# Magnetic phase diagram of $CsCuCl_3$ for in-plane magnetic fields up to 14 T

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(Received 21 August 2001; published 27 December 2001)

High-resolution specific-heat and magnetocaloric-effect measurements have been utilized to complement the magnetic phase diagram of the hexagonal antiferromagnet $CsCuCl_3$ in fields up to 14 T aligned perpendicular to the $c$ axis. The recently found additional incommensurate phase induced by thermal fluctuations could be resolved completely. It appears at about 4 T in a narrow temperature range, with a maximum width of only $\sim$70 mK and narrows towards higher fields extending up to $\sim$11 T. Within the low-temperature incommensurate phase, the magnetocaloric-effect data confirm another phase transition that may be explained by quantum fluctuations.

DOI: 10.1103/PhysRevB.65.052402 PACS number(s): 75.30.Kz, 75.40.Cx, 75.50.Ee

In $ABX_3$ hexagonal antiferromagnets—like $CsNiCl_3$, $CsMnBr_3$, and $CsCuCl_3$—the magnetic $B^{2+}$ ions form a triangular lattice within the $ab$ planes. The antiferromagnetic interaction between three neighboring spins on a triangular placquette leads to frustration and to a chiral 120° spin structure with a twofold chiral degeneracy as the lowest-energy configuration. In many systems, the superexchange coupling between the planes is much stronger than the coupling within the planes, rendering these systems quasi-one-dimensional at intermediate temperatures $T$ before at low $T$ three-dimensional magnetic order is found.

$CsCuCl_3$ exhibits ferromagnetically coupled $Cu^{2+}$ chains along the $c$ direction. The Dzyaloshinskii-Moriya interaction along the $c$ axis forces the spins to lie within the $ab$ plane ($XY$ system) and leads to a slow incommensurate spiraling of the spin chains with a pitch of about 5°.[1] The low spin ($S=1/2$) leads to quantum effects resulting in a first-order magnetic phase transition in a magnetic field $B$ aligned along $c$; at low $B$ the spins form a chiral "umbrella" structure, whereas quantum and thermal fluctuations favor a coplanar "up-up-down" structure at high fields.[2,3] We have previously reported on the anomalous critical behavior indicating a crossover close to the Néel temperature $T_N \approx 10.6$ K, i.e., below a reduced temperature $t=|T_N-T|/T_N \approx 10^{-3}$, from chiral $XY$ behavior to a weakly first-order transition,[4] and on the occurrence of an intermediate phase in a narrow $T$ window near $T_N$ appearing in a magnetic-field range between $\sim$5 and 7 T for fields applied in the $ab$ plane.[5,6]

Classically, a magnetic field applied within the basal plane elongates the spin spirals along the $c$ axis. At $B=0$, a magnetic Bragg reflex is observed at $(1/3\,1/3\,\delta)$, with $\delta=0.085$.[2] The corresponding spiral wave vector $q \propto \delta$ in this incommensurate phase (IC1) should decrease quadratically with $B$ leading to a commensurate phase with $q=0$ at $B \approx 0.5\ B_s$, where $B_s=31$ T is the paramagnetic saturation field for $T \to 0$.[7] Indeed, recent neutron-scattering results in static magnetic field have confirmed this; at $T=2$ K the commensurate phase was observed at $B \approx 15.6$ T.[8] The earlier reported value of 18 T ($T=4.2$ K) has a larger error bar since it was extracted from neutron-scattering data in pulsed fields.[9] In addition, a plateau at $\delta \approx 0.05$ occurs around 12 T indicating another intermediate phase.[2,8,9] Within a phenomenological theory this transition was ascribed to quantum fluctuations.[7]

Besides the extraordinary large effect of quantum fluctuations in $CsCuCl_3$, the equally important thermal fluctuations lead to the above-mentioned intermediate phase between the IC1 and paramagnetic phase near $T_N$. Neutron-scattering results unraveled the spin structure in this second incommensurate phase (IC2) with side peaks appearing at $\delta_{IC2}=0.074$ ($B=9.5$ T).[10,11] Based on numerical solutions of a phenomenological Landau theory the spin structure was resolved.[12] The spins on two sublattices are spiraling with a larger pitch than that of IC1, whereas the spins on the third sublattice oscillate around the field direction with halved repeat length (see the illustrations in Ref. 10). Consequently, in the IC2 phase the sublattices have no 120° structure, i.e., no chiral degeneracy.

Here we report on measurements of the specific heat and of the magnetocaloric effect of $CsCuCl_3$ up to 14 T. In previous experiments up to 7 T the magnetic ordering temperature was found to increase with field and the IC2 phase occurred above about 4 T.[5] With our present high-field data we can (i) resolve the complete IC2-phase region which is stable only between about 4 and 11 T, (ii) observe a reentrant magnetic phase boundary, and (iii) detect the phase transition to the intermediate phase at low $T$ that is induced by quantum fluctuations above about 9 T.

Single crystals of $CsCuCl_3$ were grown from aqueous solution. A freshly cut piece of 36 mg was visually aligned with the $c$ axis perpendicular to the applied magnetic field. The specific heat was measured up to 14 T in a $^4$He calorimeter by use of a standard semiadiabatic heat-pulse technique which allowed a temperature resolution of $\Delta T/T < 5 \times 10^{-6}$. The magnetocaloric effect, $\Delta T/\Delta B$, was measured in the same calorimeter. Thereby the magnetic field $B$ was changed in small steps $\Delta B$ measuring simultaneously the resulting temperature variation $\Delta T$. Taking into account the small eddy-current heating by applying field increments as well as decrements, $\Delta T/\Delta B$ was determined. For more details, see Ref. 13.

Figure 1 shows the specific heat $C$ plotted as $C/T$ vs $T$ in

 

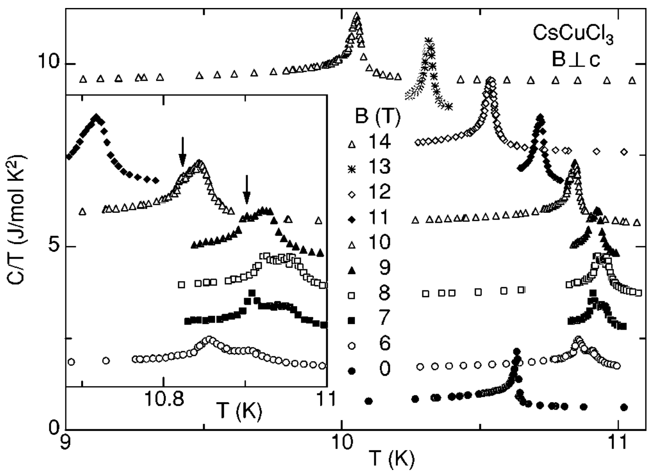


FIG. 1. Specific heat $C$ of $CsCuCl_3$ plotted as $C/T$ vs $T$ for various magnetic fields $B$ applied perpendicular to the $c$ direction. The inset shows the $C$ data between 6 and 11 T in an enlarged $T$ scale. The arrows indicate the low-$T$ anomaly corresponding to the phase transition between the incommensurate phases (IC1→IC2). Data are shifted consecutively by 1 $\mathrm{J/mol\,K^2}$ with respect to $B=0$.

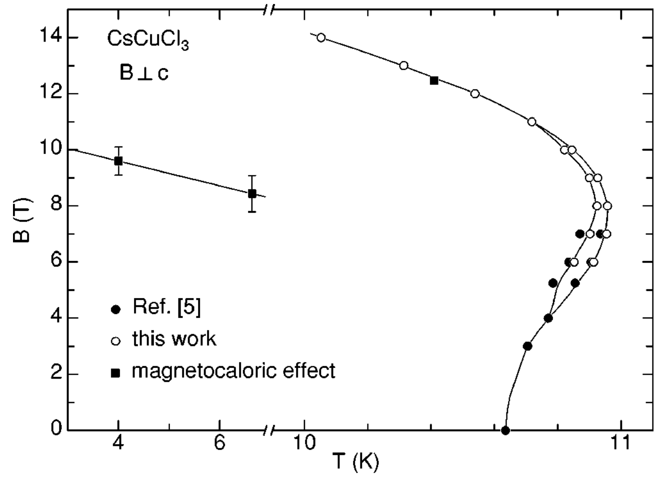


FIG. 2. Magnetic phase diagram of $CsCuCl_3$ for $B$ applied perpendicular to the $c$ axis. Circles indicate data from specific heat, squares from magnetocaloric effect.

the vicinity of $T_N$ in magnetic fields up to 14 T. The salient features are: (i) the two phase transitions observed for 6 T (separated by ~70 mK) merge together in higher fields until they cannot be resolved unambiguously above 11 T (see the inset of Fig. 1); (ii) a reentrant phase boundary is seen beyond ~8 T. The narrow incommensurate phase (IC2) was first observed in our previous work.[5] Starting at about 4.5 T a weak shoulder appears about 60 mK below the first phase transition. Both anomalies become sharper upon increasing field up to 7 T with the transition at lower $T$ (from IC1 to IC2) being apparently first order.[5] The present results (Fig. 1) confirm these findings and show in addition that the intermediate IC2 phase narrows further with higher field. At 10 T the width between the anomalies is less than 30 mK. At higher fields only one, however, broadened, peak can be resolved. These findings are perfectly in line with neutron-scattering results, although there broad peaks corresponding to the IC2 phase could be resolved up to about 14 T.[11]

Figure 2 shows the resultant $(B,T)$ phase diagram, together with the earlier data[5] and a few points determined from the magnetocaloric effect (Fig. 3). For 10.4 K a very sharp minimum in $\Delta T/\Delta B$ is observed at a field of 12.5 T, which fits nicely into the reentrant $(B,T)$ curve obtained from $C$. For 4.0 and 6.6 K, the phase transition to the saturated paramagnetic state is close to 30 T.[14] Consequently, no such sharp features in $\Delta T/\Delta B$ could be detected up to 14 T for these temperatures. The two data points at 4.0 and 6.6 K in Fig. 2 mark another transition, namely the transition to a field region where the spiral wave vector $q$ stays constant (see below). These transition fields were determined from the inflection points between the rather broad minima and the maxima in $\Delta T/\Delta B$ vs $B$ (Fig. 3). In the absence of sharp features such as the minimum for $T=10.4$ K, we take the inflection points as indicating the phase transition. The corresponding fields, 9.6(5) and 8.45(65) T, respectively, are somewhat lower (1–2 T) than the plateaus observed in high-field magnetization measurements.[14] They agree, however, perfectly with the occurrence of the $q$ plateau observed in neutron-scattering experiments[15] and are in line with structures observed in the $^{133}$Cs NMR (nuclear magnetic resonance) shift[16] and in ESR (electron-spin resonance) experiments.[17,18] Consequently, our thermodynamic data support the earlier proposed $(B,T)$ phase diagram at low $T$ and high $B$ perpendicular to $c$.

Neutron-diffraction measurements show that the spiral wave vector $q$ of the spins along $c$ gradually decreases until about 10 T ($T=4.2$ K) where a plateau up to about 14 T occurs.[2,8,9] See Ref. 11 for data close to $T_N$. All these observations appear to result from a delicate balance between the magnetic exchange energies, the Zeeman energy, and quantum fluctuations. Within a phenomenological treatment of these quantum fluctuations the plateau in $q$ could be reproduced.[7] The transition from the incommensurate to the

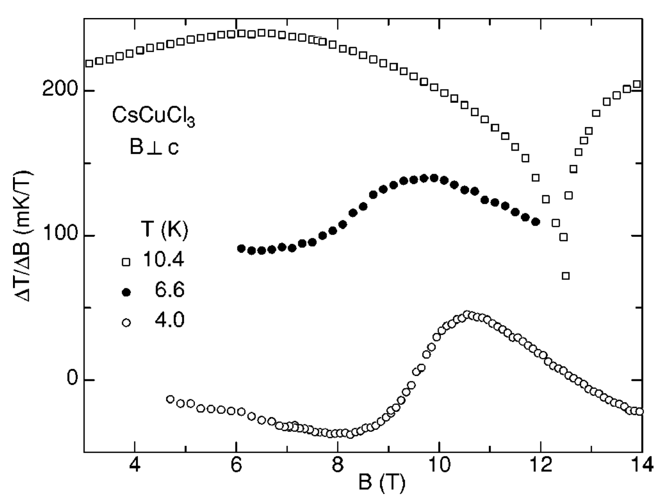


FIG. 3. Magnetocaloric effect $\Delta T/\Delta B$ vs $B$ of $CsCuCl_3$ for three different temperatures. The data points for $T=6.6$ and 10.4 K are shifted by 100 and 200 mK/T, respectively.

commensurate phase was predicted to occur at somewhat lower field (0.44 $B_s$) than observed experimentally (0.5 $B_s$).[8]

Near $T_N$, our main findings are the reentrance of the phase diagram, i.e., the initial increase of $T_N$ with field up to about 8 T, and the very narrow IC2 phase. Both effects are most probably due to thermal fluctuations in this highly frustrated triangular antiferromagnet. Indeed, within a mean-field theory that takes into account the fluctuations by means of a phenomenological biquadratic term, the occurrence as well as the very limited stability region near $T_N$ of the second incommensurate phase (IC2) can be explained.[12] This theory further accounts qualitatively for the neutron-diffraction results.[10] It fails, however, to explain the reentrant behavior of the phase diagram. Further improvements of the phenomenological theory are necessary for a more quantitative understanding.

In conclusion, we complemented our previous studies on the magnetic phase diagram of $CsCuCl_3$ with specific-heat and magnetocaloric-effect measurements up to 14 T. Our data near $T_N$ exhibit a reentrant magnetic phase boundary and allow to resolve the complete IC2 phase induced by thermal fluctuations. The very limited existence range of this phase agrees qualitatively with theoretical predictions. At low temperatures our magnetocaloric-effect data indicate a rather broad transition within the IC1 phase that is in line with structures observed in previous magnetization, NMR, ESR, and neutron-diffraction measurements. More work is required to resolve the evolution of this phase line towards $T_N$.

We are grateful to A. Hoser and N. Stüßer for supplying their neutron-scattering results prior to publication.

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