Comment on "Fluctuations and Thermodynamics of the Charge-Density-Wave Phase Transition"

In their recent analysis of the specific heat near the Peierls transition T_P in $K_{0.3}MoO_3$, Kwok, Grüner, and Brown[1] calculated the width of the critical region to be $\Delta T = \zeta_T T_P \approx 0.1$ K. As they pointed out, their result is much smaller than the experimental value $\Delta T \approx 10$ K obtained from x-ray measurements of the order parameter, susceptibility, and correlation length.[2] This Comment demonstrates that the latter, larger value not only is consistent with the specific heat but also can be deduced directly from a reanalysis of their measurements.

In the regime of three-dimensional Gaussian fluctuations $|T-T_P| > \Delta T$, C_P may be represented by

$$C_P(T) = \sum_{n=0} a_n T^n + GF(T)(T-T_P)^{-1/2} + HS(T).$$

For $T > T_P$, $F=1$ and $S=0$; for $T < T_P$, $F=\sqrt{2}$ and $S=T$. The polynomial represents a smooth background variation, G is the strength of the Gaussian term, and HT_P is the magnitude of the mean-field step. Treating a_n ($n=0$–3), G, and H as adjustable parameters, this form was fitted to data (digitized from their Fig. 2) by minimizing σ^2, the mean-square deviation per degree of freedom. The fit excluded points for which $|T-T_P| < T^*$ and was repeated for various values of T^*. The minimized σ^2 is essentially constant for $T^* > 8$ K (Fig. 1), but for smaller T^*, σ^2 increases rapidly, indicating failure of the Gaussian approximation. Correspondingly, G attains a fairly well-defined value for 16 K $> T^* >$ 8 K, but G decreases rapidly for $T^* < 8$ K because the data no longer diverge as fast as the Gaussian prediction. Therefore I experimentally identify the width of the critical region to be $\Delta T = 8$ K. This wide critical region is in good agreement with thermal-expansion[3] as well as x-ray investigations.[2]

The estimate of ΔT deduced by Kwok, Grüner, and Brown (and an even smaller estimate by Chandra[4]) fails for a simple reason: The correlation length and specific-heat step which they used are appropriate only for the hypothetical phase transition of one-dimensional chains strongly coupled together. T_P, ΔC_P, and other nonuniversal properties of the real, three-dimensional transition can be derived only from a more complicated theory containing realistic interchain-coupling parameters which are not fully known. Yet the real correlation lengths and real specific-heat step are known, and the critical region estimated from them by Aronovitz, Goldbart, and Mozurkewich[5] agrees with the experiments.

The base line extracted from the present fit is substantially lower than that used by Kwok, Grüner, and Brown.

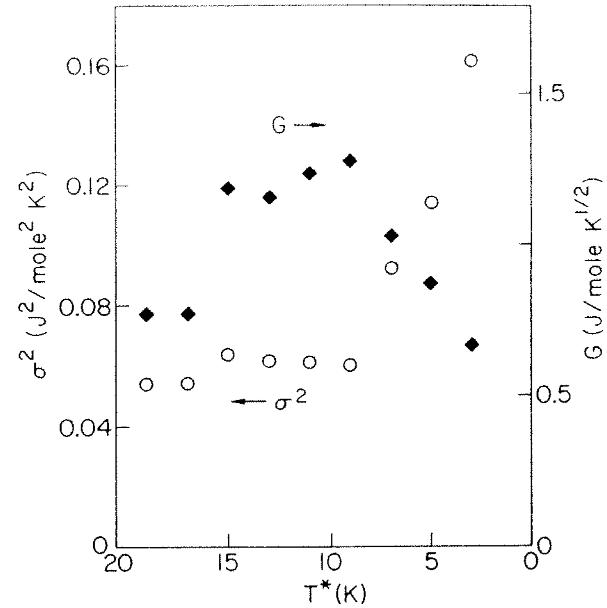

FIG. 1. Mean-square deviation σ^2 (circles, left scale) and coefficient G (diamonds, right scale) vs width T^* of the excluded temperature range.

Consequently, the entropy change is even larger than the value they quoted. Furthermore, their Fig. 3 demonstrates that the scaling between C_P and the susceptibility derivative $d\chi/dT$, which had been derived only within the regime of Gaussian fluctuations,[4] continues to hold far into the critical region. Finally, given the magnitude of ΔT, one expects no divergence in either C_P or $d\chi/dT$, even in the absence of impurity effects.

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[1]R. S. Kwok, G. Grüner, and S. E. Brown, Phys. Rev. Lett. **65**, 365 (1990).

[2]S. Girault, A. H. Moudden, and J. P. Pouget, Phys. Rev. B **39**, 4430 (1989).

[3]M. R. Hauser, B. B. Plapp, and G. Mozurkewich, Phys. Rev. B (to be published).

[4]P. Chandra, J. Phys. Condens. Matter **1**, 3709 (1989); **1**, 10067 (1989).

[5]J. A. Aronovitz, P. Goldbart, and G. Mozurkewich, Phys. Rev. Lett. **64**, 2799 (1990).

Kwok, Grüner, and Brown Reply: Mozurkewich[1] is correct when he points out that our specific-heat[2] data are not consistent with fluctuations in the Gaussian approximation. There are several reasons why we did not elaborate on this in our Letter. Most importantly, we did not believe that a specific analysis of our data would result in an unambiguous interpretation, as we will discuss below. In addition, the main point of the paper was to identify a scaling between the magnetic susceptibility χ and the specific heat c in the fluctuation regime of a Peierls transition. The calculations by Chandra,[3] which predicted the relation $d\chi/dT \sim c$, are indeed limited to the region where the Gaussian approximation is appropriate. Although detailed calculations have not been performed beyond this approximation, it was argued that the relation between the specific heat and magnetic susceptibility has a more general validity. This conjecture is supported by our results.

From the experimental side, we preferred to emphasize the scaling between the susceptibility and specific heat, rather than the issue of critical behavior. The classic experimental studies demonstrating critical behavior and the evaluation of exponents relied on one or more thermodynamic quantities obeying a power law over decades of reduced temperature.[4] Aronovitz, Goldbart, and Mozurkewich[5] recently pointed out that a correction to scaling

$$c(\tau) \sim c_{\pm}|\tau|^{-\alpha}(1+\tilde{c}_{\pm}|\tau|^{\nu\omega}) \tag{1}$$

is likely to apply to the singular part of the specific heat for the avilable experimental data. Indeed, our experimental results for $c(\tau)$ can be described by Eq. (1). However, we feel that a detailed fit of our data should not be used to determine the relativistic importance of the correction term. The reason for this is that the available data are quite restrictive from a purely numerical perspective. We showed in Ref. 2 that the intrinsic behavior in our samples is suppressed for temperatures within approximately 1 K of T_P. Assuming the width of critical behavior is 10 K, there is on the order of 1 decade, perhaps less, in reduced temperature where critical fluctuations become dominant and Eq. (1) can be fitted.

We do not mean to suggest that the relatively narrow range of temperatures from which critical exponents can be extracted from the data makes it impossible to identify critical behavior. We agree that our data can interpreted consistently in that way, and there is no doubt that the level of confidence in such an interpretation would be increased substantially with more independently measured parameters, such as the coefficients of thermal expansion.[6]

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[1]George Mozurkewich, preceding Comment, Phys. Rev. Lett. **66**, 1645 (1991).

[2]R. S. Kwok, G. Grüner, and S. E. Brown, Phys. Rev. Lett. **65**, 365 (1990).

[3]P. Chandra, J. Phys. Condens. Matter **1**, 3909 (1989); **1**, 10067 (1989).

[4]See, for example, G. Ahlers, Rev. Mod. Phys. **52**, 489 (1980).

[5]J. A. Aronovitz, P. Goldbart, and G. Mozurkewich, Phys. Rev. Lett. **64**, 2799 (1990).

[6]M. R. Hauser, B. B. Plapp, and G. Mozurkewich, Phys. Rev. B (to be published).