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Specific heat fluctuations in the vicinity of the spin–Peierls transition of $CuGeO_3$

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Abstract. We present an analysis of experimental specific heat data measured in the vicinity of the spin–Peierls transition of a $CuGeO_3$ single crystal. The aim of the investigation was to analyse the type of the transition, including the character of the fluctuations, and to give a proper determination of the critical temperature. We used and successively compared the Gaussian and critical fluctuations models to fit the experimental points detected in magnetic fields up to 21 T. Our results present new information about the influence of a magnetic field on fluctuations in the $CuGeO_3$ compound. Within the framework of the Gaussian fluctuations model, there is no significant magnetic field dependence of the fluctuations. Using this model, the critical region is estimated to be as small as 10 mK in zero field, which excludes the possibility of observation of critical fluctuations in the present experiments. In spite of this, a critical fluctuations type of analysis can also be carried out, with a critical exponent value lying between the three-dimensional XY and the Heisenberg universality classes. We also note the absence of broadening of the fluctuations regime under magnetic field. Taking into account the scatter of the data, the two models are equally suitable in the fitting process.

1. Introduction

It is now well established that the compound $CuGeO_3$ can exhibit a spin–Peierls (SP) transition driven by magnetic interactions in one-dimensional $S = 1/2$ antiferromagnetic chains. At the spin–Peierls transition ($T_{SP} = 14$ K) the uniform antiferromagnetic chains become unstable with respect to a lattice distortion which dimerizes the chains, introducing a gap into the chain–spin excitations spectrum. The examination of this transition suggests the presence of a fluctuation regime evident from both structural and magnetic measurements. In x-ray investigations, pre-transitional lattice structural fluctuations were observed above the transition temperature T_{SP} (or T_c) [1, 2]. In the paper [1], critical fluctuations were observed over a broad temperature range above T_{SP} (up to ∼40 K), with a strong anisotropy in the correlation lengths, showing a predominant quasi-1D character. In [2], pre-transitional lattice fluctuations were

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observed within 1 K above T_{SP}, with a length scale about one order of magnitude larger than that characterizing the thermal fluctuations. This was attributed to random-field defects in the near-surface region of the sample. A strong coupling between magnetic and structural fluctuations near T_{SP} was confirmed by neutron scattering experiments, as was suggested in [3]. The explanation involving magnetic fluctuations stressed the importance of next-nearest-neighbour interactions in the chain, competing with the main nearest-neighbour interactions. Moreover, the competing antiferromagnetic interactions were claimed to lead to the SP transition without spin–lattice coupling [4] described by the Cross and Fisher theory [5].

In the vicinity of T_{SP} a narrow asymptotic critical regime was observed by fitting the x-ray data with a $\beta = 0.36$ critical exponent, which is consistent with the standard three-dimensional XY or Heisenberg universality classes [6]. The analysis used so far to explain the behaviour of $CuGeO_3$ near its transition temperature T_{SP} pointed towards non-mean-field treatments [7]. But the calculated critical exponents span a wide range for different possible universality classes from tri-critical to 3D classes. For example, $\beta \sim 0.25$ was found from elastic measurements [7] as well as from earlier neutron scattering studies [8], while $\beta = 0.36$ was found from other neutron measurements [3]. Similarly, specific heat measurements have yielded estimates giving both a highly divergent heat capacity with $\alpha = 0.4$ [9], as well as $-0.15 < \alpha < 0.12$ [10] which restricts the behaviour to that described by the standard three-dimensional universality class.

Shortly after the discovery of HTSC materials, the specific heat of YBaCuO single crystal was studied. At first sight the zero-field behaviour was accounted for by a sum of a BCS-type step and 3D Gaussian fluctuations [11]. Later, after the measurements had been repeated in non-zero fields, this picture had to be changed due to the broadening of the specific heat peak at T_c, satisfying a scaling relation which is a signature of critical fluctuations, rather than Gaussian ones [12]. Finally, the authors claimed that at zero field the two approximations were equally suitable. In the work reported here, we started with the same motivation to probe the Gaussian fluctuations around the jump of the second-order mean-field transition and the critical approximation due to the expected large low-dimensional fluctuations very close to T_{SP}, by checking the specific heat under different magnetic fields up to 21 T.

From the thermodynamics point of view, at reduced temperature values $|\tau| \gg \tau_G$ (the Ginzburg criterion; see later), the usual Ginzburg–Landau mean-field results are approximately valid. Much closer to T_{SP} ($|\tau| < \tau_G$), there will be a shift from the mean-field regime towards the critical exponents regime due to large fluctuations. In the intermediate-temperature regime a proper renormalization-group solution should be necessary, but no such theory has been attempted. Here, the so-called Gaussian fluctuations theory is used, which treats small fluctuations around the second-order mean-field solution.

2. The sample and experimental technique

Experiments were performed on a single-crystalline sample (0.45 g weight) cleaved from a larger monocrystal several cm long and 5 mm in diameter, which was prepared by a floating-zone method associated with an image furnace [13]. Its value of T_{SP} in zero field was 14.25 K. The main specific heat results obtained for this sample have been published elsewhere [14,15]. In this article we present an investigation with magnetic field $\boldsymbol{H} \parallel c$-axis up to 21 T. The applied magnetic field was produced by a 12 T superconducting magnet in the CRTBT Laboratory and on a resistive Bitter-type magnet, up to 22 T, in the LCMI Laboratory, both in Grenoble. Heat capacity data were obtained with a transient-heat-pulse technique, with relative temperature increments of the order of 5% under high field, and with a high resolution of the order of 0.1% in the zero-field experiment. The high-field experiments are particularly delicate due to the noise induced by the resistive Bitter-type magnet and the magneto-resistance of the thermometers. We used film-deposited Au–Ge thermometers, characterized by a weak magneto-resistance (less than 20% of the correction for $T > 6$ K in 21 T), developed at CRTBT.

3. Analysis

Specific heat (C_p) experiments are generally limited to collecting data sufficiently close to the expected value of T_{SP}, and the experimental uncertainty of the measured values hides the detailed shape of the transition. Determination of the phase diagram requires knowing the T_{SP}-values precisely, and consequently some fitting method has to be used to find T_{SP} and the type of the transition. Usually, the fitting methods include some fluctuations contribution to treat the pronounced smearing around the transition. We applied two advantageous methods for this purpose, the so-called Gaussian and critical fluctuations models. In the Gaussian approach we supposed a BCS-type behaviour (i.e. the discontinuity of C_p at T_{SP}) and a Gaussian fluctuations contribution above (+) and below (−) T_{SP}, given by

$$C_G^{\pm} = C_0^{\pm}(\pm t)^{-(2-d/2)}$$

where $t = T/T_{SP} - 1$ is the reduced temperature and d the dimensionality of the fluctuations. We fixed d at 3 ($C_G \sim |t|^{-0.5}$, close to T_{SP}) due to this system being a 3D phonon-coupled one. This assumption is supported by studies of the spin–Peierls compound [6] and of Peierls compounds (quasi-1D electronic systems coupled to 3D phonons) [16]. For the uniform phase (where fluctuations in the specific heat are negligible) we used the simplest mean-field (MF) assumption: $C_p = \gamma T + \beta T^3$, the sum of the magnetic and lattice terms. Acoustic measurements have shown that the variation of the lattice term is negligible for calorimetric data, since it is of the order of 10^{-3} when crossing the phase boundaries [17]. Therefore we used $C_m = C_p - \beta T^3$ as the magnetic term for further analysis. At this point we applied a fit for C_m/T, where the BCS term ($T < T_{SP}$) is compatible with Mühlschlegel's results [18]:

$$\begin{aligned} C_m/T &= B_G^- + E_G^- T + C_G^-/T \qquad & T < T_{SP} \\ C_m/T &= B_G^+ + C_G^+/T \qquad & T > T_{SP} \end{aligned} \tag{1}$$

where $B_G^{\pm}$ are constants and E_G^- is the linear MF coefficient.

In the fitting procedure, we only set up one requirement—namely $C_0^+/C_0^- = \sqrt{2}$. This requirement was fulfilled by varying the value of T_{SP} and the fitting range, while verifying from log–log plots of the fluctuations term that, near the singularity, the behaviour is indeed described by a power law with the same exponent above and below T_{SP}. The 3D Gaussian fluctuations analysis gives another formula for the fluctuations which can be used to predict the appearance of critical fluctuations:

$$\begin{aligned} C_G^+/\Delta C &= \sqrt{(\tau_G/t)} \qquad & T > T_{SP} \\ C_G^-/\Delta C &= \sqrt{(\tau_G/2|t|)} \qquad & T < T_{SP} \end{aligned}$$

where ΔC is a jump at T_{SP} in zero field. We introduce here the Levanjuk–Ginzburg parameter τ_G [19,20], which has an important meaning since it represents an estimate of the relative width of the temperature region $\tau_G T_{SP}$ where critical effects (logarithmic divergence) dominate.

We did not impose conditions on $B_G^+ = \gamma$ during the fitting procedure since it should be fulfilled in the true MF regime (with no fluctuations any longer) and consequently it might be checked if $T \gg T_{SP}$, where there are not enough experimental points, particularly under high fields. For the reason that our temperature range did not extend over a large enough MF interval, the extraction of β- and γ-parameters involves some uncertainty in their values, due to the influence of the remaining fluctuations and the original scatter of the experimental data. To extract β- and γ-parameters in our present analysis, we used a linear fit to the high-temperature tail of the C_p/T versus T^2 curve, with an uncertainty related to the scatter of the data and the choice of the starting point for the high-T tail interval, which remains rather similar for the different fields (except for zero-field data) [21].

Fortunately, the manifestation of the uncertainty in β and γ in the amplitude of the Gaussian fluctuations is negligible in the vicinity of T_{SP} (within the $\sim\pm1$ K range), where we intended to apply the Gaussian fit. Note that, in zero-field measurements, the condition $B_G^+ = \gamma$ is fulfilled within 7%, as a consequence of a higher density of data points in comparison with other experiments, and in this way we can estimate the value of γ more accurately.

To perform the critical analysis we followed the usual procedure, assuming a cusp at T_{SP}. We fit C_m (without the lattice term) as

$$C_m = (A^{\pm}/\alpha)|t|^{-\alpha} + B + Et$$

with the condition that $\alpha = \alpha^+ = \alpha^-$ and that we have a linear expansion of the regular contribution close to T_{SP}, e.g. $B = B^+ = B^-$ (i.e. no discontinuity of C_m at T_{SP}) and $E = E^+ = E^-$ (i.e. differentiable smooth background) with a linear expansion of the regular contribution close to T_c [10]. We varied the T_{SP}-value to find the best least-squares fit.

4. Results and discussion

Figure 1 shows the magnetic part of the specific heat near T_{SP} at different magnetic fields. The values 0, 8.1, and 10 T correspond to the dimerized–uniform phase transition and the 18 T value to the incommensurate–uniform phase transition. Upon increasing the field, the transition temperatures shift to lower temperatures, in agreement with the phase diagram defined earlier [14], and the C_m-values become smaller [22]. These dimerized–uniform and incommensurate–uniform transitions are second order, so the experimental points around T_{SP} were not sensitive to the sweeping direction of the temperature (there are no metastable states or hysteresis at these phase boundaries). There are two fits, the dotted curve for the critical fluctuations one, and the continuous curve for the Gaussian one, including the BCS-type step (the dash–dotted curve) and the Gaussian fluctuations contribution. The critical fluctuations fit was performed directly on the C_m-data and was then scaled to display the C_m/T versus T plot. We chose the interval $\Delta T = \pm1$ K as the fitting range; then it was slightly adjusted around this value to get the best fit. Usually the fits were not sensitive to this adjustment, especially in the case of the zero-field data which show the best statistics. In the high-field cases, with poorer statistics, the fit was sensitive to the change of the number of fitting points. The first conclusion drawn from the examination of figure 1 is that the two models yield similar qualities of fitting.

Table 1 collects the results obtained in the fitting procedures for both critical and Gaussian cases. The differences in the T_{SP}-values obtained in each case differ by 1–20 mK, which is too small to be resolved in our experiments. The Gaussian fluctuations amplitude $C_0^{\pm}$ is shown to be constant in different magnetic fields, in disagreement with the theoretical calculations of Lee and Shenoy who predicted a field dependence for the Gaussian fluctuations contribution [23]. The field independence of the extracted Gaussian fluctuations data versus reduced temperature is clearly pronounced in figure 2: the data points collapse onto one branch, excluding a broadening character. The same property can be seen in figure 3 where the C_m–t data are shown. The curves shift to lower values upon increasing the field but their shape remains more or less unchanged. Furthermore, in the incommensurate phase ($B > 13$ T) the data points define one branch, showing the absence of the expected broadening behaviour.

Another important item of information obtained from the Gaussian analysis is an estimate of the critical (logarithmic divergence) range from the parameter $\tau_G T_{SP}$. These intervals are

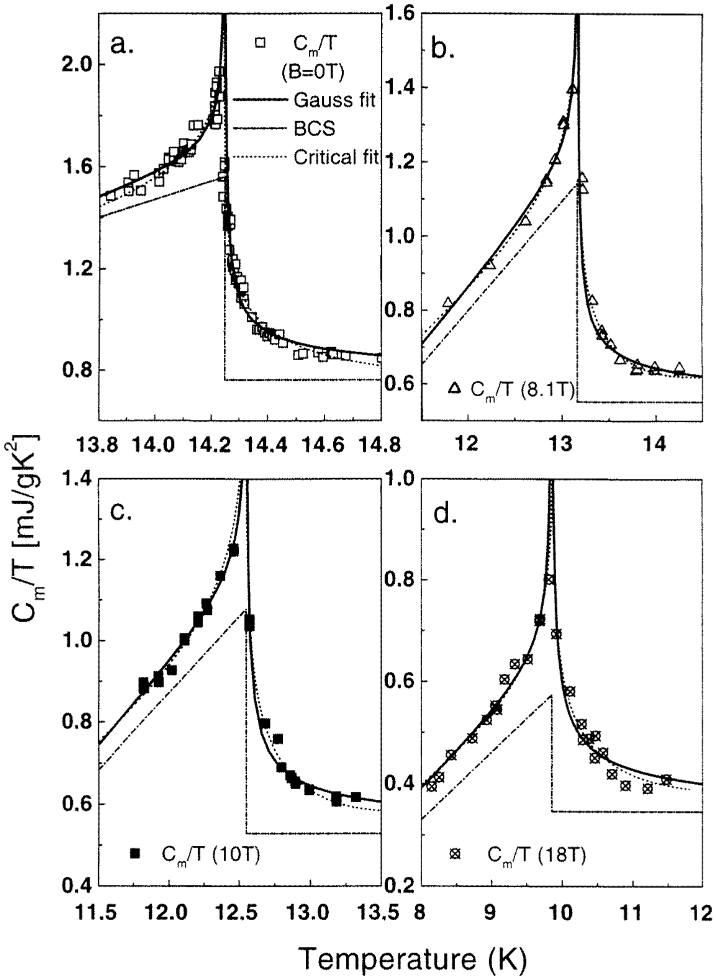

Figure 1. The magnetic specific heat scaled as C_m/T versus temperature in the vicinity of the spin–Peierls transition of single-crystalline $CuGeO_3$. The different runs (a), (b), (c), (d) were obtained in magnetic fields of 0, 8.1, 10, and 18 T, respectively. The experimental points were fitted by two methods: a Gaussian fit (continuous curve) as a sum of a BCS-type step function (dash–dotted curve) and a Gaussian fluctuations contribution, and a critical fit (dotted curve). The lattice term β used to define C_m was 1.45×10^{-3}, 1.74×10^{-3}, 1.85×10^{-3}, and 1.55×10^{-3} mJ g^{-1} K^{-4} for (a), (b), (c), (d), respectively.

too small to be checked using experimental data, even when they increase from ∼10 mK to ∼400 mK upon increasing the magnetic field (see table 1). It is difficult to find a tendency for the expected critical intervals as a function of field, but their values in the incommensurate phase are systematically larger by an order of magnitude than those in the dimerized phase. In spite of these small intervals predicted by the Gaussian model, the results of the critical analysis fitting performed on a broader interval (∼±1 K, like for Gaussian fits) are of a quality similar to that relative to the Gaussian fits. Obviously, one needs more data points with less scatter to exclude any alternative fitting possibility. The critical exponent α lies in the interval $-0.025 \geqslant \alpha \geqslant -0.044$ in different fields, so it involves a state between the standard Heisenberg (-0.12) and XY (-0.008) universality classes. This agrees well with the

Table 1. Results of the Gaussian and critical fluctuations analysis as functions of different magnetic fields. The parameter $\tau_G T_{SP}$ of the Gaussian analysis gives the expected region for the critical fluctuations. D–U and IC–U in the magnetic field column denote the transitions from dimerized to uniform and from incommensurate to uniform phases.

B (T) (magnetic field)		T_{SP} (K) Gaussian fit	T_{SP} (K) Critical fit	C_0^- (mJ g^{-1} K^{-1}) ($C_0^+ = \sqrt{2}C_0^-$)	$\tau_G T_{SP}$ (mK)	Critical exponent, $-\alpha$	Critical amplitude ratio, A^+/A^-	Data points/ fitting range
0	D–U	14.2478	14.247	0.2	8.8	0.0255	1.12	86
2.7	D–U	14.1664	14.146	0.1976	6.9	0.044	1.19	50
8.1	D–U	13.1621	13.169	0.2338	25.3	0.034	1.12	25
10	D–U	12.5505	12.55	0.2017	21.58	0.034	1.1	31
15	IC–U	10.0625	—	0.2163	370	—	—	16
18	IC–U	9.8545	9.875	0.2164	184.7	0.037	1.05	28
21	IC–U	9.754	—	0.1921	220.4	—	—	22

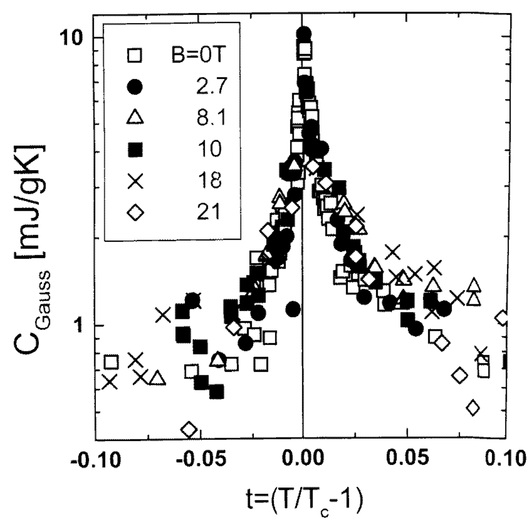

Figure 2. The Gaussian fluctuations term versus the reduced temperature in different magnetic fields after subtraction of the BCS background from the C_m-data. Note that the fluctuations amplitude below and above T_{SP}, and the broadening of the transition, do not change with magnetic field as shown by the superposition of the data.

specific heat results of reference [10], where possible values for α were obtained over a rather wide range between -0.15 and 0.12 in the zero-field measurements, and also from the x-ray measurements of reference [6]. In our zero-field analysis, due to the much better statistics in this high-resolution experiment (with $\delta T/T$ increments of $\sim$0.1%), the tolerance for suitable fits was ($-0.02 > \alpha > -0.03$), which is narrower than the literature data range. The ratio of the critical fluctuation amplitudes A^+/A^- was close to one in all of the field studies (see table 1).

Finally, we give details of the zero-field results in view of the corresponding very good statistics. The Gaussian fit was displayed on the $C_G^{\pm}$–$|t|$ plot (with $B_G^- = -3.5$; $B_G^+ = 0.761$; $E_G^- = 0.355$) shown in figure 4 in such a way that inspection of the fit was carried out during the procedure. It is worth noting that after determination of the BCS-type step function, we obtained $\Delta C/C_N \sim 1$, to be compared to the $\Delta C/C_N = 1.43$ BCS value reported earlier [14].

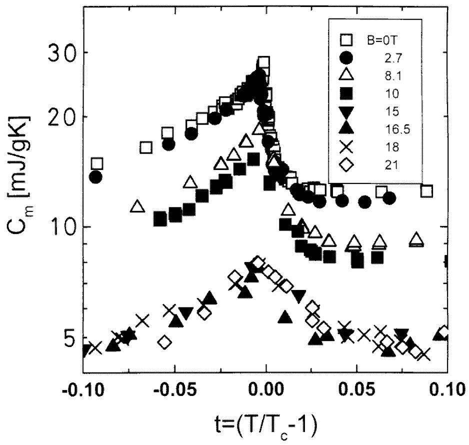

Figure 3. The magnetic part of the specific heat versus the reduced temperature in different magnetic fields. It is shown that the transition shape is independent of the field and that, in the incommensurate phase, the C_m-values are also unchanged.

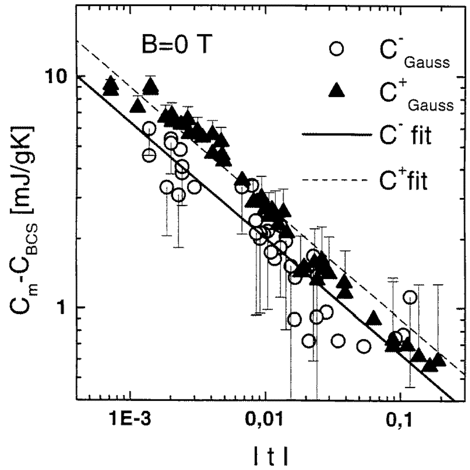

Figure 4. Zero-field Gaussian fluctuations data below and above T_{SP} versus the absolute value of the reduced temperature shown in a log–log plot in order to easily confirm the Gaussian fit after removing the BCS-type background. The error bars are set to 2.5% of the C_m-data.

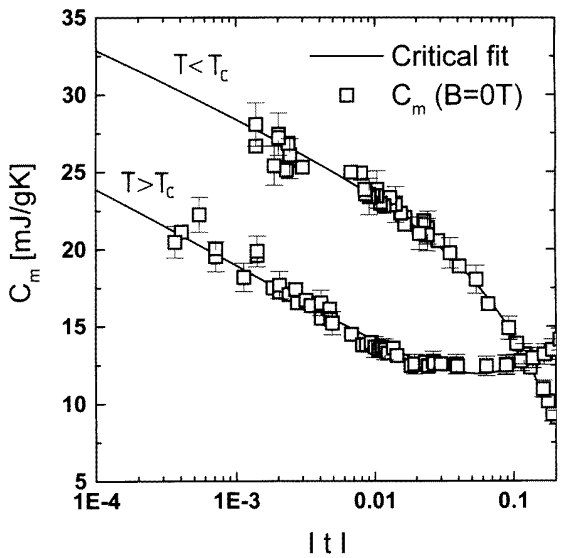

Figure 5. Magnetic specific heat versus the absolute value of the reduced temperature in zero field. The continuous curve represents the critical fit. The error bars are set to 2.5% of C_m. Note the good accuracy at low values of $|t|$ which is a consequence of the high quality of the sample.

The critical fit to the C_m–$|t|$ plot shown in figure 5 demonstrates the high quality of the sample. Usually, as $|t|$ is decreasing, the data points deviate from the fitting curve and converge to a common value [10] due to sample inhomogeneity and volume distribution of the T_{SP}-values. This limit is better than 10^{-3} for the sample under investigation. It can be seen that the critical fit works well up to $|t| = 0.1 \gg \tau_G$, disagreeing with the Gaussian prediction.

5. Summary

We have studied the specific heat data in a narrow temperature range near the SP transition. The analysis was performed by two fitting methods, of the MF Gaussian and critical types, the physical bases of which are different and even contradictory for the temperature range where the critical fluctuations were calculated well, in comparison with the interval value predicted by the Gaussian method. Within the experimental data statistics, we could not rule out either the Gaussian or the critical fit applications. The critical fit parameters and the corresponding universality class determination agree well with the results reported in the literature. Surprisingly, the magnetic field has no significant influence on the fluctuations parameters for both methods, and no pronounced magnetic field broadening has been detected.

Acknowledgments

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