First Order Phase Transition in the Frustrated Triangular Antiferromagnet $CsNiCl_3$

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By means of high-resolution ultrasonic velocity measurements, as a function of temperature and magnetic field, the nature of the different low temperatures magnetic phase transitions observed for the quasi-one-dimensional compound $CsNiCl_3$ is established. Special attention has been devoted to the field-induced 120° phase transition above the multicritical point in the H-T phase diagram where the elastic constant C_{44} reveals a steplike variation and hysteresis effects. These results represent the first experimental evidence that the 120° phase transition is weakly first order and contradict the popular notion of new universality classes for chiral systems.

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Despite increasing interest in recent years in geometrically frustrated systems [1], there still exists considerable controversy over the nature of the phase transition in the prototypical magnetic system characterized by near-neighbor antiferromagnetic exchange interactions on a stacked triangular lattice [2–4]. The prediction made 20 years ago that helical degeneracy associated with the 120° (neighboring spin vectors are $2\pi/3$ apart) magnetic order leads to new Heisenberg and XY chiral universality classes [5] found support over the following ten years or so from numerous renormalization-group studies, Monte Carlo simulations, and experimental data [4–8]. Results in favor of this scenario continue to appear [9–11]. An alternative proposal of a very weak fluctuation-induced first-order transition made soon after the original suggestion [12] has also been strengthened by further theoretical studies and numerical simulations [13–18]. The possibility of a weak first-order transition driven by magnetoelastic coupling deserves further investigation [19]. Experimental data on both rare-earth helimagnets as well as ABX_3 compounds, such as $CsMnBr_3$, have been used extensively to support each scenario. Evidence for a weak first-order transition was found in the thermal expansion data on the helimagnet Ho long before this controversy surfaced [20]. The results presented in this Letter reveal the first experimental evidence that the 120° XY transition is weakly first order. This is achieved also through magnetoelastic coupling effects, via ultrasonic sound velocity measurements in the field-induced 120° phase of $CsNiCl_3$.

$CsNiCl_3$ is one of the more widely investigated of the large class of quasi-one-dimensional hexagonal ABX_3 materials with strong antiferromagnetic c-axis exchange [4]. Along with its sister compounds $CsMnI_3$, $CsNiBr_3$ and $RbNiBr_3$, it has weak c-axis anisotropy giving rise to a linear (L) Ising-like ordered state in zero field at $T_{N_1} = 4.8$ K, with an additional in-plane ordering at $T_{N_2} = 4.4$ K, resulting in an elliptical (E) polarization of the spin density (**S**) at low temperatures [21]. These phases are characterized by a period-2 modulation along the c axis and period-3 in the basal plane. A magnetic field applied along the c axis of only 2.3 T is sufficient to induce a spin-flop phase where **S** now lies in the basal plane and forms the familiar 120° spin structure of the frustrated triangular antiferromagnet. These three phases meet at an unusual type of multicritical point [22] (at $T_m = 4.53$ K, $H_m = 2.3$ T). The transition to the Ising-like state involves a phase-factor degeneracy associated with the triangular geometry and is been predicted to belong to the XY universality class. The nature of even this transition has a history of controversy, with the most recent addition being an analysis of neutron diffraction data on a similar transition in $CsCoBr_3$ suggesting tricritical behavior [23]. The transition at T_{N_2} is generally accepted to also be of XY universality. At the multicritical point, the axial anisotropy is exactly canceled by the applied field and the system is effectively isotropic (Heisenberg-like). At higher field strengths, there is XY symmetry along with chiral degeneracy. Such systems provide a convenient platform for the investigation of a line of phase transitions (to the paramagnetic state) which can be sampled by changing the field strength. In contrast with present data, previous experimental investigations of this transition boundary support the notion of $n = 2$ chiral universality [4,24,25].

Magnetoelastic coupling has been repeatedly demonstrated to be a useful mechanism to reveal the nature of the magnetic ordering in $CsNiCl_3$ [26–28]. Landau theory can be used to show how elastic constants scale with the various order parameters and also to yield mean-field predictions of anomalies at the transition boundaries [29]. In the present work, results and analysis are presented of high-resolution measurements of various elastic constants as a function of both temperature and magnetic field, with a focus on the paramagnetic-to-120° spin phase boundary. Steplike discontinuities are found where Landau theory predicts none. Attempts at curve fitting to extract a critical exponent β show that this leads to values which are field dependent. The strongest evidence that the paramagnetic to spin-flop phase boundary is weakly first order is found in the hysteretic behavior of C_{44} as a function of temperature and field.

Contrary to previous investigations [26,28,30], where ultrasonic techniques were mainly used in order to determine phase diagrams, the emphasis of the present work is on the measurement of critical phenomena in $CsNiCl_3$. This was realized using a high-resolution pulsed ultrasonic interferometer to measure the temperature and magnetic field dependence of different acoustic modes propagating along or perpendicular to the hexagonal c axis. Measurements were carried out on a single crystal specimen of 8.9 mm in length along the c axis and approximately 2.5 mm along the perpendicular directions. The acoustic modes at 30 MHz were generated using longitudinal and transverse lithium niobate transducers.

The analysis of the temperature or field dependence of elastic properties provides a convenient way to study magnetic critical behavior in many systems. For hexagonal $CsNiCl_3$, a Landau type approach has been used to determine the relationship between the variations in the elastic constants C_{33} and C_{11} and the various order parameters [29]. This coupling occurs due to magnetoelastic contributions to the free energy of the form $\sim g e_i S^2$, where e_i is an element of the strain tensor and S is the order parameter. A similar approach can be used to include coupling terms which account for the application of a magnetic field along the c axis. One result of this new model [31] indicates that the relative variation $\Delta C_{33}/C_{33}$ can be generalized as

$$\frac{\Delta C_{33}(T, H)}{C_{33}} = -\Delta + \gamma S(T, H)^2, \tag{1}$$

where Δ and γ are constants specific to the magnetic transition of interest, while the temperature and field dependencies are directly associated with those of the order parameter S. According to (1), C_{33} is expected to show a discontinuity even in the case of a continuous phase transition. Thus, results on C_{33} cannot be used to discriminate between a continuous and weakly first-order transition. This type of behavior is to be expected whenever a linear-quadratic coupling, between the strain and the order parameter, is allowed by symmetry [29]. In order to clearly determine the character of the transition of the 120° phase, other ultrasonic modes need to be used, in particular, those that depend exclusively on quadratic-quadratic coupling terms (e^2S^2). The allowed coupling terms, compatible with hexagonal symmetry [not included in our previous analysis [29]] are simply

$$F_c(S, e_i) = \frac{g_{s_4}}{2}(e_4^2 + e_5^2)S_z^2 + \frac{g_{s_6}}{2} e_6^2 S_z^2 + \frac{g_{\beta_4}}{2}(e_4^2 + e_5^2)S_\perp^2 + \frac{g_{\beta_6}}{2} e_6^2 S_\perp^2, \tag{2}$$

where the notation of Ref. [29] has been used. As these coupling terms are quadratic in strain, the variation in the elastic constants can be written as

$$\frac{\Delta C_{44}}{C_{44}} = \frac{\Delta C_{55}}{C_{55}} = g_{s_4} S_z^2 + g_{\beta_4} S_\perp^2 \tag{3}$$

$$\frac{\Delta C_{66}}{C_{66}} = g_{s_6} S_z^2 + g_{\beta_6} S_\perp^2. \tag{4}$$

In the case of an hexagonal structure, C_{44} and C_{66} can be obtained by measuring the velocity of transverse waves propagating along and perpendicular to the c axis, respectively.

Figure 1 shows the most significant results of the temperature dependence of $\Delta C_{66}/C_{66}$ with the magnetic field applied along the c axis. At $H = 0$ T, the onset of the L-E phase transition is clearly visible ($T_{N_2} = 4.33$ K) while the variation at T_{N_1} is barely noticeable. The results show two distinct behaviors depending on whether the value of the field is lower or higher than H_m. In the elliptical phase, C_{66} softens as the temperature decreases while the opposite trend is observed in the 120° spin phase above H_m. The observed temperature dependencies of $\Delta C_{66}/C_{66}$ are perfectly consistent with the Landau predictions (4) and these data can be used to estimate the temperature dependence of the order parameter $S_\perp$. The results of this analysis, obtained at different fields, are presented in Fig. 2 as a function of the reduced temperature $\tau = 1 - T/T_{N_2}$ on a log-log plot. All curves show a well defined power law behavior over a minimum of two decades in τ. Clearly, for $H < 1.5$ T a unique scaling is observed, confirming that $\beta_E = 0.35 \pm 0.02$ is field independent in the elliptical phase. As the value of the field approach H_m, the value of the critical exponent β suddenly decreases and then gradually increases at higher fields. The inset in Fig. 2

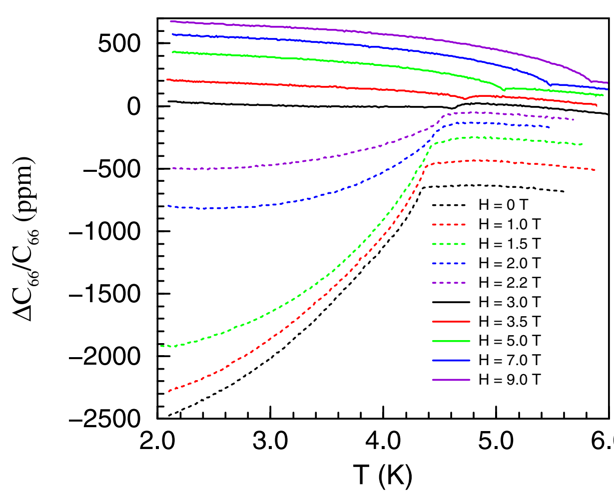

FIG. 1 (color online). Relative variation of the elastic constant C_{66} as a function of temperature. The broken and continuous lines represent results obtained below and above $H_m = 2.3$ T, respectively.

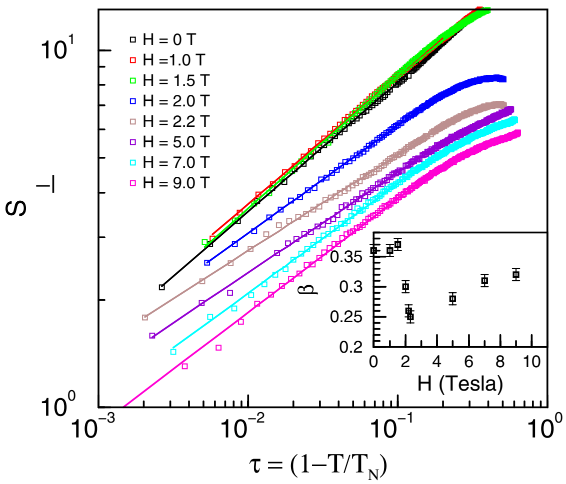

FIG. 2 (color online). Order parameter as a function of the reduced temperature $\tau = 1 - T/T_{N_2}$ calculated using (4) and the results presented in Fig. 1. The data obtained at different field are represented by symbols while lines represent fitted data at small τ using a simple power law. The inset shows the field dependence of the critical exponent β obtained from the power law fits.

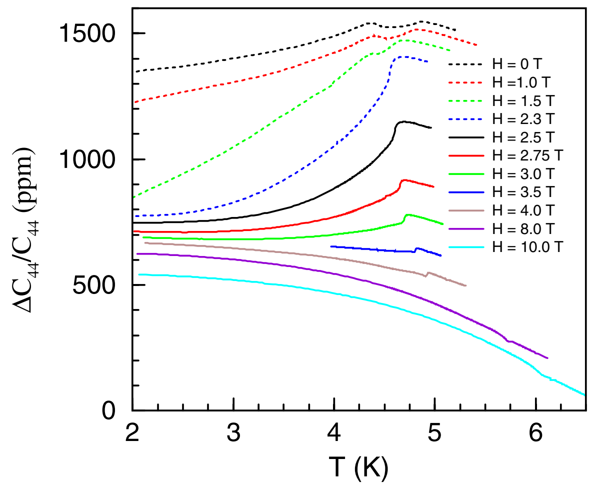

FIG. 3 (color online). Relative variation of the elastic constant C_{44} as a function of temperature. The broken and continuous lines represent results obtained below and above $H_m = 2.3$ T, respectively.

illustrates in detail how the value of β evolves as a function of a magnetic field for $CsNiCl_3$. Very close to the multicrital point, β reaches a minimum of $\beta = 0.25 \pm 0.02$ which corresponds to the predicted value for $n = 2$ chirality [5] but is also close to that of tricriticality, $\beta = 1/4$. At higher fields, β increases significantly. As noted previously [15,16], variation in the value of effective critical exponents as a function of an irrelevant parameter (in this case, H) may indicate a weak fluctuation-induced first-order transition.

Close inspection of the upper curves presented in Fig. 1 show an unexpected dip right at the para-120° phase boundary. This very small anomaly persists at all fields above H_m and could be interpreted as the effect of a weakly first-order transition. Motivated by these results, additional measurements were made using transverse waves propagating along the c axis and polarized in the basal plane to obtain C_{44}. This series of results was obtained with an exceptionally high resolution of 0.1 ppm. The data are presented in Fig. 3 as a function of temperature. At $H = 0$, two distinct features are noticeable and correspond to the onset of the phase transitions at T_{N_1} and T_{N_2}. As the field is increased, both anomalies merge at $H_m = 2.3$ T. Above the multicrital point (see continuous lines), the observed temperature dependence changes within the 120° phase as the field increases. Moreover, no power law relationship, as predicted by the Landau model (3), could be identified. More significantly, a steplike variation is noticeable at the critical temperature. These observations taken all together cannot be reconciled with a continuous phase transition.

As a test of the first-order character of the para-120° phase transition, the possibility of thermal hysteresis was investigated. A collection of thermal cycles, realized using a cooling-heating rate of 0.1 K/ min, is presented in Fig. 4. The results obtained for the 120° phase are compared to the data collected at $H = 0$ T. At zero field, where all experimental evidence presented in this Letter clearly indicates that the phase transition is continuous, no significant hysteresis is observed. However, the transition to the 120° spin phase shows a difference between the data collected during the heating and cooling processes. Those differences are small but are systematically observed at all field values. The hysteresis is maximum just below the critical temperature and persists over a tempera-

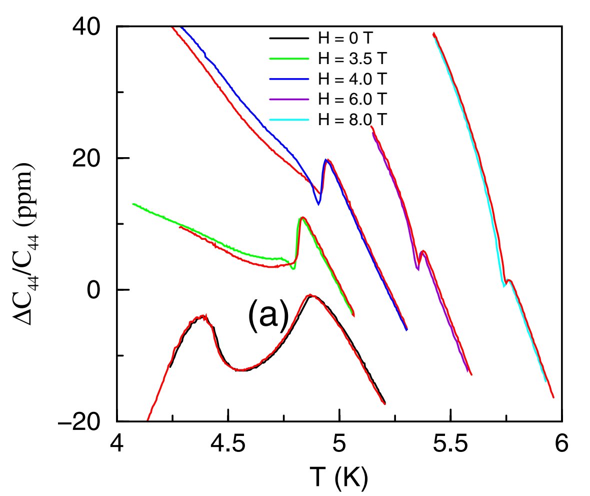

FIG. 4 (color online). Thermal cycle analysis realized at different fields using the relative variation of the elastic constant C_{44}. The data collected during the cooling process are all represented in red color for clarity. Curve (a) corresponds to the zero field transition at T_{N_2}. All other curves are associated with the transition to the 120° phase.

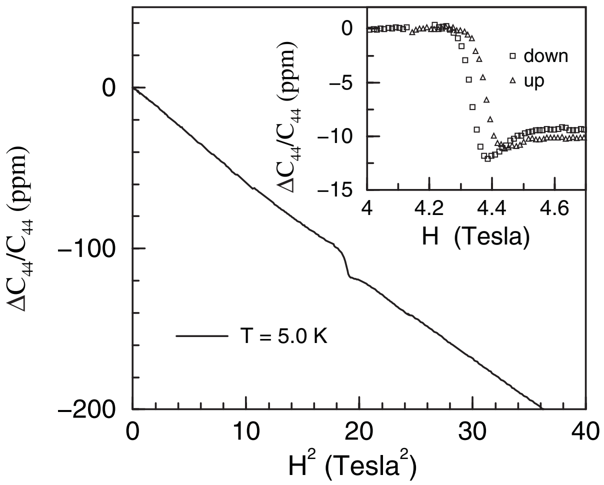

FIG. 5 (color online). Relative variation of the elastic constant C_{44} as a function of H^2 measured at $T = 5$ K. The inset shows the relative variation of C_{44} after subtracting the magnetoelastic contribution observed in the paramagnetic phase.

ture range of about 0.5 K. An additional confirmation of first-order character is obtained from the field dependence of C_{44}. The data collected at $T = 5.0$ K, presented in Fig. 5 as a function of H^2, clearly show the quadratic field dependence of C_{44} in the paramagnetic phase [32]. The field dependence of C_{44} near the 120° phase transition shown in the insert of Fig. 5 has been isolated by subtracting this magnetostriction. It is clear that the steplike variation of C_{44}, along with the observed hysteresis, at the 120° phase boundary cannot be accounted for in the context of a continuous phase transition.

The data and analysis presented in this work serve to fill a long-standing gap regarding experimental support for the growing body of theoretical and numerical work that the phase transition in the prototypical geometrical frustrated system, the stacked triangular antiferromagnet, is fluctuation-induced first order in nature. $CsNiCl_3$ provides a convenient field-temperature phase diagram for this purpose with a phase boundary line to the 120° spin structure which may be sampled at various points. Sound velocity measurements have proven to be an accurate tool for obtaining high-resolution data on the various order parameters (similar experiments are planned for $CsMnI_3$). The possibility to extract effective (field dependent) critical exponents, the weak nature of the discontinuities and small hysteresis, taken together, provide evidence for the weakness of the first-order character of this transition.

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[1] R. Moessner and A. P. Ramirez, Phys. Today **59**, No. 2, 24 (2006).
[2] J. Villian, J. Phys. (France) **38**, 385 (1977).
[3] G. Toulouse, Communications in Physics **2**, 115 (1977).
[4] M. F. Collins and O. A. Petrenko, Can. J. Phys. **75**, 605 (1997).
[5] H. Kawamura, J. Phys. Soc. Jpn. **56**, 474 (1987).
[6] H. Kawamura, J. Phys. Condens. Matter **10**, 4707 (1998).
[7] *Magnetic Systems with Competing Interactions*, edited by H. T. Diep (World Scientific, Singapore, 1994).
[8] H. Weber *et al.*, Int. J. Mod. Phys. B **9**, 1387 (1995).
[9] V. P. Plakhty, J. Kulda, D. Visser, E. V. Moskvin, and J. Wosnitza, Phys. Rev. Lett. **85**, 3942 (2000).
[10] G. C. DeFotis, M. L. Laccheo, and H. A. Katori, Phys. Rev. B **65**, 094403 (2002).
[11] A. Peles and B. W. Southern, Phys. Rev. B **67**, 184407 (2003).
[12] P. Azaria, B. Delamotte, and T. Jolicoeur, Phys. Rev. Lett. **64**, 3175 (1990).
[13] M. L. Plumer and A. Mailhot, J. Phys. Condens. Matter **9**, L165 (1997).
[14] *Frustrated Spin Systems*, edited by H. T. Diep (World Scientific, Singapore, 2004).
[15] B. Delamotte, D. Mouhanna, and M. Tissier, Phys. Rev. B **69**, 134413 (2004).
[16] A. Peles, B. W. Southern, B. Delamotte, D. Mouhanna, and M. Tissier, Phys. Rev. B **69**, 220408(R) (2004).
[17] K. Kanki, D. Loison, and K. D. Schotte, J. Phys. Soc. Jpn. **75**, 015001 (2006).
[18] P. Calabrese, A. Pelissetto, and E. Vicari, Nucl. Phys. **B709**, 550 (2005).
[19] D. J. Bergman and B. I. Halperin, Phys. Rev. B **13**, 2145 (1976).
[20] D. A. Tindall, M. O. Steinitz, and M. L. Plumer, J. Phys. F **7**, L263 (1977).
[21] M. L. Plumer, K. Hood, and A. Caillé, Phys. Rev. Lett. **60**, 45 (1988).
[22] H. Kawamura, A. Caillé, and M. L. Plumer, Phys. Rev. B **41**, 4416 (1990).
[23] M. Mao, B. D. Gaulin, R. B. Rogge, and Z. Tun, Phys. Rev. B **66**, 184432 (2002).
[24] D. Beckmann, J. Wosnitza, H. v. Lohneysen, and D. Visser, Phys. Rev. Lett. **71**, 2829 (1993).
[25] M. Enderle, R. Schneider, Y. Matsuoka, and K. Kakurai, Physica (Amsterdam) **234–236B**, 554 (1997).
[26] D. P. Almond and J. A. Rayne, Phys. Lett. **55A**, 137 (1975).
[27] P. B. Johnson, J. A. Rayne, and S. A. Friedberg, J. Appl. Phys. **50**, 1853 (1979).
[28] M. Poirier, A. Caillé, and M. L. Plumer, Phys. Rev. B **41**, 4869 (1990).
[29] G. Quirion, T. Taylor, and M. Poirier, Phys. Rev. B **72**, 094403 (2005).
[30] Y. Trudeau, M. Poirier, and A. Caillé, Phys. Rev. B **46**, 169 (1992).
[31] G. Quirion (to be published).
[32] J. A. Rayne, J. G. Collins, and G. K. White, J. Appl. Phys. **55**, 2404 (1984).