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ARTICLES

X-ray-diffraction study of critical phenomena at the spin-Peierls transition in $CuGeO_3$

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We have performed x-ray-diffraction measurements of the critical phenomena associated with the spin-Peierls phase transition in $CuGeO_3$. Measurements of the order parameter indicate a value of the critical exponent β of 0.345 ± 0.03 consistent with conventional three-dimensional (3D) behavior and in closest agreement with 3D XY universality, as expected on theoretical grounds. This work also indicates a rather narrow asymptotic critical region which explains much of the inconsistency reported in previous critical exponent estimates. Measurements of the relative changes in lattice constants have also been carried out to allow for detailed comparison between the spontaneous strains present below the transition temperature and the order parameter. The order parameter and lattice constant measurements were performed in identical thermal environments on the same sample to allow for direct comparison with no adjustment of transition temperature. This comparison suggests good agreement between the two except near the transition temperature where fluctuation effects are observed in the spontaneous strain which are less evident in the order parameter. [S0163-1829(98)02622-8]

I. INTRODUCTION

Quantum fluctuations in low-dimensional magnetic systems are known to result in unique and exciting phenomena. One particularly interesting effect is the spin-Peierls (SP) transition which occurs in quasi-one-dimensional $S=1/2$ Heisenberg spin chains with antiferromagnetic interactions. In the presence of strong magnetoelastic coupling, the chains are found to undergo a dimerization at low temperatures and a concomitant gap in the magnetic excitation spectrum separating a nonmagnetic singlet ground state from a triplet of excited states. The presence of this gap yields an isotropic drop in the magnetic susceptibility below the transition temperature (T_{sp}).

Experimentally realized SP systems are rare as three-dimensional (3D) magnetic interactions usually drive the system to a Néel ordered state before the magnetoelastic SP transition can occur. Previously, the only known systems to undergo such a transition were composed of large, complex organic molecules,[1] such as MEM(TCNQ)$_2$ and TTF(CuBDT), with a very low density of magnetic moment. However, interest in this phase transition has been renewed with the discovery of a structurally simple, inorganic SP system, $CuGeO_3$. It is now well established that $CuGeO_3$ undergoes a SP transition at $T_{sp}\sim 14$ K.[2–6] The isotropic magnetic-susceptibility drop and characteristic decrease in T_{sp} in the presence of a magnetic field were observed by Hase, Terasaki, and Uchinokura.[2] The gap in the excitation spectrum has been directly observed with neutron scattering[3] and the singlet-to-triplet nature of the gap has been confirmed under application of a magnetic field.[4] Finally, the dimerization has been observed using x-ray,[5] neutron,[5] and electron diffraction.[6]

$CuGeO_3$ has an orthorhombic unit cell with space group $Pbmm$ and room-temperature lattice constants of $a=4.81$ Å, $b=8.47$ Å, and $c=2.94$ Å.[7] (Recent measurements suggest a different but related crystal structure for $CuGeO_3$ with space group $P2_12_12$ and lattice constants $a=9.60$ Å, $b=8.47$ Å, and $c=11.78$ Å.[8] However for the remainder of this paper we will refer to the conventional crystal structure.) The structure consists of chains of CuO_4 octahedra stacked along the c axis which are separated from each other by chains of GeO_3 tetrahedra. The one-dimensional (1D) spin chains are formed by Cu^{2+} ions stacked along the c axis and the one-dimensionality arises from a strong superexchange interaction mediated through the O atoms. There exist, however, non-negligible interchain couplings with $J_b\sim 0.1J_c$ and $J_a\sim -0.01J_c$.[3] It has been proposed that the c-axis dimerization is out of phase between neighboring chains[9] and this, together with slight displacements of the O atoms results in a doubling of the unit cell along the a axis in addition to the expected dimerization of the spin chain. Consequently, the unit cell is doubled along both a and c and superlattice reflections of the form $(h/2,k,l/2)$ with h and l odd have been observed.

The measurements to date of the critical phenomena associated with the SP transition in $CuGeO_3$ have produced a rather murky picture with exponents spanning several universality classes. Early neutron measurements produced results consistent with tricritical behavior ($\beta\sim 0.25$),[10,11] whereas more recent neutron-diffraction studies on a crystal with a reduced T_{sp} (~ 13.26 K) have determined a value of β consistent with 3D universality (0.33 ± 0.03).[12] Thermal-expansion measurements have yielded estimates of β ranging from 0.30 to 0.35,[13,14] while ultrasonic attenuation has produced a β estimate of 0.25.[15] Specific-heat measurements have resulted in an equally unclear picture with an early measurement producing a rather large value of $\alpha\sim 0.4$,[16]

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while later measurements estimate values of α consistent with conventional 3D universality, $-0.15 \leqslant \alpha \leqslant 0.12$.[17] While no clear picture as to the true universality of the SP transition in CuGeO$_3$ has existed, one thing that is clear is that the results for CuGeO$_3$ are not the same as those for the previously studied organic SP systems where critical phenomena consistent with mean-field behavior have been observed.[18,19] The immature status of this experimental field led us to carefully examine the temperature dependence of the superlattice peak intensity using x-ray diffraction with high-temperature stability. A preliminary report of these results has been published previously.[20]

Previous neutron[21] and x-ray-diffraction[10] measurements indicated a spontaneous strain in the b-axis lattice constant which develops below T_{sp} and scales with the square of the order parameter. The x-ray-diffraction results also seemed to indicate a slight upturn in the a-axis lattice constant but the resolution was insufficient to ascertain whether this spontaneous strain also scales with the order parameter.[10] Later neutron work[22] and high-resolution capacitance dilatometry measurements[13] indicated spontaneous strains along all three crystal axes. In order to understand the relationship between the order parameter and the spontaneous strains, we have performed high-temperature stability, high-resolution x-ray-diffraction measurements of the temperature dependence of all three lattice constants. Our apparatus provides a unique opportunity to perform the spontaneous strain and order parameter measurements on the same sample in identical sample environments with identical thermometry. Both measurements can be performed with very high-temperature stability and the results can be compared directly with no compensation for temperature calibration. This should allow for detailed comparisons to be made and systematic deviations between the two quantities can be observed.

II. EXPERIMENTAL DETAILS

The single crystal used in these measurements was grown from a CuO flux by slow cooling from 1220 °C. The dimensions of the crystal were approximately $2 \times 1 \times 0.5$ mm^3 and the sample was of good quality with a mosaic spread of about 0.04° half width at half maximum (HWHM). For both the order parameter and thermal-expansion work, the sample was mounted in a Be can in the presence of a He exchange gas. This can was connected to the cold finger of a closed-cycle He refrigerator and a temperature stability of about 0.005 K was obtained over the temperature range of interest. The incident radiation was Cu $K\alpha$ radiation from an 18 kW rotating anode x-ray generator. For the order-parameter measurements, a vertically focusing PG (0,0,2) monochromator crystal was used in order to maximize the number of photons incident on the sample. For the lattice constant measurements, a flat, perfect single crystal of Ge (1,1,1) was used as the monochromator and the incident radiation consisted of Cu $K\alpha_1$ only with Cu $K\alpha_2$ being removed by distance collimation before the sample.

III. ORDER PARAMETER

A. Experimental results

The temperature dependence of the (1/2,5,1/2) superlattice Bragg peak was examined in order to measure the order parameter associated with the SP transition in CuGeO$_3$. This reflection was chosen due to its relative strength when compared to other possible reflections.[9] It is important to note that our measurements, as well as previously reported structure factor calculations,[9] indicate that this superlattice peak is reduced in intensity by a factor of $\sim 10^{-4}$ when compared to principal Bragg peaks such as (0,4,0) and, consequently, extinction effects should be negligible.

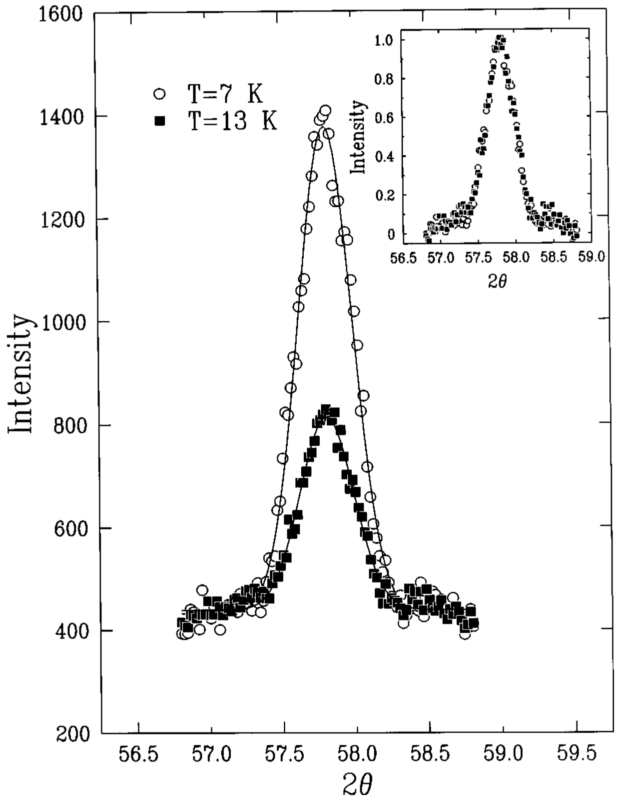

FIG. 1. Longitudinal scans through the (1/2,5,1/2) superlattice reflection at temperatures of 7 and 13 K. The solid lines represent best fits to a single Gaussian resulting in peak positions of 57.805(5) at 7 K and 57.807(5) at 13 K with corresponding widths of 0.44(1) and 0.44(1). The inset shows the two curves background subtracted and normalized to unity.

Prior to performing our measurements, the effect of spontaneous strains present below T_{sp} on the peak position and line shape of the superlattice peak were examined carefully. Both longitudinal and transverse scans through (1/2,5,1/2) were performed at temperatures near the transition and also well below the transition and the resulting longitudinal scans at 7 and 13 K are shown in Fig. 1. The solid lines represent best fits to a single Gaussian with resulting peak positions of 57.804(5) at 7 K and 57.807(5) at 13 K and corresponding widths of 0.44(1) at 7 K and 0.44(1) at 13 K. We certainly expected any changes in position or line shape which occur below the transition temperature to be negligible given the relatively low-Q resolution configuration employed in these measurements. However, to emphasize this point, the inset shows the same data background subtracted and normalized to unity. Once again, there is no noticeable change in position or line shape. Consequently, the peak intensity will be proportional to the square of the order parameter and the

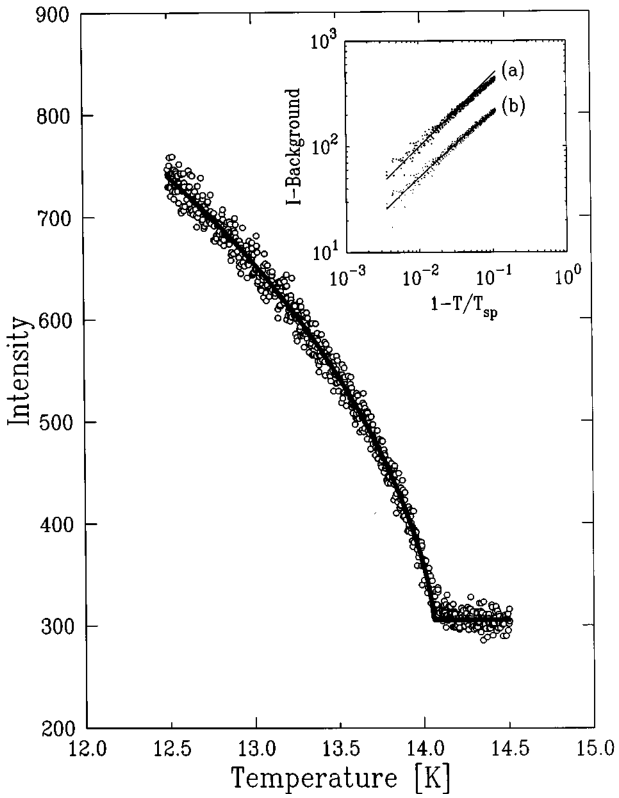

FIG. 2. X-ray-scattering peak intensity of the (1/2,5,1/2) superlattice reflection as a function of temperature. The solid line represents the best fit to a power law with the first correction-to-scaling term added [Eq. (2)]. The inset shows the same data, background subtracted, on a logarithmic scale [(a) and (b) have been displaced vertically]. The solid line in (b) represents the same fit as in the main panel, while that in (a) represents a fit of the data at small reduced temperature t to a simple power law.

observed temperature dependence of the peak intensity for the (1/2,5,1/2) reflection is shown in Fig. 2.

B. Analysis and discussion

In order to determine the critical behavior of the order parameter, the measured data was fit to a power law in the reduced temperature $t=1-T/T_{\mathrm{sp}}$:

$$\mathrm{Intensity}=I_0 t^{2\beta}+\mathrm{Background}. \qquad (1)$$

This power law is expected to be valid in the so-called asymptotic critical region, near T_{sp}, where the length scale associated with fluctuations in the order parameter dominates over all other relevant length scales in the system. As one moves below the asymptotic region in temperature, the expected power-law behavior must be modified by successive correction-to-scaling confluent singularity terms,[23] the first of which is shown in Eq. (2).

$$\mathrm{Intensity}=I_0 t^{2\beta}(1+At^{\Delta})+\mathrm{Background}, \qquad (2)$$

where the exponent Δ has an approximate value of 0.5. In fitting the data to Eq. (2), the exponent Δ was first treated as a variable parameter, but was never found to deviate from 0.5 in any significant manner. As a result, Δ was fixed at 0.5 for the remainder of the analysis.

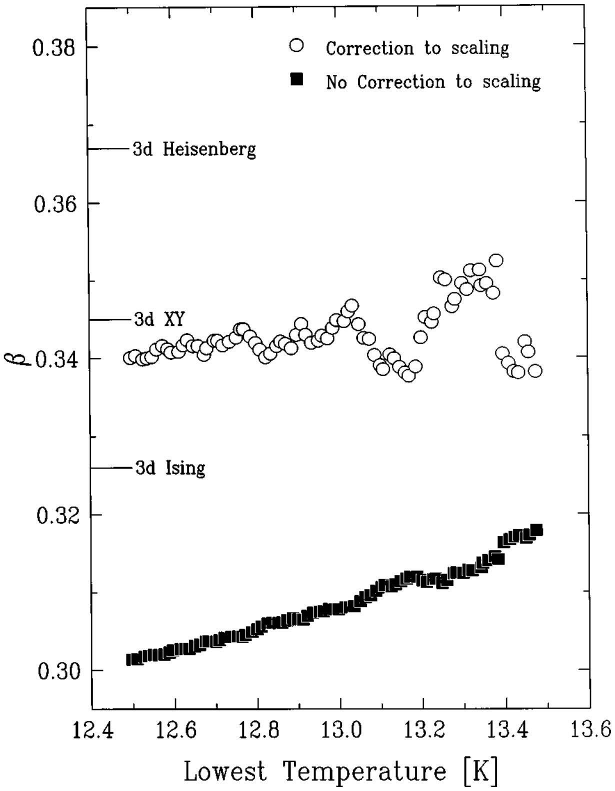

FIG. 3. The dependence of the critical exponent β on the range of data included in the fits for fits to a simple power law [Eq. (1)] and to a power law with the first correction-to-scaling term added [Eq. (2)]. All fits are performed with the same highest temperature. For reference, the predicted values of β for 3D Ising, XY, and Heisenberg universality are also included.

An important point of note is that the sign of the correction amplitude A should be negative resulting in a correction term $(1+At^{\Delta})$ which is less than unity for temperatures below T_{sp}. This point is discussed in detail in the Appendix.

The fit represented by the solid line in Fig. 2 represents the best fit using the modified power law [Eq. (2)] and yields an exponent β of 0.345 ± 0.03 at a transition temperature of 14.05 ± 0.01 K. The inset of Fig. 2 represents the same peak intensity data, background subtracted, plotted on logarithmic scales with fits to the simple power law (a) as well as the power law with the first correction-to-scaling term included (b). The corrected power law describes the data very well over the entire temperature range whereas the ordinary power-law fit is seen to deviate from and exceed the data for reduced temperatures in excess of about 0.03. To correct for this deviation, one clearly needs a correction term which will be less than unity for temperatures below T_{sp} and thus the correction amplitude A in Eq. (2) must be less than zero as expected.

The deviation of the data from the simple power law at low temperatures motivated us to examine in more detail the dependence of the fits on the range of data included. Thus, fits were carried out as a function of the lowest temperature included as this temperature is varied from about 12.5 K up to about 13.5 K. The results could not be extended much beyond 13.5 K as the uncertainty in the fits became excessive. The obtained results for β as a function of lowest temperature are shown in Fig. 3 for fits to both the ordinary power law [Eq. (1)] as well as the power law with the first correction-to-scaling term included [Eq. (2)]. Expectations for the 3D Ising, 3D XY, and 3D Heisenberg universality classes are included in the figure as a point of reference.[24] The value of β obtained from the ordinary power law varies continuously over the entire temperature range of interest and we feel that this strong variation is largely responsible for the wide range of values of critical exponents reported in previous measurements. The fits to the corrected power law [Eq. (2)] show little dependence on the range of data included. The fact that the value of β obtained from the ordinary power law varies over the entire temperature range is taken as direct evidence that the asymptotic region is rather narrow. The robust nature of the corrected power-law fits indicates that only the first-order correction term is necessary to adequately describe the data at least over the temperature range which was investigated. Fits were also performed using a power law with the first two correction-to-scaling terms included and, as expected, no significant differences were observed.

The extraction of the exponent β is generally made much more difficult due to the presence of critical scattering from fluctuations in the order parameter in the immediate vicinity of the transition temperature. These fluctuations provide additional scattering at the ordering wave vector which attains its maximum at the transition temperature where the size of the correlated regions diverge. This causes substantial curvature in the order parameter near the transition temperature and makes the data in its immediate vicinity unusable. However, in contrast to more traditional SP systems, there has been a great deal of difficulty in observing these critical fluctuations in $\mathrm{CuGeO_3}$,[5,9–11] although recent measurements have made progress in this respect.[12,25] Detailed scans were performed through the (1/2,5,1/2) position at temperatures near T_{sp} and no evidence of critical scattering was observed. The absence of critical scattering in our measurements makes it impossible to determine exponents associated with the Q-dependent susceptibility $\chi(Q)$ and the correlation length ξ. It does, however, allow for a much more accurate determination of the exponent β associated with the order parameter than is usually possible.

The dependence of the value of β on the chosen transition temperature T_{sp} was investigated in some detail as this largely determines the accuracy of most critical exponent estimates. This dependence is shown in Fig. 4 where β as well as the goodness-of-fit parameter χ^2 are plotted versus the chosen value of transition temperature T_{sp}. As can be seen the value of β obtained from these fits is a smooth function of T_{sp}, indicating that, as expected, it is the uncertainty in T_{sp} and not the statistical quality of the diffraction data that is responsible for the uncertainty in β.

For reference, the expected values of β for tricritical, 3D Ising, 3D XY, and 3D Heisenberg universality are indicated. The plot of χ^2 versus T_{sp} has a very pronounced minima at a T_{sp} of about 14.05 K with a corresponding β value of about 0.345. The value of β obtained from these measurements is consistent with conventional 3D behavior and strongly supports recent theoretical work[26] based on a Landau-type description of the free energy, where the displacements of both Cu and O are taken into consideration, which predicts 3D XY universality for which β has been estimated theoretically to be 0.3455 ± 0.002.[27]

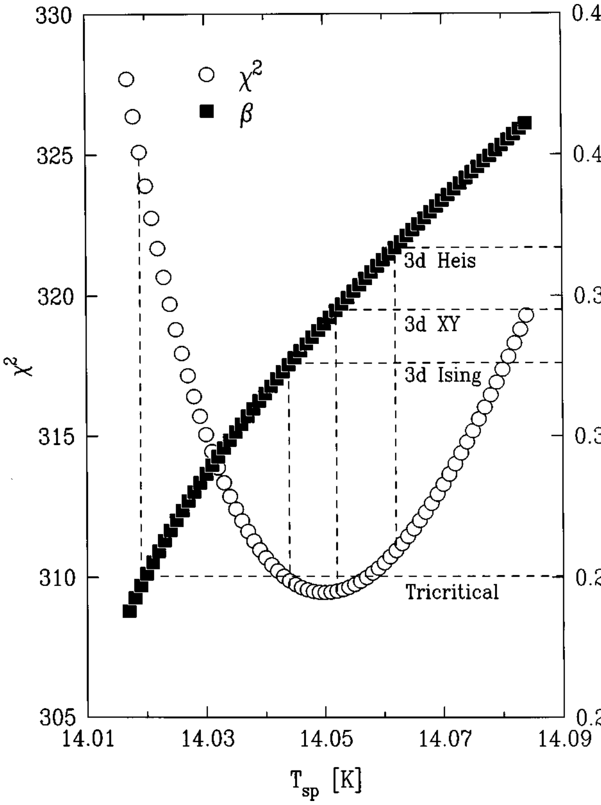

FIG. 4. The dependence of the goodness-of-fit parameter, $\chi^2 = \Sigma_i\{[I_{\mathrm{calc}}(T_i) - I_{\mathrm{obs}}(T_i)]/\sigma(I_{\mathrm{obs}}(T_i))\}^2$ and the critical exponent β on the chosen value of the transition temperature T_{sp}. The results were obtained from fits to the power law with first correction-to-scaling term included [Eq. (2)]. The predicted values of β for 3D Ising, XY, and Heisenberg universality, as well as for tricritical mean-field behavior are included.

IV. LATTICE CONSTANTS

Our first set of measurements of the lattice parameters in $\mathrm{CuGeO_3}$ using a conventional approach led us to conclude that such measurements would lack the resolution necessary for detailed comparison to the order parameter. The limiting factor was the mosaic quality of the single crystal and the subsequent lowering of Bragg peak intensity. The crystal used in these measurements has a mosaic spread of about 0.04° HWHM. (As a point of reference, the crystal used in the diffraction measurements of Harris *et al.* had a reported mosaic of 0.009° HWHM.[10]) The conventional approach consists of performing detailed longitudinal scans of the relevant Bragg peaks and then extracting peak positions from line-shape analysis.

A. Experimental description

The alternative approach we implemented is shown schematically in Fig. 5. As the temperature is changed, the peak in a longitudinal scan shifts position from point A to point B, and thus the intensity at point C undergoes a rather large change ending at point D. In this way small changes in peak

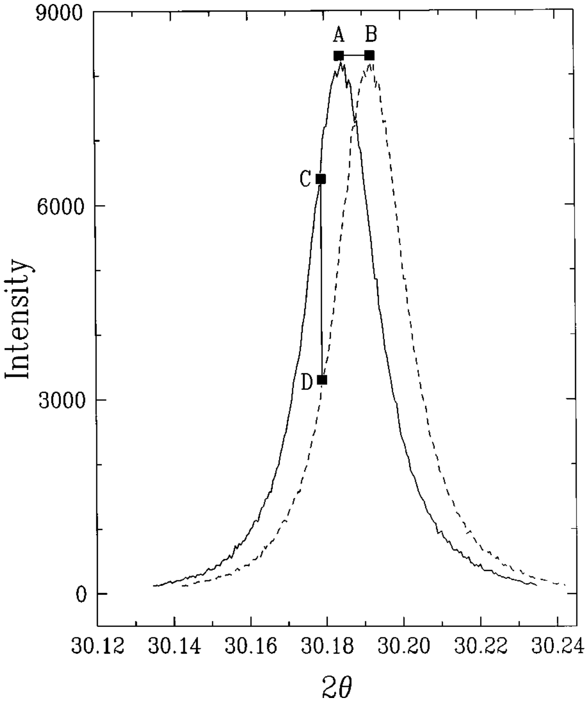

FIG. 5. A sample longitudinal scan through the (0,0,1) Bragg reflection. With a shift in peak position from *A* to *B*, the intensity at point *C* changes by a large amount, to that at point *D*. The changes in peak position represented by this figure are exaggerated and are shown to demonstrate the approach employed in the lattice constant measurements.

position correspond to rather large intensity changes for those positions on the longitudinal scan whose slope is large. Large changes in position, such as those shown in Fig. 5, could easily be measured using conventional techniques, but this alternative approach has significant advantages for measuring very small changes in lattice constant such as those which occur in $CuGeO_3$ (the shift in peak position shown in Fig. 5 has been exaggerated to allow for easier description of the technique). The technique allows high statistic measurements to be made as the time allotted per temperature now is the time involved in measuring a single point as opposed to that required for a detailed line shape. We estimate that this approach provided about an order of magnitude increase in sensitivity, resulting in measured $\Delta L/L \sim 10^{-6}$.

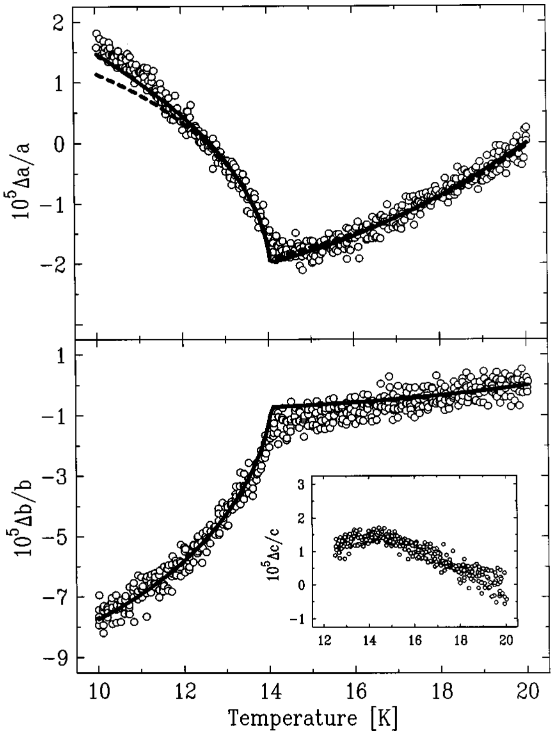

FIG. 6. Relative changes in the *a*, *b*, and *c* lattice constants as a function of temperature normalized to produce a $\Delta l/l$ of zero at 20 K. The solid line represents the background obtained from measurements on a 5% Zn-doped sample in addition to the order parameter squared, as obtained from fits to the superlattice reflection data shown in Fig. 2. The dashed line in the upper panel represents the results obtained with a background fit using the data on the pure sample for temperatures between 16 and 20 K, well above the transition temperature.

The actual determination of the temperature dependence of the lattice constants consisted of the following procedure. The longitudinal line shape of a Bragg peak, such as that shown in Fig. 5 for the (0,0,1) reflection, was measured in detail. An appropriate position on the line shape (such as point *C* in Fig. 5) was selected so as to maximize changes in intensity. The temperature dependence of the intensity at that point was then measured. Initially, on ramping the temperature, successive runs showed essentially the same relative changes, but from one run to the next, there were often small offsets in intensity. This was attributed to slight twists of the sample-mount-cryostat system and to correct this, following each change in temperature, transverse scans were performed and the position was recentered in the transverse direction. This alleviated the offset problem as evidenced by the reproducibility of runs taken with both temperature increasing and decreasing. The resulting data, shown in Figs. 6 and 7, were typically made up of 8–10 runs with half done on warming and half on cooling. Finally, changes in peak position were determined from changes in intensity using the detailed line-shape measurement.

Potential problems exist with this approach, such as systematic changes in the line shape due to, for example, slight realignment of the grains which make up the mosaic single crystal. Throughout our measurements, we periodically performed longitudinal scans, such as those shown in Fig. 5, as a check for these and related effects. In addition, as mentioned above, the results were reproducible over many independent warming and cooling runs.

B. Results and discussion

The results obtained for the temperature dependence of the three lattice constants of $CuGeO_3$ are shown in Fig. 6. The results are presented as relative changes in lattice constant normalized to give a $\Delta l/l$ of zero at a temperature of 20 K. For all lattice constants, the highest *Q* reflection possible was measured to maximize resolution. The *a* lattice constant was measured using the (4,0,0) reflection while the *b* lattice constant was measured using (0,8,0). The *c* lattice constant was measured from changes in the (0,0,1) peak position as this was the highest attainable (0,0,*L*) reflection due to geometrical constraints. The low-*Q* reflection used in measuring *c*, coupled with the smaller magnitude of the spontaneous

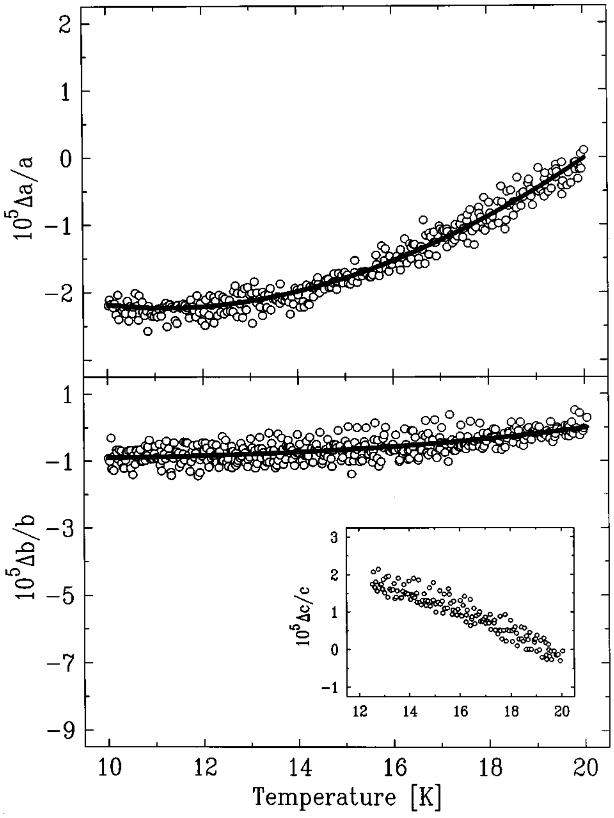

FIG. 7. Relative changes for the a, b, and c lattice constants as a function of temperature for a single crystal of $Cu_{1-x}Zn_xGeO_3$ with $x \sim 0.05$. Again the data was normalized to produce a $\Delta l/l$ of zero at 20 K. The solid lines represent the best polynomial description of the data. This was taken as an independent measure of the thermal expansion of pure $CuGeO_3$ in the absence of the SP transition.

strain along this direction,[13] is responsible for the inferior results obtained for this lattice constant compared with the other two.

As is evident from Fig. 6, there exist spontaneous strains below T_{sp} for all three lattice constants. As a further consistency check, the magnitude of the changes in length were compared to those obtained in previous capacitance dilatometry measurements.[13] We obtain relative length changes between 12.5 and 14 K of 0.002, 0.004, and 0.0004 % for a, b, and c, respectively, and these are in very close agreement with dilatometry measurements where changes of 0.002, 0.004, and 0.0003 % were obtained.[13] We are therefore very confident that the approach employed in measuring the spontaneous strains is free of systematic error.

It is important to note that this represents a substantial improvement over previous x-ray-diffraction results where measurements of the a-axis lattice constant indicated only a small upturn below T_{sp} and it had been suggested that the changes in the c-axis lattice constant were too small to be observed using such techniques.[10] Our results show clear changes in both a and c and the spontaneous strains along both a and b have been measured with sufficient accuracy to allow for quantitative analysis.

A difficulty in extracting the spontaneous strain from the relative changes in lattice constant comes from determining the background, representing the expected thermal expansion in the absence of the phase transition. This contribution must be subtracted from the overall signal to isolate both the spontaneous strain below T_{sp} and any possible fluctuation effects near T_{sp}. Typically, the data well above the transition temperature would be fit to a suitable polynomial and this fit would be taken to represent this background. In order to provide an independent measure of this background, lattice constant measurements were also performed on a $Cu_{1-x}Zn_xGeO_3$ single crystal with $x \sim 0.05$. The first studies on the influence of Zn impurities on the SP transition in $CuGeO_3$ indicated that this level of doping was sufficient to suppress the SP transition completely with only an antiferromagnetic phase transition at much lower temperatures.[28] However, later measurements suggest that a sample with this concentration of Zn should exhibit a SP transition at a temperature of about 11 K (Ref. 29) in addition to a lower temperature Néel phase. While the precise nature of the phase diagram for the $Cu_{1-x}Zn_xGeO_3$ system is somewhat controversial, it is clear that Zn doping at the 5% level should be disruptive to the SP state displayed by the pure material, and thus this doped system may well serve for an appropriate background determination. The temperature dependence of the three lattice constants in the 5% Zn-doped sample was measured using the approach described above and the resultant relative changes are shown in Fig. 7. No evidence of spontaneous strains can be seen for temperatures between 10 and 20 K indicating the absence of a SP transition over this temperature range. This appears inconsistent with the presence of a SP transition at 11 K, as suggested by Sasago *et al.*,[29] and is consistent with the absence of such a transition as suggested by the earlier measurements of Hase *et al.*[28] Of course, any comparison between our present results and those of both Sasago *et al.*[29] and Hase *et al.*[28] rely on accurate determinations of the Zn concentration present in the crystals employed in these studies.

The solid lines in Fig. 7 represent the best polynomial fit describing the strain data for the 5% Zn-doped sample. The b lattice constant was fit to a T^4 behavior as expected for the low-temperature thermal expansion of an insulator where the thermal-expansion coefficient exhibits a T^3 behavior:[10]

$$b = b_0(1 + AT^4). \tag{3}$$

The a lattice constant could not be described by such an expression as it is observed to increase slightly at lower temperatures. These data were fit to

$$a = a_0[1 + A(T - T_0)^2]. \tag{4}$$

The best-fit line shown yields a value of T_0 of about 11.5 K indicating an increase in the a lattice constant for temperatures below this value. One may argue this upturn to be indicative of a SP transition at this temperature, as would be expected from the phase diagram of Sasago *et al.*[29] However, no evidence of such a transition is seen in the b lattice constant where the magnitude of the spontaneous strain is greatly enhanced and hence, we conclude that no SP transition occurs in this sample over the temperature range of interest.

These best-fit polynomial lines were taken to represent the thermal expansion of the pure material in the absence of the SP transition. Thus, the solid lines shown in Fig. 6 represent this background with the order parameter squared added for temperatures below $T_{\rm sp}=14.05$ K. The order parameter was obtained from the best fit to the superlattice reflection data shown in Fig. 2 using the modified power law [Eq. (2)]. As the measurements were carried out on the same crystal using the same thermometry, no adjustment of the transition temperature was required and the only tunable parameter is the overall amplitude [I_0 in Eq. (2)]. This was scaled to provide agreement at $T\sim 12.5$ K as this is the lowest temperature included in the order-parameter measurements. The solid line in Fig. 6 gives a good description of the data for both the a-axis and b-axis lattice constants and, consequently, we conclude that the spontaneous strain does indeed scale well with the order parameter squared.

The importance of the independent background measurement can be appreciated by consideration of the dashed line in the upper panel of Fig. 6. This dashed line assumes a background which is taken from a polynomial fit to the high temperature (16–20 K) data for the a lattice constant on the pure sample. One can see that this provides an inferior description of the data and it is evident that the independent background determination is necessary to properly describe the data. The better agreement with the background obtained from the Zn-doped sample indicates that the upturn in the a-axis lattice constant observed for this sample is, in fact, a good representation of the true background occurring in pure $\mathrm{CuGeO_3}$. This line still lies somewhat lower than the data, suggesting that the true increase in background strain for the a-axis lattice constant below about 11.5 K in the pure material is slightly greater than that observed in the 5% Zn-doped sample.

We have examined systematic deviations of the spontaneous strains from the order parameter squared. The data shown in Fig. 6 are subtracted from the model calculation represented by the solid lines in the same figure. The resulting subtracted data were binned into groups of 5 and the results for both the a axis and b axis are shown in Fig. 8. As a point of reference, the difference between the superlattice reflection data and the order parameter fit, as shown in Fig. 2, is plotted in the inset. For the order parameter, significant deviations from the fit are only observed for temperatures within about 0.1 K of the transition temperature consistent with the absence of fluctuations. However, for both the a-axis and b-axis spontaneous strain measurements, significant deviations are observed within about 1 K of $T_{\rm sp}$ for the a axis and within about 2 K for the b axis. We interpret these differences as the presence of fluctuation effects in the spontaneous strain data which are less evident in the order-parameter data. It is important to note that critical scattering from fluctuations in the order parameter has been observed in several previous measurements[5,12,25] and the absence of such scattering in our order-parameter measurements is likely a consequence of poor signal-noise. However, this effect is much more clearly observed in the spontaneous strain measurements. Deviations are also observed in the case of the a-axis lattice constant at low temperatures (<12 K), however, this is a consequence of the slight difficulty in the background subtraction, as previously discussed. It is important to note that this slight difference in background does not alter the fluctuation effects observed in the vicinity of $T_{\rm sp}$ as this is largely determined by the shape of the order parameter and the value of the transition temperature.

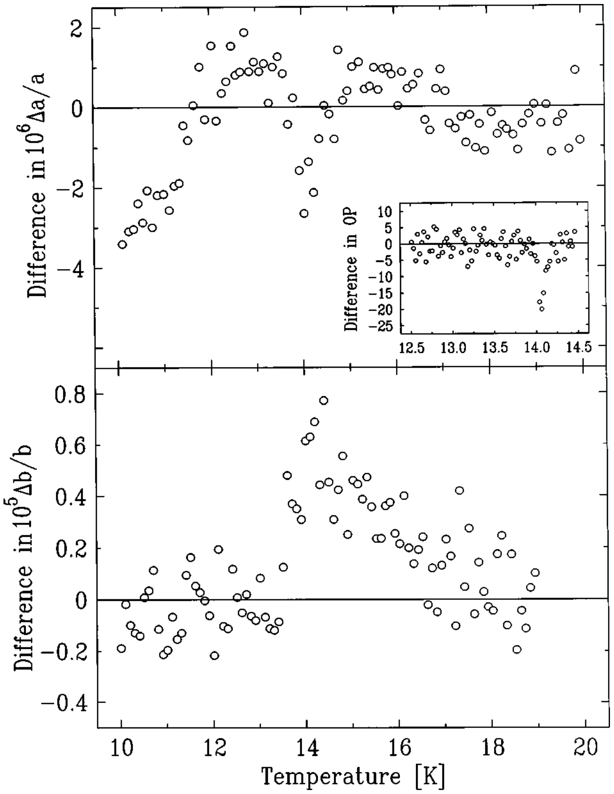

FIG. 8. Difference between the data and the model of the spontaneous strain being proportional to the square of the order parameter (shown as the solid lines in Fig. 6). The inset shows the difference between the superlattice reflection data and the best fit to the power law with correction-to-scaling included, which is the solid line shown in Fig. 2. For both the thermal expansion and order parameter data, the resulting differences have been binned into groups of five to improve statistics.

V. SUMMARY

In summary, we have performed high-temperature stability measurements of the order parameter associated with the SP transition in $\mathrm{CuGeO_3}$ in the vicinity of $T_{\rm sp}$ and obtain a value of the exponent β of 0.345 ± 0.03 at a transition temperature of 14.05 ± 0.01 K. This value of β is consistent with conventional 3D universality and strongly supports the theoretical argument[26] for 3D XY behavior, where the predicted value of β is 0.3455 ± 0.002.[27] Our results also demonstrate that the asymptotic critical region is rather narrow and this factor is most likely responsible for the inconsistency of critical exponent estimates obtained from previous measurements.

In addition, high-resolution, high-temperature stability x-ray-diffraction measurements of relative lattice constant changes have been performed and this has allowed for a detailed comparison between the spontaneous strains present below $T_{\rm sp}$ and the order parameter. This comparison shows the spontaneous strains to be well accounted for by the order parameter squared with fluctuation effects present in the spontaneous strains, near $T_{\rm sp}$, over a temperature range of at least 1 K. These fluctuation effects, easily observed in the spontaneous strain measurements, are much more difficult to observe in the order parameter with little evidence seen in our results. The nature of this additional contribution to the spontaneous strain is not clear, but the peak observed in the difference plots shown in Fig. 8 are reminiscent of those typically seen in measurements of heat capacity or the Q-dependent susceptibility due to the build up of critical fluctuations near typical continuous phase transitions.

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APPENDIX: THE FIRST CORRECTION-TO-SCALING AMPLITUDE

For a modified power law with the first correction-to-scaling term included, the amplitude of this term [represented as A in Eq. (2)] should be less than zero.

To appreciate this, let us consider the case of mean-field theory where one commonly considers the solution to be

$$m \sim t^{1/2}, \tag{A1}$$

where m is the order parameter and $t = 1 - T/T_{\mathrm{sp}}$. This result is only valid near the asymptotic critical region with the temperature near the transition temperature. In fact within mean-field theory, the full solution of the order parameter as a function of temperature is known:[30]

$$m = \tanh\left(\frac{T_{\mathrm{sp}}}{T}\, m\right), \tag{A2}$$

where the order parameter is normalized to unity at $T = 0$. The lowest order expansion of this transcendental equation for temperatures near T_{sp}, where m is small, results in

$$m = 3^{1/2}\left(\frac{T}{T_{\mathrm{sp}}}\right) t^{1/2}. \tag{A3}$$

So one does obtain the commonly used form shown in Eq. (A1), but even the lowest-order expansion is modified by a term T/T_{sp}. One would expect the correction-to-scaling term in Eq. (2), when applied to mean-field theory, to modify the order parameter in a manner consistent with the T/T_{sp} term shown in Eq. (A3). As this will act to reduce the order parameter for temperatures below T_{sp}, one would expect the same for the correction term $(1 + A t^{\Delta})$ in Eq. (2) and, hence, the first correction-to-scaling amplitude A should be less than zero.

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