alamos, using 99% pure K_2MoO_4 and high-purity MoO_3 from Cerac Chemical Company. The largest single crystals were used for the specific-heat and magnetic studies, while samples of various sizes were used for the resistivity measurements.

The resistivity study was performed to establish the range of temperature over which the behavior can be regarded as intrinsic, i.e., dominated by fluctuations and not due to impurity-induced smearing of the phase transition. Standard four-wire measurements were made on three samples from two different batches. In Fig. 1, we show $d(\ln\rho)/dT$ vs T near the phase transition. A peak in the derivative of the resistance is identified as the critical point[6] by analogy to continuous antiferromagnetic transitions.[7] Large temperature dependences of $d\rho/dT$ are observed for all of the samples, and except to within a few degrees kelvin of T_p, appear identical. Very close to the transition there appears to be some sample-dependent broadening, which we believe is a result of varying impurity levels in the samples. The two types of behavior can therefore be described as "intrinsic" (where every sample gives the same results) and "extrinsic" (where the samples are different).[8] The fact that the intrinsic fluctuation regime is so large, at least 30 K wide, is important for the analysis of the thermodynamic quantities, C_p and χ.

The heat capacity was determined by[9] first measuring the thermal conductivity κ, followed by the thermal

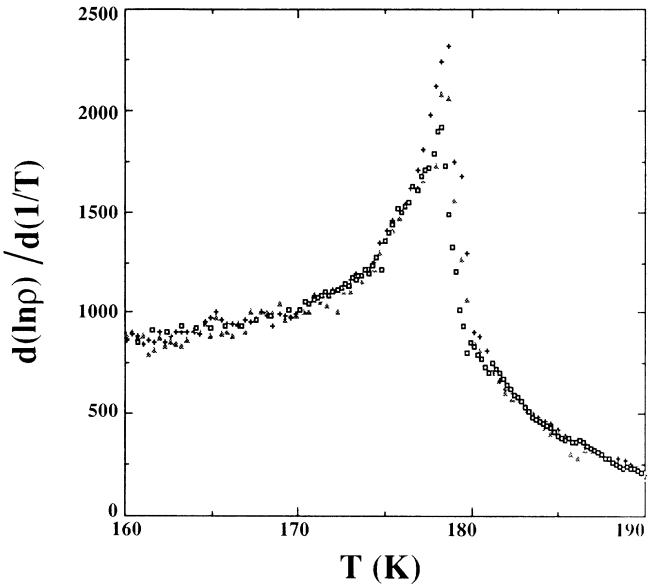

FIG. 1. Derivative of $\ln\rho$ with respect to $1/T$ in arbitrary units. The three different symbols denote measurements of three different samples.

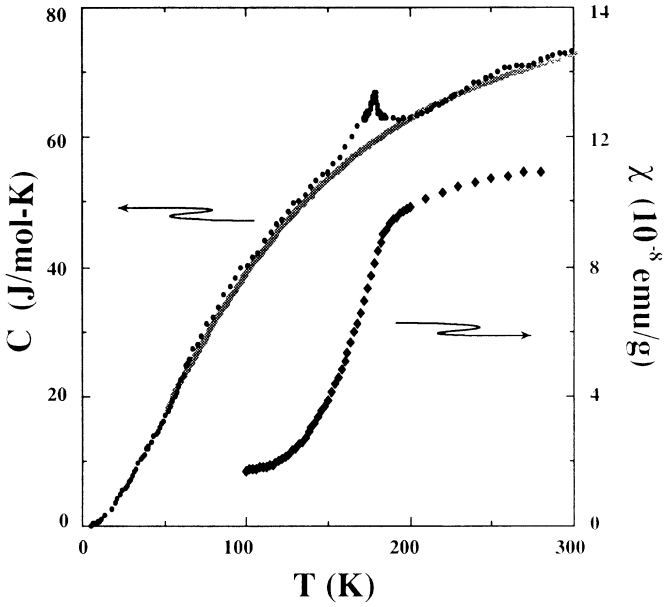

FIG. 2. Temperature dependence of the specific heat and magnetic susceptibility. The solid line is a polynomial fit through the background of the specific data as discussed in text.

diffusivity D. The specific heat is proportional to κ/D. The sample is chosen so that the aspect ratio is large, with the long axis coinciding with the chain direction. It is thermally anchored to a heat reservoir at one end with a resistive wire heater wound around the other. A temperature-controlled radiation shield of the appropriate geometry surrounds the sample, as described elsewhere.[10] A heater at the end of the sample is switched off and on repeatedly at a rate that is comparable to D. After averaging many cycles, the temperature versus time profile was fitted by an appropriate numerical model of the one-dimensional heat diffusion equation. The susceptibility was measured in a Quantum Design SQUID magnetometer at a field of 50 kG.

Results for C_p measured over the range 4–300 K are shown in Fig. 2. At low temperatures, C_p varies as T^3 as reported previously.[11] It continues to increase in a Debye-like fashion, but with several notable features. First, there is an anomaly associated with T_p that is large, considering that the CDW state is described in mean-field theory to be an electronically driven phase transition. Rather than appearing to asymptotically approach the Dulong-Petit limit, the data seem to be leveling off at about $2R$, where R is the gas constant. The observation is common to compounds comprised of MoO_6 octahedra[12] (such as Mo_4O_{11} or other molybdenum bronzes), and must indicate the presence of high-energy phonon modes.

A major difficulty in analyzing specific-heat features at high temperatures is the substantial contribution from background thermal excitations that must be subtracted from the total. We have adopted a procedure for accomplishing the subtraction that we believe is reasonable for this case, and most of the conclusions that we draw do not depend on the details. First, a polynomial fit to the background (shown as the solid line in Fig. 2) was made by forcing the error to be small at temperatures far from T_p. The subtraction of the fit from the measurement gives a crude estimate of the excess specific heat ΔC_p associated with CDW formation. The entropy is obtained by integrating $\Delta C_p/T$ over temperature, resulting in 1.5 J/(mol Mo) K.

To see the significance of the large entropy, it is necessary to calculate the expected electronic contribution $\gamma_0 T_p$, where γ_0 is the standard electronic specific-heat coefficient $(\pi^2/3)k_B^2 D(\epsilon_F)$, which can be evaluated[13] from the spin susceptibility χ shown in Fig. 2. The slow decrease in χ from room temperature has been attributed to fluctuations. At T_p, there is a sharp increase in the slope. The change in χ over the whole temperature range reflects the opening of a gap at the Fermi level, so that the Pauli spin contribution vanishes at low temperatures. Johnston[13] found that the change over the whole temperature range gave $D(\epsilon_F) \simeq 1$ state/eV (formula unit), which leads to $\gamma_0 T_p \simeq 0.3$ J/mol K for the electronic contribution to the entropy, significantly smaller than the value estimated above.

This discrepancy can be understood qualitatively by including some contribution from the lattice, as suggested by McMillan.[14] In his description of the CDW phase transition, the lattice plays a crucial role in the thermodynamics in systems where the correlation lengths are

short. In reciprocal space, it is equivalent to a substantial number of phonon modes being involved in the transition. A surprising conclusion arrived at by McMillan was that in the limit of very short length scales, the phonon entropy, because of the large number of modes, would actually dominate over the contribution from single-electron excitations across the gap. To support the case for significant phonon entropy in the blue bronze, we first note that the affected modes will occupy a volume in reciprocal space $\delta k^3 \sim (1/\xi)^3$, where ξ is the correlation length. At zero temperature, we get $\xi_0 \sim v_F/2\Delta(0)$, where $2\Delta(0) \simeq 1200$ K is the energy gap[13] at $T=0$ K and $v_F \sim 2\epsilon_F/k_F$ is the Fermi velocity. From the quoted values,[15] we get $\epsilon_F \simeq 0.7$ eV, $k_F \simeq 0.35$ Å^{-1}, and $\xi_0 \simeq 40$ Å; therefore δk^3 covers approximately $\frac{1}{50}$ of the Brillouin-zone volume. The small value for ξ_0 is also consistent with the hypothesis that the specific-heat behavior in the neighborhood of T_p cannot be interpreted as a jump or a smeared-out jump.

A consistency check for our results can be made by estimating the phonon contribution S_{ph} as[16]

$$S_{ph} \sim N_{ph} k_B (T_{mf} - T_p)/T_{mf}, \quad (1)$$

where N_{ph} is the number of degrees of freedom in the soft mode multiplied by the appropriate Bose factor near the transition temperature, k_B is Boltzmann's constant, and T_{mf} is the mean-field transition temperature. Equation (1) reflects the increase in phonon entropy when more modes are involved. If $T_p = T_{mf}$, then only one mode at $q = 2k_F$ can participate, and $S_{ph} = 0$. When $T_p = 0$, all of the states in the soft mode are important (the coherence length goes to zero). Optical measurements of the gap,[17] resistivity measurements,[18] and structural studies[19] all indicate that $T_{mf} \simeq 320$ K. Using the phonon energy $\omega_0 \sim 2\pi \times 10^{12}$ s^{-1} from neutron-scattering studies,[19] we obtain approximately 3.3 for the Bose factor at 180 K. This gives $S_{ph} \simeq 1.2$ J/mol K, in good agreement with our measurement (total entropy 1.5 J/mol K).

Chandra[3] extended Fisher's theory[4] with a charge-conservation argument and concluded that the ionic fluctuations, which are responsible for ΔC_p, also lead to variations in $D(\epsilon_F)$ and therefore are reflected in the spin susceptibility. In particular, $d\chi/dT$ will be proportional to the lattice specific heat close to T_p, in analogy to similar results described by Fisher for antiferromagnetic transitions. The magnetic system is somewhat simpler because the same degrees of freedom are important for both the specific heat and the susceptibility, namely, the spin entropy. In the case of blue bronze, the specific heat is significantly enhanced by the lattice contribution, while χ is solely related to the electronic density of states. We have found that the expression $d(\chi T)/dT$ compares favorably to C_p over a broad range of temperatures where fluctuations contribute significantly to C_p, as shown in Fig. 3. The values for $d(\chi T)/dT$ are plotted in arbitrary units, but there is no adjustable parameter or

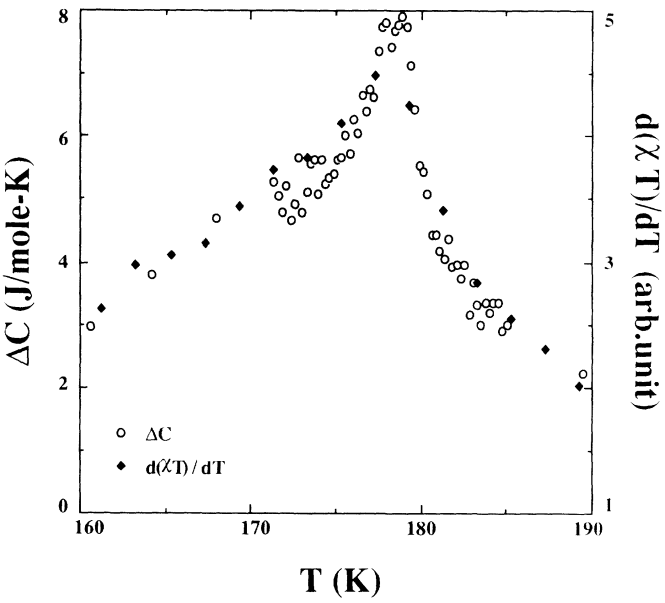

FIG. 3. The excess specific heat (open circles) and $d(\chi T)/dT$ (solid diamonds) near the Peierls transition.

background subtracted as there is for C_p. It is possible that the experimentally determined fit is not in conflict with the theoretical prediction because the theoretical work covers temperatures close to T_p. However, the comparison made here extends over a wide range of temperatures. Also, Fisher[4] found that a similar expression for antiferromagnets was more appropriate. Of more consequence is the unfortunate, yet unavoidable, subtraction of the background specific heat from the total. Nevertheless, our choice of the best fit to find the excess specific heat ΔC_p matches $d(\chi T)/dT$ extremely well.

Chandra's theory is based on the three-dimensional (3D) Gaussian fluctuations close to the 3D ordering temperature T_p. Therefore, the scaling relation $d\chi/dT \sim \Delta C_p$ is expected to be valid over the same temperature regime where fluctuations of the order parameter can be treated by the Gaussian approximation. We use the Ginzburg criterion[20] to estimate the width of the critical region $\zeta_T T_p$ in which fluctuations are so large that the Gaussian approximation would break down. Near the 3D ordering temperature T_p, ζ_T is related to the Landau correlation length ξ_0 by[21]

$$\zeta_T = [(2\pi\xi_0)^3 \Delta C/k_B]^{-2}, \quad (2)$$

where $\Delta C = 1.43\gamma_0 T_p \simeq 0.4$ J/mol K is the mean-field specific-heat jump. Substituting $2\pi\xi_0 \simeq 40$ Å into Eq. (2) gives $\zeta_T T_p \sim 0.1$ K. Taken literally, the criterion implies that the region within 0.1 K of T_p may be critical but outside of that Gaussian fluctuations should dominate. However, recent x-ray studies[19] suggested that the critical fluctuations extend to ~ 20 K beyond T_p. It is possible that the Ginzburg criterion in its usual form is

not adequate for the Peierls transition because of the large effects from the lattice degrees of freedom. We are presently working to improve our resolution so that details of the fluctuations can be examined more closely.

In conclusion, we have investigated transport and thermodynamic properties of the charge-density-wave system $K_{0.3}MoO_3$ around the transition temperature T_p. Our resistivity measurements demonstrated that scattering of single electrons from intrinsic fluctuations dominates the temperature dependence over a wide temperature interval around T_p, and impurity effects are negligible except in the close vicinity of T_p. In this intrinsic regime, a specific-heat anomaly significantly larger than the mean-field prediction is observed, and we interpret it as a consequence of short coherence lengths. We have also shown that the thermodynamic quantities $d(\chi T)/dT$ and C_p have the same temperature dependence. The particular form of the scaling relation is modified from the one proposed by Chandra,[3] although there is no significant distinction between them for temperatures close to T_p.

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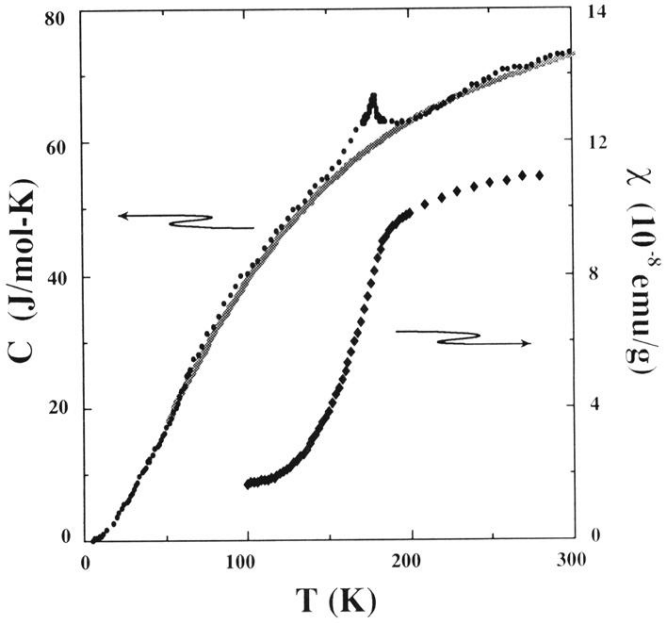

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