Quenched chirality in RbNiCl₃: Linear birefringence and neutron diffraction

Maikel C. Rheinstädter* and Mechthild Enderle
Institut Laue-Langevin, 6 rue Jules Horowitz, BP 156, 38042 Grenoble Cedex 9, France
and Technische Physik, Universität des Saarlandes, PSF 1551150, 66041 Saarbrücken, Germany

Garry J. McIntyre
Institut Laue-Langevin, 6 rue Jules Horowitz, BP 156, 38042 Grenoble Cedex 9, France
(Received 6 June 2004; published 16 December 2004)

The critical behavior of stacked-triangular antiferromagnets has been intensely studied since Kawamura predicted new universality classes for triangular and helical antiferromagnets. The new universality classes are linked to an additional discrete degree of freedom, chirality, which is not present on rectangular lattices, nor in ferromagnets. However, the theoretical as well as experimental situation is discussed controversially, and generic scaling without universality has been proposed as an alternative scenario. Here we present a careful investigation of the zero-field critical behavior of RbNiCl₃, a stacked-triangular Heisenberg antiferromagnet with very small Ising anisotropy. From linear birefringence experiments we determine the specific-heat exponent \( \alpha \) as well as the critical amplitude ratio \( A'_+/A^- \). Our high-resolution measurements point to a single second-order phase transition with standard Heisenberg critical behavior, contrary to all theoretical predictions. From a supplementary neutron diffraction study we can exclude a structural phase transition at \( T_c \). We discuss our results in the context of other available experimental results on RbNiCl₃ and related compounds. We arrive at a simple intuitive explanation which may be relevant for other discrepancies observed in the critical behavior of stacked-triangular antiferromagnets. In RbNiCl₃ the ordering of the chirality is suppressed by strong spin fluctuations, yielding a different phase diagram, as compared to, e.g., CsNiCl₃, where the Ising anisotropy prevents these fluctuations.

DOI: 10.1103/PhysRevB.70.224420 PACS number(s): 75.25.+z, 75.50.Ee, 75.40.Gb, 75.10.Jm

I. INTRODUCTION

On a hexagonal lattice, an antiferromagnet can never entirely satisfy its interactions, they will be at least partially frustrated. A stacked set of triangular planes will nevertheless develop long-range order for any finite interplane interaction. In the perfectly isotropic case (Heisenberg antiferromagnet), neighboring spins on a triangle compromise the antiferromagnetic interaction by including 120°. Neighbors along the hexagonal \( c \) axis are aligned antiparallel. The magnetic structure is then defined by two continuous degrees of freedom (the polar and azimuthal angle of one chosen spin) and one additional discrete degree of freedom, the chirality, the sense of rotation of the spin direction on a chosen triangle. This chirality vanishes in collinear structures, on rectangular lattices and in ferromagnets. It is still present for easy-plane antiferromagnets, and in the spin-flop phases of antiferromagnets with a small Ising-anisotropy. A large family of hexagonal compounds with a chiral degree of freedom can be described by the Hamiltonian

\[
H = J \sum_{i,j} S_i \cdot S_j + J' \sum_{i,k} S_i \cdot S_k - D \sum_i (S^2_i)^2. \tag{1}
\]

Here, \( J > 0 \) denotes the antiferromagnetic exchange interaction between nearest neighbors along the symmetry axis and \( J' > 0 \) the antiferromagnetic interaction between nearest neighbors on a triangle. The single ion anisotropy constant \( D \) favors an easy axis \( (D > 0) \) or plane \( (D < 0) \). Kawamura predicted that the chiral degree of freedom provokes not only a different topology of the field-temperature phase diagrams, but also new types of universal critical behavior, the \( n=2 \) chiral and the \( n=3 \) chiral universality classes. This prediction is discussed controversially, and arguments have been given for quite different scenarios, such as, e.g., generic nonuniversal behavior.\(^2\) Table I lists Kawamura’s predictions for the critical exponents \( \alpha, \beta, \gamma, \) and \( \delta \) and the ratio \( A'_+/A^- \) of the amplitudes above and below \( T_N \) for antiferromagnets on rectangular and triangular lattices as a survey. Here rectangular stands for all collinear structures, as they usually develop on a square or orthorhombic lattice.

\( ABX_3 \) compounds with easy-axis anisotropy, such as CsNiCl₃, RbNiCl₃, CsMnI₃, and CsNiBr₃ are well described by the Hamiltonian in Eq. (1) and have developed into model systems for low-dimensional fluctuations and ordering, see, e.g., Ref. 3 for a recent review. These compounds show quasi-one-dimensional (1D) magnetic behavior, because the intrachain interaction \( J \) is much larger than the interchain interaction \( J' \), typically \( J'/J = 10^{-2} \). One-dimensional short-range antiferromagnetic order within the 1D spin chains develops below about 40 K. At lower temperatures there is a phase transition into a three-dimensionally (3D) magnetically ordered structure.

Without an external field, Heisenberg antiferromagnets with an Ising anisotropy on a triangular lattice undergo two successive phase transitions, where ordering of the spin components parallel and perpendicular to the hexagonal \( c \) axis occurs at \( T_{N1} \) and \( T_{N2} \) \((< T_{N1})\), respectively. Below \( T_{N2} \), the spins form a 120° structure in the \( ac \) plane. The predicted \( B-T \) phase diagram is schematically shown in Fig. 1.
The two zero-field phase transitions should show 3D XY critical behavior.\(^1\) On a rectangular lattice, there is just one transition with Ising-type critical behavior.\(^3\)–\(^5\)

In order to clarify the number of phase transitions in RbNiCl\(_3\), and their criticality, we performed linear magnetic birefringence (LMB) experiments with high temperature resolution to measure the critical exponent \(\alpha\) and the amplitude ratio \(A^+/A^-\). The paper is organized as follows. The properties of RbNiCl\(_3\) are discussed in Sec. II. Experimental details of the birefringence setup are presented in Sec. III, the LMB results and the outcome of a supplementary neutron diffraction study are shown and discussed in Sec. IV. The anomalous behavior of RbNiCl\(_3\) as compared to other members of the abovementioned \(ABX_3\) family, is discussed in Sec. V.

II. \(ABX_3\)

RbNiCl\(_3\) is a quasi-1D \(S=1\) Heisenberg antiferromagnet with a weak Ising anisotropy on a triangular lattice (hexagonal space group \(P6_3/mmc\)). As in other members of the \(ABX_3\) family, CsNiCl\(_3\), CsMnI\(_3\), CsNiBr\(_3\), and RbNiBr\(_3\), the magnetic Ni\(^{2+}\) ions form strongly coupled chains along the crystallographic \(c\) axis. The chains are characterized by an intrachain exchange parameter \(J\), which is much larger than the interchain exchange parameter \(J'\) because magnetic exchange in the basal plane is mediated via two \(X\) ions compared to only one along \(c\), as pictured in Fig. 2. \(J'/J = 0.38\ K/23.8\ K = 1.6 \times 10^{-2}\) in RbNiCl\(_3\).\(^6\) The magnetic behavior therefore is quasi-1D.

At \(T_N \approx 11\) K, there is a phase transition into a 3D magnetically ordered structure. Magnetic ordering in RbNiCl\(_3\) can be discussed in the context of other members of the \(ABX_3\) family. In, e.g., CsNiCl\(_3\), two successive phase transitions are found in neutron scattering, magnetic birefringence, and specific heat capacity experiments and display 3D XY-critical behavior with the corresponding critical exponents,\(^3\)\(^,\)\(^7\) as predicted by Kawamura. For RbNiCl\(_3\), most experimental report only one transition. The criticality of this transition is not clear: Different methods obtained disagreeing values of the critical exponents and accordingly different universality classes have been proposed for the transition. The experimentally determined values do not coincide with 3D XY critical behavior. Table II summarizes experimental techniques and the values determined for \(T_N\), \(\alpha\) and \(\beta\), as found in the literature. Apart from a neutron scattering study by Oohara et al.,\(^8\) all measuring techniques report only one phase transition. The temperature resolution in all experiments was better than 0.02 K, considerably smaller than 0.15 K, claimed as the distance between \(T_{N1}\) and \(T_{N2}\) in the neutron scattering study. The anomalies in all techniques (except for Ref. 8) appear very sharp while the overlap of two close lying divergences would lead to a rounded and broad anomaly. Furthermore, the measured critical exponents do

### Table I. Critical exponents for antiferromagnets on square and triangular lattices after Kawamura, see Refs. 3–5, and references therein.

<table>
<thead>
<tr>
<th>(\alpha)</th>
<th>(\beta)</th>
<th>(\gamma)</th>
<th>(\nu)</th>
<th>(A^+/A^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ising</td>
<td>0.1098(29)</td>
<td>0.325(1)</td>
<td>1.2402(9)</td>
<td>0.6300(8)</td>
</tr>
<tr>
<td>XY</td>
<td>-0.0080(32)</td>
<td>0.346(1)</td>
<td>1.3160(12)</td>
<td>0.6693(10)</td>
</tr>
<tr>
<td>Heisenberg</td>
<td>-0.1160(36)</td>
<td>0.3647(12)</td>
<td>1.3866(12)</td>
<td>0.7054(11)</td>
</tr>
<tr>
<td>(n=2), chiral</td>
<td>0.24(8)</td>
<td>0.30(2)</td>
<td>1.17(7)</td>
<td>0.59(2)</td>
</tr>
<tr>
<td>(n=3), chiral</td>
<td>0.24(8)</td>
<td>0.30(2)</td>
<td>1.17(7)</td>
<td>0.59(2)</td>
</tr>
</tbody>
</table>

**FIG. 1.** Predicted phase diagram for \(ABX_3\) with easy-axis anisotropy. In zero magnetic field, two successive phase transitions are expected, connected with ordering of the spin components parallel and perpendicular to the hexagonal \(c\) axis at \(T_{N1}\) and \(T_{N2}<T_{N1}\), respectively. Both transitions should show \(XY\) critical behavior.

**FIG. 2.** In RbNiCl\(_3\) magnetic exchange \(J\) along the easy axis is two orders of magnitude larger than exchange in the basal plane \(J'\), which involves two \(Cl^-\) ions (as compared to one along \(c\)).
not coincide with the predicted 3D $XY$-critical behavior. If the two transitions would fall together at the same temperature, the transition from the paramagnetic directly into the chiral ordered state should show $n=3$ chiral exponents, against the experimental evidence.

RbNiCl$_3$ has a very small Ising anisotropy $D$, as compared to other members of the $ABX_3$ family. We argue that the pronounced Heisenberg character plays the key role for the understanding of phase transitions and criticality in RbNiCl$_3$. In the next section, we present and discuss the results of our high resolution LMB experiments.

### III. EXPERIMENTAL

Single crystals of RbNiCl$_3$ were grown by the Bridgman method. The slightly hygroscopic samples were prepared by cleaving in a glovebox under He atmosphere. The natural cleavage planes contain the $c$ axis, and correspond probably to $\{10\overline{1}0\}$. The typical sample size was $4 \times 4 \times 1.5$ mm$^3$ (with thickness $d=1.5$ mm). The linear birefringence $n_{ac} = n_c - n_a$ has been measured using a Sénarmont setup$^{9,10}$ with a He-Ne laser at $\lambda=632.8$ nm. The cleft samples were used without further polishing and were mounted stress free in an optical $^4$He continuous flow cryostat with a temperature stability of 0.001 K. The sample temperature was measured with a Cernox semiconductor thermometer in lock-in technique with a relative accuracy of 0.001 K. Before and behind the sample, apertures with a diameter of 0.3 mm were installed. The sensitivity of the Sénarmont setup was increased by modulating the incoming polarisation with 50 kHz and lock-in detection of the intensity.

Under certain conditions, the derivative $dn_{ac}/dT$ is proportional to the magnetic part of the specific-heat capacity, see, e.g., Ref. 11 and references therein. This relation is in particular valid close to the phase transitions of the antiferromagnetic triangular $ABX_3$ compounds with and without easy-axis anisotropy, such as CsNiCl$_3$ and RbNiCl$_3$. In the temperature range of the phase transition in RbNiCl$_3$ at $T_N \approx 11$ K, the specific-heat capacity is already dominated by contributions of the crystal lattice. The critical properties of the magnetic specific heat are therefore difficult to measure in a standard specific heat capacity setup. Here the birefringence is an elegant way to determine the critical exponent $\alpha$ as well as the amplitude ratio $A^+/A^-$ of the critical part of the specific heat capacity above and below the phase transition.

### IV. RESULTS

Figure 3 shows the temperature dependence of $n_{ac}$ over a broad temperature range. At high temperatures, $n_{ac}$ linearly decreases with lowering temperature. Below about $T=70$ K there is distinct deviation from linear behavior due to the onset of short-ranged 1D correlations along the Ni chains.$^{12}$ The inset in Fig. 3 shows the temperature range of the 3D phase transition in magnification. The onset of 3D correlations close to $T_N=10.89$ K, which finally leads to a 3D mag-

![FIG. 3. Temperature dependence of the birefringence $n_{ac}=n_c-n_a$ over a broad temperature range. The inset shows the range of the phase transition in magnification. The transition is marked by an arrow.](image-url)
for a the hexagonal basal plane. This scenario has been discussed

\[ T_N \]

ting the degeneracy of the magnetic exchange interactions in

\[ -T_N \]

estion of the critical part of the birefringence \( dn_{ac}/dT \), which is proportional to the magnetic specific heat. The solid line is the resulting fit with Eq. (2).

etically ordered structure, is indicated by the drop of the birefringence below 11 K.

Close to the phase transition the derivative of the birefringence with respect to temperature is described by a power law

\[
\frac{dn_{ac}}{dT} = A \left( \frac{T - T_N}{T_N} \right)^{-\alpha} + \text{noncritical contribution. (2)}
\]

Figure 4 shows \( dn_{ac}/dT \), the solid line is a fit after Eq. (2). The noncritical contribution due to 1D correlations and lattice natural birefringence was taken into account by a polynomial of the form \( a + bT + cT^2 + dT^3 + eT^4 \) which was subtracted from the data. We observe only one transition as the fitted transition temperatures for the range below and above \( T_N \) perfectly coincide. The good temperature resolution allows one to measure as close to the phase transition as \( 10^{-4} \) in reduced temperature, considerably closer than all previous experiments. Even if two different transition temperatures were allowed for the high- and the low-temperature side, they converge to a single one in the fit. We do not observe any signs of crossover effects.

To check the quality of the fits, Fig. 5 shows log-log plots of the critical part of \( n_{ac} \) vs reduced temperature \( |t| = |(T - T_N)/T_N| \) for \( T > T_N \) and \( T < T_N \). Solid lines are fits with Eq. (2), the fitted values for \( \alpha^+ \), \( T_N \) and the ratio \( A^+/A^- \) are given in the figure.

for other \( ABX_3 \) compounds in, e.g., Ref. 3 and 13. Considering the crystal structure of RbNiCl\(_3\), as pictured in Fig. 2, a lift of degeneracy is inseparable from changes in the crystal lattice. We therefore carried out supplementary single-crystal neutron diffraction experiments at the new Vivaldi Laue-diffactometer at the high flux reactor of the ILL in Grenoble, France, to detect a possible change in the lattice symmetry below \( T_N \). Vivaldi’s large image-plate detector allows us to survey large areas of reciprocal space to detect possible superlattice reflections in the ordered phase.

Typical sample crystals of about \( 1 \times 1 \times 2 \) mm\(^3\) were mounted in a helium cryostat. We took exposures at \( T = 20 \) K, in the paramagnetic, and in the ordered phase, at 2 K. The corresponding Laue patterns are shown in Fig. 6. The reflections of the \( T = 20 \) K exposure in Fig. 6(a) could be indexed by a primitive hexagonal cell with lattice parameters \( a = 6.93 \) Å and \( c = 5.89 \) Å. The reflections in the magnetically ordered phase in Fig. 6(b) can be described in terms of a tripled hexagonal cell \( (a, a, 3c, c) \). Figure 6(c) shows the measured reflections at \( T = 2 \) K and the corresponding simulated Laue patterns superposed. We could not detect any splitting of the reflections below the phase transition within the experimental angular resolution of \( 10' \) nor the appearance of

\[
\alpha^+ = -0.084 \pm 0.001
\]

\[
T_N = 10.89 K
\]

\[
A^+/A^- = 1.38
\]

\[
\alpha^- = -0.080 \pm 0.007
\]

\[
T_N = 10.89 K
\]

\[
A^+/A^- = 1.38
\]
Close lying divergences due to two close lying phase transitions from most of the previously reported experimental results. From our high resolution birefringence measurements as well as from the structural data. If there was only one transition, connected with ordering of the spin components parallel and perpendicular to the 1D axis but no static ordering of the chirality, the corresponding transition should indeed show conventional Heisenberg critical behavior similar to antiferromagnets on rectangular lattices. We argue in the following that spin fluctuations suppress long-ranged chiral order in RbNiCl$_3$ below $T_N$.

The chirality, which basically takes into account the sense of rotation of the spin direction on a chosen triangle, is defined as

$$\kappa = \frac{2}{3\sqrt{3}}(S_i \times S_j + S_j \times S_k + S_k \times S_i).$$

Figure 7 shows the ordered spin structure of RbNiCl$_3$ in the hexagonal basal plane, as proposed in the literature by Yelon and Cox. The spins lie in a [001] [110] plane with 2/3 of the spins canted away from $c$ by an angle $\theta$. $\theta$ depends on the ratio $D/J'$ and is determined to $\theta = 57.5^\circ$ (Ref. 14) in RbNiCl$_3$, very close to the ideal value of 60°. In this model, the chirality $\kappa$ is long-ranged ordered and changes sign from one triangle to the neighboring triangle. Note that antiphase domains of the chirality contribute equally in a neutron-scattering experiment.

Oohara and Iio investigated the RbNi$_{1-x}$Co$_x$Cl$_3$ system$^{17}$ with LMB. By replacing Ni$^{2+}$ by Co$^{2+}$, the magnitude of the Ising anisotropy $D$, which is very small in pure RbNiCl$_3$ (70% that of CsNiCl$_3$), can gradually be increased. With increasing $D$, two anomalies become visible in the LMB experiments and the distance $T_{N1}-T_{N2}$ increases. The latter study clearly shows that the small Ising anisotropy $D$ plays the crucial role for the understanding of criticality and phase transitions in RbNiCl$_3$. It also proves that LMB is capable of detecting the upper transition, if it exists.

The anisotropy $D$ confines the 120° spin structure to the $ac$ plane. Depending on the ratio $D/J'$, the structure might exhibit an additional degree of freedom connected with the rotation of the 120° structure in the $ac$ plane. This quaside-
general chirality has been predicted\(^{18}\) and experimental evidence was found for the case of CsNiCl\(_3\).\(^{19}\) The energy barrier for a rotation of the spin-star in the \(ac\) plane is of the order of \(D(D/6J)'\)^2.\(^{20}\) Miyashita\(^{18}\) suggested that this quasidegeneracy exists if \((D/J)' < 1\) \((D/J)' = 0.06\) in RbNiCl\(_3\)). Even though \(D_{\text{RbNiCl}_3} = 0.7D_{\text{CsNiCl}_3}\), \(D(D/6J)'^2\) for RbNiCl\(_3\) is just 7\% of that of CsNiCl\(_3\); the quasidegeneracy should therefore be strongly enhanced in the paramagnetic phase of pure RbNiCl\(_3\).

NMR and measurements of the specific-heat capacity (see Table II) give evidence for strong spin fluctuations also in the ordered phase of RbNiCl\(_3\). Figure 8 schematically shows the two basic spin relaxation mechanisms. Type I fluctuations are rotations of the spin star around an axis perpendicular to the spin plane, i.e., parallel to the chirality vector \(\hat{\kappa}\). This is the quasidegeneracy that has been discussed above. As indicated in the figure, these fluctuations preserve the chirality of the triangle; \(\hat{\kappa}\) can still show long-ranged order.

All fluctuations with axis of rotation perpendicular to \(\hat{\kappa}\) (type-II fluctuations) change the sign of \(\hat{\kappa}\). If these fluctuations occur incoherently, \(\hat{\kappa}\) cannot order. The phase transition should be of conventional type, as suggested by the LMB experiment.

Type-II fluctuations seem not to depend directly on the Ising anisotropy \(D\) because the canting angle of the respective spins does not change during the rotation. Their incoherent occurrence in the ordered structure, however, may be emphasized by the presence of type-I fluctuations. When the Ising anisotropy is enlarged in CsNiCl\(_3\) or in the RbNi\(_{1-x}\)Co\(_x\)Cl system, the contribution of type-II fluctuations is obviously negligible, as these compounds show chiral ordering as predicted by theory. This seems to imply that type-II fluctuations play a major role only when type-I fluctuations are already strongly enhanced (as in pure RbNiCl\(_3\)).

The basic idea of fluctuations which on the one hand preserve (type I) and on the other hand suppress (type II) long-ranged chiral order seems to account well for phase transitions and critical behavior observed in RbNiCl\(_3\). The separate ordering of the spin components parallel to the 1D axis is presumably suppressed by type-I fluctuations; type-II fluctuations do not affect the projection of the magnetic moment onto the \(c\) axis. But fluctuations of type-II might suppress ordering of the chirality \(\hat{\kappa}\) at the phase transition \(T_N\) where the magnetic moment shows 3D ordering (whereas type-I fluctuations have no effect on the sign of \(\hat{\kappa}\)). If both types of fluctuations are strongly enhanced, we imagine that the domain walls between chirality domains of opposite sign move freely through the otherwise magnetically long-range ordered structure. If the chirality domain walls in the ordered phase behave liquid-like, the transition should show conventional Heisenberg critical behavior, as is observed in the LMB experiment. In this language, the chirality domain walls in CsNiCl\(_3\) or CsMnBr\(_3\) are quasistatic. This liquid-like behavior of the domain walls, which leads to a different phase diagram and different critical behavior, as compared to other members of the \(ABX\)\(_3\) family, must crucially depend on the almost perfect Heisenberg character of RbNiCl\(_3\).

VI. CONCLUSIONS

We present a linear magnetic birefringence study in RbNiCl\(_3\). Our high-resolution determination of the critical parameters \(\alpha\) and the amplitude ratio \(A'/A\) show conventional Heisenberg critical behavior similar to antiferromagnets on rectangular lattices (which have no ordered chirality) as opposed to theoretical predictions. There is just one phase transition in RbNiCl\(_3\). From a neutron-diffraction study we can exclude a structural phase transition and a lift of the degeneracy of the magnetic exchange interactions in the basal plane at \(T_N\). We discuss RbNiCl\(_3\) in the framework of previous experimental and theoretical results and other members of the \(ABX\)\(_3\) family. We finally argue that spin fluctuations lead to the unusual behavior of RbNiCl\(_3\). A separate phase transition of the spin component parallel to the easy axis might be suppressed by spin fluctuations with axis of rotation parallel to the chirality vector \(\hat{\kappa}\) (type-I fluctuations). Fluctuations of type II, with axis of rotation perpendicular to \(\hat{\kappa}\), presumably suppress long-ranged order of the chirality \(\hat{\kappa}\) below \(T_N\). The resulting single phase transition shows conventional Heisenberg critical behavior, as evidenced by the critical exponents and phase transitions observed in the LMB experiment.

ACKNOWLEDGMENTS

We are indebted to and thank K. Knorr for hospitality and fruitful discussions. This work has been partially funded by the Universität des Saarlandes, Saarbrücken, Germany. We thank H. Tanaka for providing us with the high-quality samples.
QUENCHED CHIRALITY IN RbNiCl$_3$: LINEAR...

Present address: Institut Laue-Langevin, 6 rue Jules Horowitz, BP 156, 38042 Grenoble Cedex 9, France. Electronic address: rheinstaedter@ill.fr