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The specific heat and critical behaviour of VBr_2, a Heisenberg antiferromagnet with chiral symmetry

J Wosnitza†, R Deutschmann†§, H v Löhneysen† and R K Kremer‡

† Physikalishes Institut der Universität Karlsruhe, Engesserstraße 7, 76128 Karlsruhe, Germany

‡ MPI für Festkörperforschung, Heisenbergstraße 1, 70569 Stuttgart, Germany

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Abstract. We present high-resolution measurements of the specific heat, C, of the Heisenberg antiferromagnet VBr_2 with layered-triangular lattice in the temperature range between 1.5 and 35 K and in fields up to 6 T The critical exponent α extracted from C has been obtained as $\alpha = 0.30 \pm 0.05$. This value is fully consistent with the theoretically expected exponent of $\alpha = 0.24 \pm 0.08$ for three-dimensional Heisenberg systems with chiral symmetry.

As early as almost ten years ago on the basis of symmetry arguments and Monte Carlo simulations two new universality classes for the critical behaviour of frustrated antiferromagnets on a three-dimensional (3D) stacked-triangular lattice were proposed [1]. These special magnetic systems exhibit a non-collinear spin structure with an additional symmetry characterized by a new degree of freedom, the chirality. For the chiral symmetry with easy-plane anisotropy (XY like) which means that the spins are confined within the triangular plane and the number of components of the order parameter is $n = 2$, recent new Monte Carlo estimates [2] yield critical exponents of $\alpha = 0.34 \pm 0.06$ for the specific heat, $\beta = 0.253 \pm 0.01$ for the magnetization, $\gamma = 1.13 \pm 0.05$ for the susceptibility and $\nu = 0.54 \pm 0.02$ for the correlation length. The values of these exponents differ significantly from the well established values for conventional 3D systems [3]. Experimental support for the above predictions has recently been obtained by a variety of neutron-diffraction and specific-heat studies for $CsMnBr_3$ [4–6].

However, for the other predicted new universality class with Heisenberg ($n = 3$) chiral symmetry, where Monte Carlo estimates yield [2] $\alpha = 0.24 \pm 0.08$, $\beta = 0.30 \pm 0.02$, $\gamma = 1.17 \pm 0.07$ and $\nu = 0.59 \pm 0.02$, only very few experimental verifications exist. One reason for this is the rare realization of the pure $n = 3$ chiral symmetry because some anisotropy is often present in stacked-triangular antiferromagnets. In particular, an easy-plane anisotropy leads to the above-mentioned XY chiral symmetry seen, e.g., in $CsMnBr_3$ and possibly also in $RbMnBr_3$ [7]. An easy-axis (Ising-like) anisotropy, on the other hand, causes a splitting of the antiferromagnetic phase transitions into two separate transitions associated with the successive ordering of the spin components parallel (T_{N1}) and perpendicular ($T_{N2} < T_{N1}$) to the c-axis. This is believed to result in ordinary XY criticality [8] which was indeed seen in recent specific-heat measurements of $CsMnI_3$ [9] and $CsNiCl_3$ [10]. In the latter experiment, however, the application of a magnetic field parallel to the easy-axis (parallel to c) allows us in an elegant way to change the degrees of freedom of

§ Present address: Siemens AG, ZFE-STKM51, Otto-Hahn-Ring 6, 81739 München, Germany.

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the order parameter. In particular, at the tetracritical point full isotropy in spin space is reached and the critical behaviour is excellently described by the $n = 3$ (Heisenberg) chiral universality class [10].

In spite of this increasing number of experimental confirmations showing the existence of new chiral universality classes the predictions of [1] and [2] are still the subject of controversy. Other authors, for example, are doubtful about the proposed new chiral universality and suggest rather a tricritical mean-field behaviour for the spin-order both for the XY [11] and for the Heisenberg case [12]. The tricritical mean-field critical exponents are $\alpha = 0.5$, $\beta = 0.25$, $\gamma = 1$ and $\nu = 0.5$.

Two other candidates for the chiral Heisenberg type of critical behaviour are VCl_2 and VBr_2. The former material has a weak Ising-like anisotropy of the order of $D/J \simeq 3 \times 10^{-3}$, where D is the anisotropy of the magentic ions and J represents the intralayer nearest-neighbour exchange interaction [13]. For VCl_2 this anisotropy causes a tiny splitting of T_N into $T_{N1} = 35.88$ K and $T_{N2} = 35.80$ K [13]. For VBr_2 a comparable anisotropy of $D \simeq 0.1$ K has been estimated from the measured g factor [14]. However, no splitting of T_N or other manifestations of this anisotropy have been observed. Therefore, VBr_2 is a prime candidate for an $n = 3$ chiral symmetry.

So far only one experimental study of the critical behaviour of VBr_2, that in the specific heat, is known [15]. In this work, however, the usual fit procedure (as described below) for the determination of α was not used. Instead, an attempt to subtract the regular background was made by scaling the specific heat of the non-magnetic compound $CdCl_2$ measured separately. As the authors of [15] themselves point out this 'evaluation of the lattice contribution seems to be tricky'. Indeed it is known that before starting the fitting procedure the subtraction of some background, of whatever origin, often fails and leads to ambiguous results [16]. Therefore, it seems of no surprise that in [15] two different critical exponents $\alpha^+ = 0.59 \pm 0.05$ for the data above $T_c (= T_N)$ and $\alpha^- = 0.28 \pm 0.05$ for the data below T_c were found contrary to the renormalization group prediction $\alpha^+ = \alpha^-$ [17].

In order to clarify this unsatisfactory situation and to test for the predicted 3D Heisenberg chirality we, therefore, measured the specific heat, C, of VBr_2 with high accuracy in $B = 0$ and $B = 6$ T applied parallel to c. For both magnetic fields we extract for the data close to the phase transition the critical exponent α and the amplitude ratio A^+/A^-. The critical exponent of the specific heat α shows the largest relative change between the values of the conventional and the new universality classes. A careful analysis of C close to T_c promises, therefore, a reliable determination of the type of critical behaviour.

VBr_2 has the crystal structure of CdI_2. The V^{2+} ions with $S = \frac{3}{2}$ are arranged in the ab-plane on the triangular lattice. Adjacent stacks of V^{2+} planes in the c-direction are separated by two Br^- planes. The cations form chains along c surrounded by Br^- anion octahedra. From measured spin-wave dispersion relations the nearest-neighbour exchange interaction within the ab-plane $J/k_B = -16$ K and the next-nearest-neighbour exchange interaction in the c-direction $J'/k_B = -0.2$ K were obtained [14]. The antiferromagnetic ordering occurs at approximately $T_N = 29$ K. The exact magnetic structure, especially the angle φ of the magnetic moments with respect to c is unresolved. Either a fixed value of φ or a magnetic liquid without a well determined φ might be possible [14]. Because of the frustration of the spins on the triangular lattice, however, VBr_2 is chirally degenerate and due to the Heisenberg character of the moment falls into the $n = 3$ chiral universality class.

The investigated VBr_2 single crystal was grown from powder using the Bridgman technique. VBr_2 powder was prepared according to standard methods [18]. To avoid hydrolysis the dark brown and flaky crystals were kept under Ar atmosphere except for the short time (~ 5 min) necessary for mounting the crystal in the cryostat. The specific heat in

$B = 0$ and 6 T, applied parallel to c, was measured between 1.5 and 35 K with a standard semiadiabatic heat-pulse method in a ^{4}He cryostat. The high-temperature resolution of $\delta T/T < 10^{-5}$ allowed relative temperature increments near T_c of $\Delta T/T < 10^{-3}$ to be resolved with high accuracy.

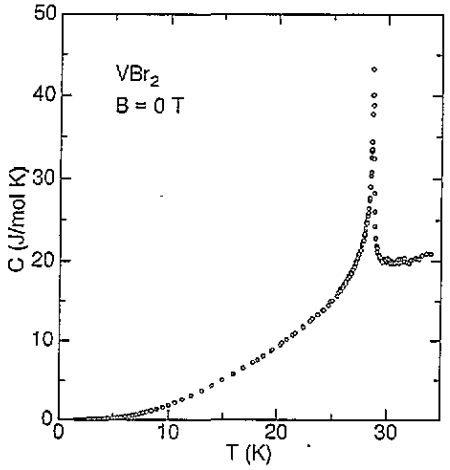

Figure 1. The specific heat C against temperature T of VBr_2.

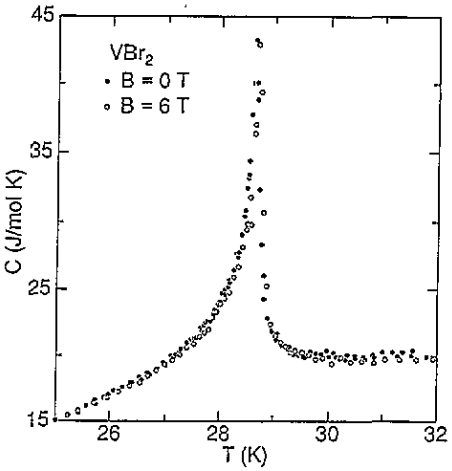

Figure 2. The specific heat of VBr_2 close to the antiferromagnetic phase transition in magnetic fields $B = 0$ and $B = 6$ T applied parallel to c.

Figure 1 shows the specific heat of VBr_2 in $B = 0$ over the whole investigated temperature range on a linear scale. Between 2 and 10 K the specific heat is approximately proportional to T^3. The antiferromagnetic ordering at $T_N = 28.66$ K is clearly visible as a sharp anomaly in C. An enlargement of this critical region near T_N between 25 and 32 K is shown in figure 2. The λ-type anomaly at T_N rises by a factor of approximately three above the background value. In $B = 6$ T the phase transition has only slightly shifted towards the higher temperature $T_N(6\text{ T}) = 28.74$ K (figure 2). The overall shape of the C anomaly, however, is not changed in the applied field. Within the experimental resolution C in $B = 6$ T outside the temperature region of figure 2 is identical to C in $B = 0$. The absolute value of T_N and the temperature dependence of C are in fairly good agreement with previously reported measurements [15, 19].

First we briefly want to discuss the low-temperature part of the measured C. In figure 3 the data below 5 K are plotted on an enlarged linear scale. In this range the measured data can be very well described by

$$C = a_{hf}T^{-2} + \beta_D T^3. \tag{1}$$

The solid line in figure 3 shows this fit with the parameters $a_{hf} = (12.1 \pm 0.5)$ mJ K mol^{-1} and $\beta_D = (1.69 \pm 0.01)$ mJ mol^{-1} K^{-4}. The second term of (1) describes the Debye contribution to C with the Debye temperature $\Theta_D = 151$ K. The first term stands for the high-temperature tail of a Schottky anomaly due to the splitting of the ^{51}V nuclear spins in a hyperfine field B_{hf}. The coefficient a_{hf} is connected with B_{hf} through [20].

$$a_{hf} = R\sum_i a_i \frac{I_i + 1}{3I_i}\left[\frac{\mu_t B_{hf}}{k_B}\right]^2 \tag{2}$$

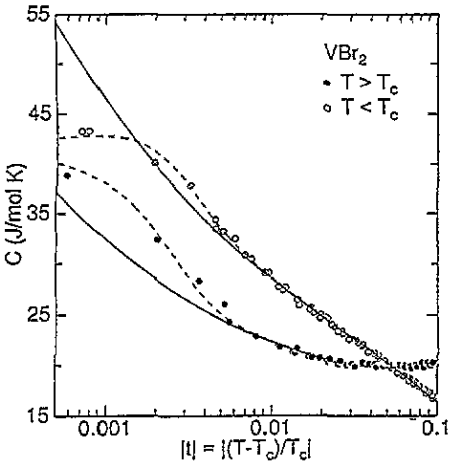

Figure 3. The specific heat of VBr_2 in zero field below 5 K. The solid line is a fit according to (1) with parameters as described in the text.

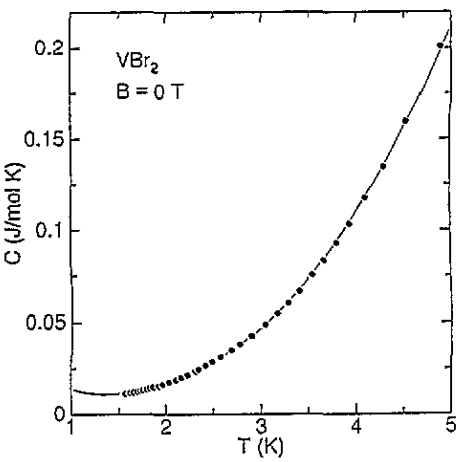

Figure 4. The specific heat against reduced temperature near the phase transition at $B = 0$. The solid line is a fit according to (3) with parameters as listed in table 1. The dashed line is the same fit with an included Gaussian-distributed smearing of T_c ($\Delta T_c/T_c = 1.7 \times 10^{-3}$).

where R is the gas constant, k_B the Boltzmann constant, I_i is the nuclear spin, μ_i the nuclear moment and a_i the relative abundance of the isotope i. For ^{51}V a_{51} is 99.75%, $I_{51} = \frac{7}{2}$ and $\mu_i = 5.1514\mu_N$, with μ_N the nuclear magnetic moment. With the above-stated fit value of a_{hf} this results in a hyperfine field of 31 T. Although a_{hf} agrees within the error bars with the value of [19], in [19] a hyperfine field of 8.2 ± 1.2 T was deduced using a similar formula as (2) but presumably taking the wrong value of $g_i = 5.14$ instead of $g_i = \mu_i/I_i = 1.472$. A value of the hyperfine field of 9.1 T obtained by NMR measurements [21] is cited in [19]. This value, however, is far too small to explain the observed large T^{-2} contribution to C. The origin of this discrepancy is not yet clear.

Table 1. Parameters of equation (3) describing the critical behaviour at the phase transition $T_c = T_N$. The units of A^+, B and E are joules per mole per kelvin.

B (T)	T_N (K)	α	A^+/A^-	A^+	B	E
0	28.66 ± 0.02	0.30 ± 0.05	0.60 ± 0.05	0.79 ± 0.05	11.4 ± 0.2	38.1 ± 0.5
6	28.74 ± 0.02	0.30 ± 0.05	0.58 ± 0.05	0.78 ± 0.05	11.1 ± 0.2	38.4 ± 0.5

For the determination of the critical exponent α the data close to the phase transition the usual formula

$$C = (A^{\pm}/\alpha)|t|^{-\alpha} + B + Et \tag{3}$$

where $t = (T - T_c)/T_c$ and T_c is the critical temperature, is employed as a fit function to the data. The first term in (3) represents the leading contribution to the singularity in C with amplitudes A^+ for $t > 0$ and A^- for $t < 0$. The regular contributions are approximated by a linear t dependence, which is known to be sufficient to describe the data in the restricted fit range near T_c adequately. In the present case the fit range was limited to the interval

$[|t_{min}|, |t_{max}|]$ with $|t_{min}| = 0.006$ to exclude data very close to T_c where rounding effects due to sample inhomogeneities are visible (see figure 4) and $|t_{max}| = 0.1$ in order to eliminate data outside the critical region. The resulting fit curves with the parameters as listed in table 1 are shown as the solid lines in figure 4, where C is plotted against $\ln|t|$. To account for the deviation of the data from the theoretical fit for $|t| < 5 \times 10^{-3}$ a Gaussian-like smearing of T_c was assumed [22]. With the fairly large value $\Delta T_c/T_c = 1.7 \times 10^{-3}$ for this smearing compared to other crystals [6 (Deutschmann *et al* 1992), 10] the whole data set, even close to T_c, is very well described as can be seen by the dashed line in figure 4.

The obtained values of $\alpha = 0.30 \pm 0.05$ and of the amplitude ratio $A^+/A^- = 0.60 \pm 0.05$ for $B = 0$ are in very good agreement with the theoretically predicted exponent $\alpha = 0.24 \pm 0.08$ and the ratio $A^+/A^- = 0.54 \pm 0.2$ for the $n = 3$ chiral case [2] and definitely different from the values for the conventional universality classes [3] or the tricritical mean-field behaviour as predicted in [12]. Of course, the experimental value would also be compatible with the $n = 2$ chiral exponent $\alpha = 0.34 \pm 0.06$ [2]. However, a weak Ising-like anisotropy, which in VCl_2 leads to two very close successive ordering temperatures, presumably would lead to a crossover to conventional XY behaviour similar to that observed in $CsNiCl_3$ [10] and $CsMnI_3$ [9]. In a sufficiently high field applied parallel to c the spin components should be forced to lie in the ab-plane leading to the $n = 2$ chiral criticality. Within our experimental uncertainty, however, no change of the critical behaviour in $B = 6$ T could be detected. Keeping in mind the minor change in T_N of only approximately 0.3% the applied field of 6 T still might be too small to observe a clear change.

In summary, we have presented a high-accuracy specific-heat measurement of VBr_2 showing an anomaly at T_N, which is definitely incompatible with the conventional universality classes and also with a tricritical mean-field behaviour. Analysis of the data within 10% around T_N using the well established formula (3) leads to the values $\alpha = 0.30 \pm 0.05$ for the critical exponent and $A^+/A^- = 0.60 \pm 0.05$ for the amplitude ratio of the specific heat. This is in good agreement with the values expected for the phase transition assumed here with $n = 3$ chiral symmetry. Besides $CsNiCl_3$ at the tetracritical point [10], VBr_2 seems to be so far the only system where clear evidence for the predicted Heisenberg chirality in $B = 0$ T has been found. Up to fields of 6 T this critical behaviour is unchanged. To date no other critical exponents of this material have been reported [23].

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