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Specific heat of α'-NaV$_2$O$_5$ at its spin-Peierls transition

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We have measured the specific heats of small ($\approx$1 mg) crystalline flakes of α'-NaV$_2$O$_5$. A large sharp peak is observed at its (33 K) spin-Peierls transition. The size of the peak ($\Delta c_P \approx R$) is more than an order of magnitude greater than the value estimated from mean-field theory, consistent with large fluctuations expected from its one-dimensional magnetic structure. However, the peak is somewhat sample dependent and does not have the symmetry about T_c expected for either Gaussian or critical fluctuations, suggesting either that the samples are near a multicritical point or that there is some heterogeneous broadening, in which case we are underestimating the true size of the anomaly. The low-temperature behavior is consistent with a Debye temperature between 345 and 414 K, depending on the size of magnetic contributions to the specific heat. [S0163-1829(98)50330-X]

Because of quantum spin fluctuations, a crystal containing isolated chains of antiferromagnetically coupled ($S=\frac{1}{2}$) spins, with spin Hamiltonian $H_{\text{spin}}=J\Sigma \mathbf{S}_i \cdot \mathbf{S}_{i+1} (J>0)$, cannot magnetically order. Coupling to phonons, however, allows the spins to form singlets by dimerizing along the chains, resulting in a nonmagnetic ground state. While such ''spin-Peierls'' transitions have been of continuing interest for over two decades, all known spin-Peierls materials prior to 1993 were quasi-one-dimensional organic materials, and because of difficult sample morphologies and reactivities, experimental investigations were limited.[1]

Therefore, the discovery in 1993 of a $T_c=14$ K spin-Peierls transition in CuGeO$_3$,[2] of which large, robust crystals could be prepared, led to a huge number of measurements over the past five years.[3] A number of properties of CuGeO$_3$ which differed from theoretical expectations for the spin-Peierls state have been attributed to the existence of substantial interchain[3,4] and next-nearest-neighbor[5,6] spin interactions. Indeed, the measured spin excitation gap[4] $E_{\text{gap}}/k_{\text{B}} = 24\text{ K} \approx 1.76\, T_c$ (*its mean-field value*),[1] and the specific heat anomaly at T_c is also very close to mean field in magnitude,[7,8] suggesting that interchain interactions are sufficient to suppress the expected large one-dimensional fluctuations.

In 1996, Isobe and Ueda reported that α'-NaV$_2$O$_5$ also has magnetic behavior consistent with a spin-Peierls transition.[9] Above $T_c \approx 34$ K, the magnetic susceptibility is well described by the Bonner-Fisher behavior[10] characteristic of chains of antiferromagnetically coupled spins, with nearest-neighbor exchange interaction $J/k_{\text{B}}=560$ K and *negligible* interchain interactions.[6,9,11] The susceptibility drops rapidly at T_c, although there remains a significant Van Vleck contribution at low temperature.[9,11] The low-temperature spin excitation gap has been measured with inelastic neutron scattering;[12] $E_{\text{gap}}/k_{\text{B}}=114\text{ K}=3.4\, T_c$, i.e., twice the mean-field value, so that fluctuation effects will presumably be much larger than in CuGeO$_3$.

In this paper we report on the specific heat of several crystalline samples of α'-NaV$_2$O$_5$. We observe large peaks, more than an order of magnitude larger than a mean-field estimate, at T_c. In fact, the observed sample dependence of the low-temperature specific heat may indicate that our observed anomalies are heterogeneously broadened, so the intrinsic anomalies may be even sharper and larger.

α'-NaV$_2$O$_5$ has an orthorhombic unit cell.[13] The structure consists of pairs of edge-sharing chains of VO$_5$ pyramids, running along **b**, separated by chains of sodium ions. Initially, it was thought that the sizes of the two edge-sharing pyramids differed,[13] so that one chain contained ($S=0$)V^{5+} ions and the other ($S=\frac{1}{2}$)V^{4+} ions, thus giving one spin per formula unit.[9] More recent structural determinations suggest that the two chains may be identical,[14] so that all vanadium ions have a formal valence of +4.5. The single spin would then be delocalized along V-O-V rungs of ladders, running along **b** (again giving one spin per formula unit).[14]

The samples of α'-NaV$_2$O$_5$ used in our study were synthesized as follows. NaVO$_3$ was first prepared by heating a stoichiometric mixture of Na$_2$CO$_3$ (99.997% Alfa) and V$_2$O$_5$ (99.995% Alfa) at 580 °C for 48 h in air. A stoichiometric mixture of Na$_2$VO$_3$, V (99.5% Alfa), and V$_2$O$_5$ was pressed into a pellet and heated at 640 °C in an evacuated quartz tube for 48 h. This yielded a coarse powder (typical crystalline mass $\leqslant$1 μg) of α'-NaV$_2$O$_5$. Larger, flake-shaped samples ($\approx$1 mg, with a typical thickness of 50 μm), that appeared to consist of several intergrown crystals, were prepared by mixing this powder with NaVO$_3$ flux (in 1:4 mass ratio) and placing it in an alumina crucible, which was sealed in an evacuated quartz tube and heated at 750 °C for 2 h, then cooled to 700 °C at a rate of 5 °C/h, cooled at 1 °C/h to 580 °C and 10 °C/h to room temperature.

Both the original powder and the products of the flux growth were characterized by powder x-ray diffraction and temperature-dependent magnetic susceptibility. The diffraction patterns of both agree well with the published results,[13]

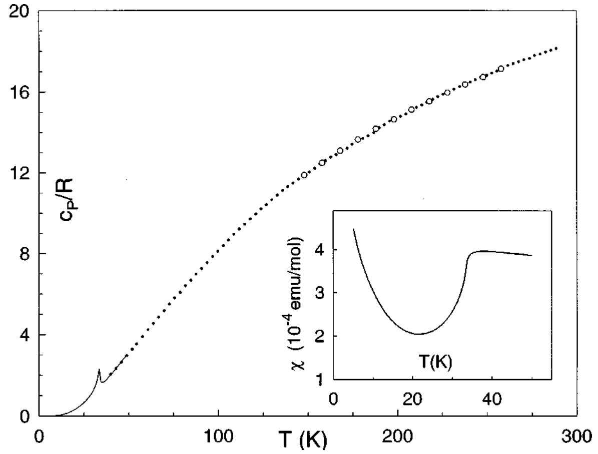

FIG. 1. Specific heat vs temperature of α'-NaV_2O_5 measured by differential scanning calorimetry (open circles) and ac calorimetry (solid curve: sample #1; dotted curve: sample #2), spanning the temperature range $13\,K < T < 300\,K$. Inset: Temperature dependence of magnetic susceptibility of a collection of randomly oriented flux-grown samples (total mass=21 mg, field=1 T).

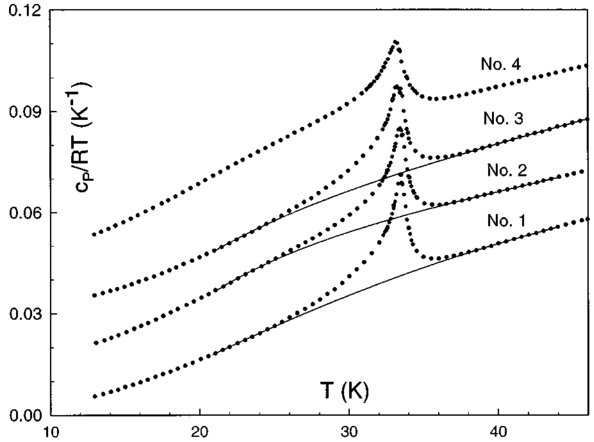

FIG. 2. Low-temperature specific heat, plotted as c_P/RT, vs temperature for four samples of α'-NaV_2O_5 measured by ac calorimetry; for clarity, successive curves are vertically offset by $0.015\,K^{-1}$ and less than half the data points for each sample are plotted. The solid curves for sample Nos. 1–3 are the polynomial backgrounds used to analyze critical behavior in Fig. 4.

with no indication of the presence of other polytypes or materials. The magnetic susceptibility of the powder is similar to that of slightly sodium deficient material ($Na_yV_2O_5$, with $0.98 < y < 0.99$);[11] i.e., the susceptibility above T_c is ≈10% larger than that for $y = 1.00$ material, the Curie tail is consistent with a defect spin concentration ≈1%, and the transition is broad and suppressed (T_c varying between 26 and 30 K for different sample growths). For the flux-grown samples, while the magnetic susceptibility, shown in the inset to Fig. 1, indicates a sharp transition at 33.4 K, consistent with $y \approx 1.00$, the Curie tail still suggests a defect concentration of ≈1%, and $\chi(T > T_c)$ is 16% larger than the Isobe and Ueda value,[11] indicating the extreme sensitivity of the susceptibility to defects.

The heat capacity was measured for four flux-grown samples, with masses varying from 0.5 to 1.3 mg and thicknesses varying from 40 to 100 μm, using ac calorimetry.[7,15] The sample was heated with light chopped at a frequency ω, and the oscillating temperature $\Delta T(\omega)$ was measured with a fine thermocouple glued to the sample. For $\tau_2 \ll 1/\omega \ll \tau_1$, where τ_1 and τ_2 are the external and internal thermal time constants of the sample, $\Delta T(\omega) \propto 1/C$, the total heat capacity of the sample and its (known) addenda. The low-temperature heat capacities of all four samples were too small to take quantitative data below 13 K with this technique.

Since the optical power absorbed by the samples is constant but not determined, the absolute value of the specific heat (c_P) was determined by normalizing[15] the data of sample No. 2, which had the best high temperature time constants, to the specific heat of a pellet (prepared from the coarse powder), which was measured with differential scanning calorimetry (with an accuracy of ≈2%).[16] The agreement between the ac calorimetry and differential scanning calorimetry results are shown in Fig. 1, in which we plot c_P/R, where R=gas constant$=8.314\,J\,K^{-1}$/mol (formula unit). The specific heat of the other three samples were normalized to that of No. 2 at 50 K, also as indicated in Fig. 1 for sample No. 1.

The low-temperature specific heats of all four samples, plotted as c_P/RT vs T, are shown in Fig. 2. The specific heats of all samples are similar above T_c, and all exhibit well-defined peaks at temperatures varying between 33.1 and 33.4 K. As shown below (see Fig. 4), the peaks for samples 1, 2, and 3 are very similar, especially on their low-temperature sides, but the peak for No. 4 is significantly broadened. Below T_c, the measured specific heats of all four samples differ; while sample No. 1 has $c_P \sim T^3$ below 30 K, the other three samples exhibit a broad hump in c_P/T near 25 K. While the significance of this hump is not understood, we note that its associated entropy is quite large; for example, the difference in the molar entropies of samples No. 4 and No. 1, given by $\int^{30\,K}[c_P(4) - c_p(1)]dT/T \approx 0.2R$, comparable to the entropy in the peak at the transition, so it is unlikely that these humps are simply due to entropy being shifted from the peak to lower temperature due to sample inhomogeneity.

Because it has the smallest low-temperature specific heat, as well as time constants most strongly in the $\tau_2 \ll 1/\omega \ll \tau_1$, limits, we chose to analyze the results for sample No. 1. In Fig. 3, we compared its molar specific heat with that of $CuGeO_3$;[7] the specific heat is plotted as c_P/RT vs T^2, with both axes scaled by T_c to facilitate direct comparison. While there are qualitative similarities, there are important quantitative differences. The peak (Δc_P) at the transition is much sharper and more symmetric in α'-NaV_2O_5, whereas the peak in $CuGeO_3$ is more ''mean field'' in shape. In the mean-field theory for a spin-Peierls transition with *only* an intrachain, nearest-neighbor exchange interaction J, $\Delta c_P(MF)/R = 0.92\,k_BT_c/J$.[1] While this expression cannot be directly applied to $CuGeO_3$, due to the non-negligible interchain and next-nearest-neighbor interactions, from the peak in the susceptibility one would estimate an effective $J_{\mathrm{eff}}/k_B \approx 88$ K,[2] so $\Delta c_P(MF)/R \approx 0.15$, close to the average of the values observed by several investigators,[8] $\Delta c_P(\mathrm{ave})/R = 0.21 \pm 0.10$. That the transition in $CuGeO_3$ is mean field is consistent with the measured gap value,[4] mentioned above. Similarly, the specific heat anomalies in organic spin-Peierls materials are also quite close to their

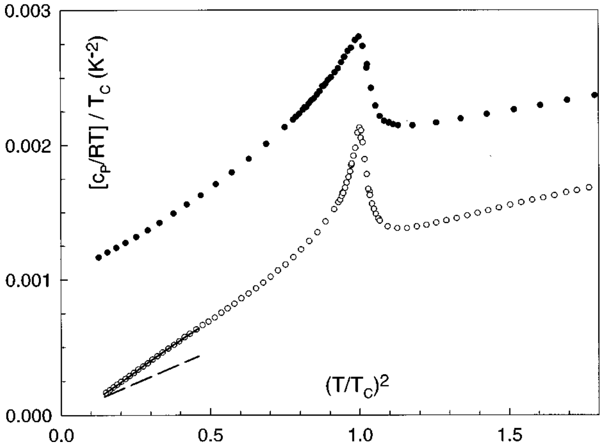

FIG. 3. Specific heats of α'-NaV$_2$O$_5$ (sample No. 1, open circles) and CuGeO$_3$ (Ref. 7, closed circles, offset by 0.001 K^{-2}), plotted as $(c_P/\mathrm{RT})/T_c$ vs $(T/T_c)^2$. (Less than half the data points are plotted for clarity.) The solid curve through the α'-NaV$_2$O$_5$ data shows the fit to Eq. (1); the dashed line shows the phonon ($\beta_1 T^3$) contribution of this fit.

mean-field estimates.[17] In contrast, the mean-field estimate of the specific heat anomaly in α'-NaV$_2$O$_5$, with[11] $J/k_B = 560$ K, is $\Delta c_P(MF)/R \approx 0.055$, while the measured anomaly is $\Delta c_P/R = 1.0$. Because of the large measured spin gap, we expected to find that $\Delta c_P > \Delta c_P(MF)$, but the order of magnitude difference in their values was very surprising. For example, in charge-density-wave Peierls transitions in quasi-one-dimensional conductors, one typically observes $\Delta c_P/\Delta c_P(MF) \approx 3$.[18] The large value of $\Delta c_P/\Delta c_P(MF)$ for α'-NaV$_2$O$_5$ suggests that critical behavior might be observed.

To investigate possible critical behavior, it is necessary to determine the baseline behavior of the specific heat. Because the transition temperature is relatively high, the baseline behavior could not be determined theoretically. Therefore, for sample Nos. 1–3, the measured specific heats away from the transition, 20.5 K$<T<$25.5 K and 38 K$<T<$44 K, were fit to third-order polynomials, shown in Fig. 2, to determine the approximate backgrounds near T_c. In Fig. 4 are plotted $\log_{10}(\Delta c_P)$ vs $\log_{10}|t|$, where $t \equiv T/T_c - 1$, $\Delta c_P \equiv c_P - c_P(\mathrm{background})$, and T_c is taken as the peak temperature. Because of the arbitrariness of the backgrounds, the plots may not be significant for small Δc_P [e.g., $\log_{10}(\Delta c_P/R) < -1.5$]. Figure 4 reveals the following:

(i) The anomalies for the three samples are remarkably alike below T_c but only qualitatively similar above T_c.

(ii) The spin-Peierls transition should belong to the three-dimensional (3D)-Ising class,[18] with critical exponent $\alpha_{\mathrm{ISING}} \approx 0.11$. From the Ginzburg criterion, the sample should be in the critical region for $|t| \ll [R/\pi \Omega_\xi \Delta c_P(MF)]^2/32$, where Ω_ξ is the coherence volume (normalized to the volume of a formula unit).[19,20] Figure 4 suggests that we may be approaching critical behavior at $|t| < 10^{-2}$, giving $\Omega_\xi > 10$. However, the lack of symmetry between positive and negative t, while much less than for CuGeO$_3$, makes interpretation in terms of critical behavior difficult.

(iii) While $\Omega_\xi > 10$ is not unreasonable, we also expect to be entering the critical region as the specific heat anomaly becomes slightly larger than its mean-field value,[19,20] e.g., $\Delta c_P/R > 0.1$. At this value, the observed slopes $\alpha(t) \equiv -d\,\log_{10}(\Delta c_P)/d\,\log_{10}|t| > 1.2 \gg \alpha_{\mathrm{ISING}}$.

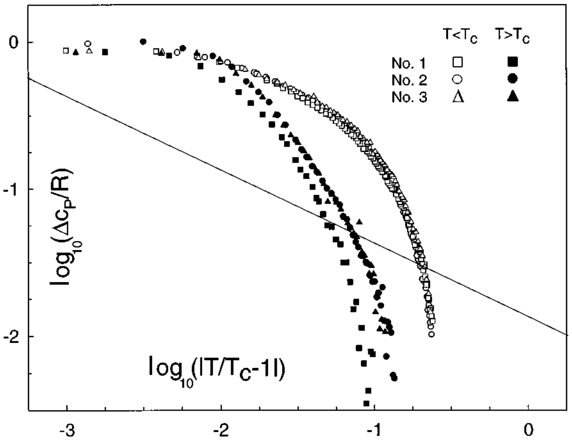

FIG. 4. Logarithmic plot of $\Delta c_P/R$ vs $|T/T_c - 1|$ for α'-NaV$_2$O$_5$ sample Nos. 1–3, where Δc_P is the measured specific heat minus the background shown in Fig. 1. (Less than half the data points are shown for clarity.) The line with slope$=-\frac{1}{2}$, appropriate for three-dimensional Gaussian fluctuations, is shown for reference.

(iv) For $0.01 < -t < 0.1$, $\alpha(t) \approx \frac{1}{2}$, suggesting that we are dominated by (3D) Gaussian fluctuations. However, in this case,[20] we also expect $\alpha(t) = \frac{1}{2}$ for $t > 0$ and $\Delta c_P(t>0)/\Delta c_P(t<0) = \sqrt{2}$, neither of which is observed.

Hence, we conclude that we are observing neither critical nor Gaussian fluctuations in our measurements. The temperature and sample dependence of α suggests that we may be near a multicritical point,[19] which may occur if states other than the spin-Peierls are favored by interchain interactions or the presence of defects. However, despite the large size of the specific heat anomaly, we also cannot rule out the possibility that the shapes of the observed anomalies are not intrinsic, but are due to sample inhomogeneities. Such is suggested not only by the sample dependence observed for $T > T_c$, but the different behaviors exhibited for $T < 30$ K. In this case, the intrinsic anomaly would be even *larger and sharper* than those we observed.

Finally, we discuss the temperature dependence of c_P for $T \ll T_c$ for sample No. 1. An upper limit to the Debye temperature can be found by assuming that in addition to the phonon T^3 term, there is a contribution from spin excitations with a *constant* gap E_{gap}:

$$c_P/R = \beta_1 T^3 + z(E_{\mathrm{gap}}/k_B T)^2 \exp(-E_{\mathrm{gap}}/k_B T). \qquad (1)$$

As shown in Fig. 3, we fit c_P for $T < 22$ K to this expression, fixing $E_{\mathrm{gap}}/k_B = 114$ K, the triplet excitation gap observed with neutron scattering,[12] and varying β_1 and z. For one triplet excitation per spin dimer, we expect $z = \frac{3}{2}$. The best fit gave $z = 0.95$ and $\beta_1 = 2.5 \times 10^{-5}$ K^{-3}, and hence a Debye temperature (per atom) of $\Theta_1 = 414$ K. However, this should be considered an upper limit to the Debye temperature, because the contribution of spin excitations to the specific heat is greatly reduced if one considers dispersion of the triplet band. One expects the width of the triplet band to be $W \approx J$; for a cosine band, the magnetic term in Eq. (1) is reduced by a factor of order $(k_B T/W)^{1/2} \approx 0.2$. Indeed, the low-temperature specific heat for sample No. 1 can be fit well by phonons alone: $c_P/R=\beta_0 T^3$, with $\beta_0=4.5\times 10^{-5}$ K^{-3}, giving a lower limit to the Debye temperature of $\Theta_0=345$ K.

In conclusion, we have measured the specific heat of a few crystalline samples of α'-NaV$_2$O$_5$. Analysis of the low-temperature specific heat indicates that $345\text{ K}<\Theta<414\text{ K}$. A surprisingly large anomaly, almost twenty times its mean-field estimate and indicating the existence of large fluctuation effects, is observed at its $T_c=33$ K spin-Peierls transition. However, we could not extract critical exponents from our data.

Note added. Implicit in our analysis of the c_P anomaly is that the transition is continuous, as theoretically expected[1] and observed[1,7,8,17] for all previous spin-Peierls transitions. Köppen *et al.*,[21] however, have recently reported thermal expansion (α) data indicating that there may be first-order character to the transition in α'-NaV$_2$O$_5$. In particular, in the sample examined, they observed two anomalies in α, separated by only 0.3 K, the upper one of which appears to involve discontinuities in lattice constants. If the presence of two transitions depends on sodium concentration, this may account for the multicritical behavior we suggest above. However, it is also possible that the large anomalies we observe are due to latent heat, spread out over a finite temperature interval due to inhomogeneities (e.g., in sodium concentration) in the samples.[15] Since the volume change reported in Ref. 21 is small ($\Delta V/V\approx 5\times 10^{-6}$, principally along **a**, i.e., the ladder-rung direction), the pressure dependence of the transition temperature, estimated from the Clausius-Clapeyron equation, would need to be small ($dT_c/dp\approx +0.1$ K/kbar) to account for all the transition entropy ($\Delta S\approx R/10$) we observe. We also note that Köppen *et al.*[21] measured the specific heat of their crystal, and observed an anomaly similar in shape to ours, although their specific heat is 20 to 60% larger than ours at all temperatures.

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[1] For a review of the spin-Peierls transition, see J. W. Bray, L. V. Interrante, I. S. Jacobs, and J. S. Bonner, in *Extended Linear Chain Compounds 3,* edited by J. S. Miller (Plenum, New York, 1982), pp. 353–415.

[2] Masashi Hase, Ichiro Terasaki, and Kunimutsu Uchinokura, Phys. Rev. Lett. **70**, 3651 (1993).

[3] J. P. Boucher and L. P. Regnault, J. Phys. I **6**, 1939 (1996).

[4] M. Nishi, O. Fujita, and J. Akimutsu, Phys. Rev. B **50**, 6508 (1994).

[5] G. Castilla, S. Chakravarty, and V. J. Emery, Phys. Rev. Lett. **75**, 1823 (1995); Jose Riera and Sergio Koval, Phys. Rev. B **53**, 770 (1996); Ralph Werner and Claudius Gros, *ibid.* **57**, 2897 (1998).

[6] Hisatoshi Yokoyama and Yasuhiro Saiga, J. Phys. Soc. Jpn. **66**, 3617 (1997).

[7] Y.-K. Kuo, E. Figueroa, and J. W. Brill, Solid State Commun. **94**, 385 (1995).

[8] J. C. Lasjaunias *et al.*, Solid State Commun. **101**, 677 (1997).

[9] Masahiko Isobe and Yutaka Ueda, J. Phys. Soc. Jpn. **65**, 1178 (1996).

[10] J. C. Bonner and M. E. Fisher, Phys. Rev. **135**, A640 (1964).

[11] Masahiko Isobe and Yutaka Ueda, J. Alloys Compd. **262–263**, 180 (1997).

[12] Yasuhiko Fujii *et al.*, J. Phys. Soc. Jpn. **66**, 326 (1997).

[13] A. Carpy *et al.*, J. Solid State Chem. **5**, 229 (1972).

[14] Holger Smolinski *et al.*, Phys. Rev. Lett. **80**, 5164 (1998); Auke Meetsma *et al.*, Acta Crystallogr. (to be published).

[15] M. Chung *et al.*, Phys. Rev. B **48**, 9256 (1993).

[16] Y. Wang, M. Chung, T. N. O'Neal, and J. W. Brill, Synth. Met. **46**, 307 (1992).

[17] T. Wei *et al.*, Solid State Commun. **21**, 595 (1977); S. Huizinga *et al.*, Phys. Rev. B **19**, 4723 (1979); W. H. Korving *et al.*, Physica B & C **145B**, 299 (1987); J. C. Bonner *et al.*, Phys. Rev. B **35**, 1791 (1987).

[18] J. W. Brill, in *Physics and Chemistry of Low-Dimensional Inorganic Conductors*, edited by Claire Schlenker *et al.* (Plenum, New York, 1996), pp. 345–355.

[19] P. M. Chaikin and T. C. Lubensky, *Principles of Condensed Matter Physics* (Cambridge University Press, Cambridge, 1995).

[20] Shang-Keng Ma, *Modern Theory of Critical Phenomena* (Benjamin/Cummings, Reading, PA, 1976).

[21] M. Köppen *et al.*, Phys. Rev. B **57**, 8466 (1998).