Pressure-induced stabilization of an intermediate phase in the triangular lattice

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LETTER TO THE EDITOR

Pressure-induced stabilization of an intermediate phase in the triangular lattice antiferromagnet CsNiCl$_3$

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Abstract
Pressure effects on the magnetic properties of the triangular lattice Heisenberg antiferromagnet CsNiCl$_3$ have been studied through heat capacity measurements up to the pressure of 6.6 kbar. With increasing pressure, two successive phase transitions at $T_{N1} = 4.74$ K and $T_{N2} = 4.24$ K at 0 kbar, which result from a small Ising-type anisotropy of $S = 1$ moments on Ni^{2+} ions, shift to higher temperatures in proportion to the pressure. Moreover, the pressure dependence of the entropy indicates that the intermediate phase AF$_1$ ($T_{N2} < T < T_{N1}$) is stabilized. These results suggest that the pressurization enhances the Ising-type anisotropy in the spin moments.

There has been considerable interest in magnetic properties of geometrically frustrated spin systems such as pyrochlore lattice [1] and triangular lattice magnets [2, 3]. The hexagonal ABX$_3$ compounds have exhibited novel experimental properties for triangular lattice antiferromagnets (TL-AF). The B ions form a magnetic chain along the c-axis via three halogen (X) ions and a triangular lattice in the XY basal plane. The intrachain exchange interaction along the c-axis is usually much larger than the interchain interaction in the XY basal plane. This gives rise to a quasi-one-dimensional behaviour in the high temperature region, while in the low temperature region the interchain interaction plays an important role in the magnetic properties and the system is thought to show the features of a TL-AF. The magnetic properties of such compounds are described by the following Hamiltonian:

$$H = -J_0 \sum_i^{\text{chain}} \boldsymbol{S}_i \cdot \boldsymbol{S}_{i+1} - J_1 \sum_{\langle i,j \rangle}^{\text{plane}} \boldsymbol{S}_i \cdot \boldsymbol{S}_j + D \sum_i (S_i^z)^2, \tag{1}$$
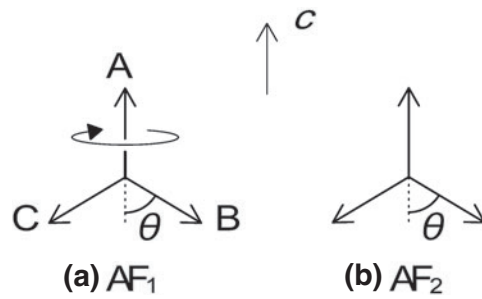
Figure 1. The schematic spin structure of the intermediate phase AF_1 (a) and the low temperature phase AF_2 (b). A, B and C denote the three sublattice spins. θ stands for the canting angle of the B, C sublattice from the c-axis.

where J_0 and J_1 are the intrachain and interchain exchange interaction, respectively, and D is the single-ion (Ising-type) anisotropy. It is noted that D can be neglected in the $S = 1/2$ system.

The compound $CsNiCl_3$ is a typical TL-AF with $S = 1$, which has $J/k_B = -16.6$ K, $J_1/k_B = 0.28$ K [4] and $D/k_B = -0.046$ K [5]. It exhibits two antiferromagnetic phase transitions at $T_{N1} \simeq 4.7$ and $T_{N2} \simeq 4.3$ K at zero field and $P = 0$ kbar [4–9]. The two successive transitions are associated with the spin components parallel and perpendicular to the c-axis. In the intermediate phase AF_1 ($T_{N2} < T < T_{N1}$), the spin moments at A sublattice sites in (a) of figure 1, which constitute one third of the total number of spins, are ordered in parallel with the c-axis, while the other two thirds, at B and C sublattice sites, are canted away from the c-axis with $\theta = 59°$ with the remaining degree of freedom in the XY components [10]. In other words, only the spin components parallel to the c-axis are ordered, while the canted spins still have a rotary degree of freedom around the c-axis as shown in figure 1(a). In the low temperature phase AF_2 ($T < T_{N2}$) (figure 1(b)), the degree of freedom in the XY components is also ordered; i.e., the spins at A, B and C sublattice sites are ordered with the so-called 120° structure in the basal plane.

Theoretical studies on the magnetic properties of TL-AF have been carried out extensively [2, 3]. The properties in $CsNiCl_3$ mentioned above are well explained by assuming that the anisotropy is of easy-axis type (Ising-like). On the other hand, if the anisotropy is of the easy-plane type (XY-like), the spins form the 120° structure at an antiferromagnetic transition temperature T_N, accompanied with critical indices for a new universality class due to the chiral degeneracy. These features stimulated us to study the magnetic properties at low temperatures, which might be substantially modified by the type of single-ion anisotropy. If the anisotropy was controlled artificially, one could investigate the novel phase transitions in TL-AF in detail.

With this motivation, we have studied the pressure effects on $CsNiCl_3$. In this letter, we report the pressure dependence of the heat capacity up to the pressure of 6.6 kbar. It will be shown that the Ising-type anisotropy in $CsNiCl_3$, rather than the XY anisotropy, is enhanced with increasing pressure, leading to a slight suppression of the canting angle.

A single crystal of $CsNiCl_3$ prepared by the Bridgman method was used for the present experiments. The heat capacity C_P under hydrostatic pressure P was measured by the conventional adiabatic heat pulse method with a piston–cylinder-type clamp cell made of Cu–Be. The sample (1.145 g), the Apiezon-J oil (0.422 g) used as the pressure-transmitting oil and a few milligrams of Sn metal as a pressure manometer were inserted directly into the sample space in the sample cell to ensure good thermal contact between the cell and the
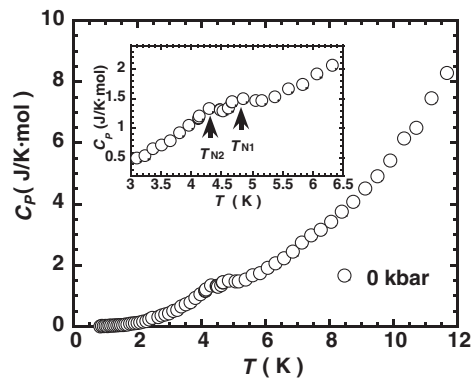
Figure 2. The temperature dependence of the heat capacity C_P of CsNiCl$_3$ at $P = 0$ kbar. An inset shows a C_P versus T plot for 3.0 K $\leqslant T \leqslant$ 6.5 K. T_{N1} and T_{N2} are indicated by the arrows.
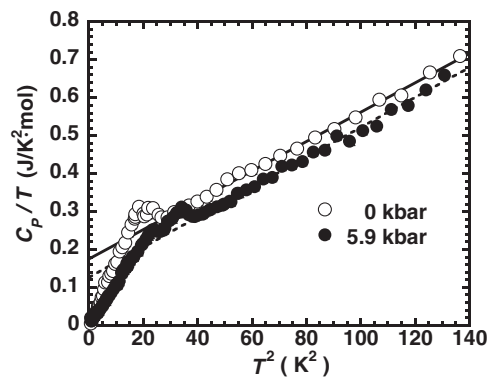

Figure 3. The magnetic heat capacity of CsNiCl$_3$ plotted as C_P/T versus T at $P = 0$ and 5.9 kbar. The solid and dashed lines are the best fits with equation (1) using the parameters $\alpha = 0.18$ and 0.13 J K^{-2} mol^{-1}, $\beta = 0.0039$ and 0.0040 J K^{-4} mol^{-1} for $P = 0$ and 5.9 kbar, respectively.

sample. The pressure dependence of the heat capacity of the Apiezon-J oil was estimated from the data in [11]. The pressure was determined within an error of 0.1 kbar by the pressure dependence of the superconducting transition temperature of Sn measured by means of the ac susceptibility. The contribution of the sample heat capacity to the total, which includes the sample, the pressure cell and the pressure-transmitting oil, is within 10–30% in the present experimental temperature range 0.7 K $\leqslant T \leqslant$ 12 K.

The temperature dependence of C_P in CsNiCl$_3$ at $P = 0$ kbar is shown in figure 2. Two distinct anomalies of C_P can be seen at $T_{N1} = 4.74$ K and $T_{N2} = 4.29$ K as reported in the previous studies [4–9]. It was found that C_P obeys the following formula in the temperature range above T_{N1}, 6 K $\leqslant T \leqslant$ 12 K, as shown in figure 3:

$$C_P = \alpha T + \beta T^3. \tag{2}$$

The T-linear term is interpreted as the spin wave excitation due to one-dimensional antiferromagnetic correlations [5], and the T^3-dependence comes from the lattice heat capacity of CsNiCl$_3$. In this case, $\alpha = 0.18$ J K^{-2} mol^{-1} and $\beta = 0.0039$ J K^{-4} mol^{-1} are obtained for 0 kbar. This formula is valid for pressure up to 6.6 kbar, which enables us to extract the magnetic heat capacity from C_P under pressure.
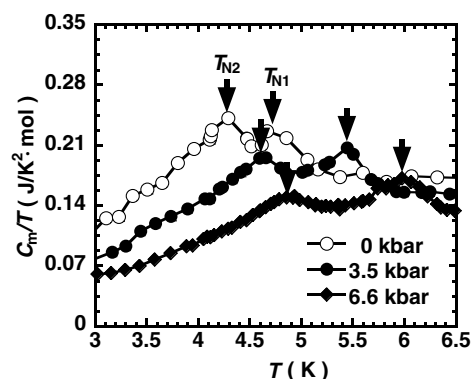
Figure 4. The magnetic heat capacity of $CsNiCl_3$ plotted as C_m/T versus T under various pressures $P = 0$, 3.5 and 6.6 kbar. Arrows point to the transition temperatures T_{N1} and T_{N2}.
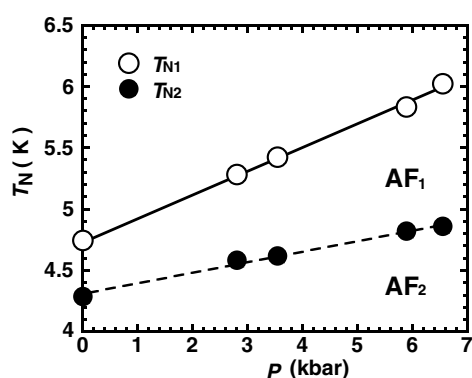

Figure 5. The pressure dependence of T_{N1} and T_{N2}. The solid and dashed lines are guides to the eyes for the experimental results.

Figure 4 shows the temperature dependence of the magnetic heat capacity divided by the temperature, C_m/T, at $P = 0$, 3.5 and 6.6 kbar. With increasing pressure, T_{N1} and T_{N2} shift to higher temperatures. The pressure dependence of T_{N1} and T_{N2} determined by the anomalies in C_m/T is shown in figure 5. It is seen that T_{N1} and T_{N2} increase in proportional to the pressure in the present experimental range. The expansion of the AF_1 and AF_2 phases might be caused by enhancement of J_0 and/or J_1 as a function of pressure. The rate of increase of T_{N1} caused by pressure, dT_{N1}/dP ($=1.91 \times 10^{-4}$ K bar^{-1}), is about twice that of T_{N2}, dT_{N2}/dP ($=0.87 \times 10^{-4}$ K bar^{-1}). This means that AF_1 is more stabilized than AF_2 by pressurization. According to Kawamura and Miyashita, AF_1 is more stabilized for the system with the stronger Ising-type anisotropy [2]. From these results, we can understand pressurization giving rise to the enhancement of the Ising-type anisotropy D in $CsNiCl_3$.

In order to investigate how the spin structure changes upon pressurization, we analyse the pressure dependence of the magnetic entropies, S_{XY}, S_I and S_{total} using the following equations:

$$S_{XY} = \int_0^{T_{N2}} \frac{C_m}{T} \, dT, \tag{3}$$
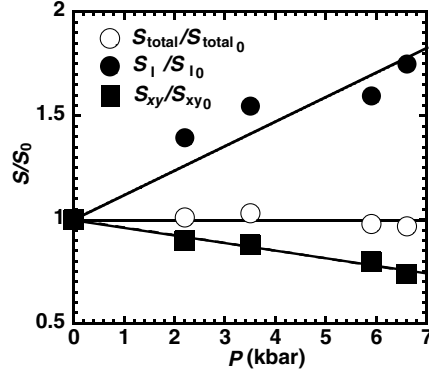
$$S_I = \int_{T_{N2}}^{T_{N1}} \frac{C_m}{T} \, dT \tag{4}$$

Figure 6. The pressure dependence of the magnetic entropies, S_{total}, S_{I} and S_{XY}, in pressure range 0 kbar $\leqslant P \leqslant$ 6.6 kbar normalized against the values at 0 kbar, S_{total_0}, S_{I_0} and S_{XY_0}, respectively. The solid lines are guides to the eyes for experimental results.

and

$$S_{\text{total}} = S_{XY} + S_{\text{I}} = \int_0^{T_{\text{N1}}} \frac{C_{\text{m}}}{T} \, \mathrm{d}T. \tag{5}$$

The values of S_{XY} and S_{I} reflect the degrees of freedom for the XY and Ising components in the respective magnetic phases. Thus we can get information about the spin structure of $CsNiCl_3$ under pressure. Figure 6 shows the pressure dependences of S_{I}, S_{XY} and S_{total} for pressure up to 6.6 kbar, which are normalized by the values at 0 kbar: $S_{\text{I}_0} = 9.88 \times 10^{-2}$, $S_{XY_0} = 3.35 \times 10^{-1}$ and $S_{\text{total}_0} = 4.34 \times 10^{-1}$ J K^{-1} mol^{-1}, respectively. S_{total_0} is 5% of the total entropy $R \ln 3$ (R: gas constant), which is expected for magnetic systems with $S = 1$ due to the Ni^{2+} ions and essentially unchanged by pressure. It is noted that the pressure dependence of $S_{\text{total}}/S_{\text{total}_0}$ is unchanged under pressure, suggesting that the degree of freedom of the spin moments released below T_{N1} is also independent of the pressure. On the other hand, the pressure dependences of S_{XY}/S_{XY_0} and $S_{\text{I}}/S_{\text{I}_0}$ are changed substantially by pressurization; $S_{\text{I}}/S_{\text{I}_0}$ increases with increasing pressure while S_{XY}/S_{XY_0} decreases, linearly. We obtained $(1/S_{\text{I}_0}) \, \mathrm{d}S_{\text{I}}/\mathrm{d}P = 1.18 \times 10^{-4}$ and $(1/S_{XY_0}) \, \mathrm{d}S_{XY}/\mathrm{d}P = -0.37 \times 10^{-4}$ bar^{-1} from the slope of the solid line in figure 6. These results suggest that the degree of freedom ascribed to the Ising component is enhanced with increasing pressure. In other words, the angles θ described in figure 1(a) decrease upon pressurization. Assuming that the value of S_{I} (S_{XY}) continues to increase (decrease) in proportion to P up to the higher pressures around 20–30 kbar, we expect to have $\theta \simeq 0$ in the present system. Although it has been reported that $CsNiCl_3$ has a quantum fluctuation of the spin moment due to the one-dimensional Heisenberg antiferromagnetism with $S = 1$ [12–16], the quantum fluctuation might be strongly reduced in the higher pressure range. We are anxious to carry out microscopic measurements based on neutron scattering measurements for $CsNiCl_3$ under the pressure. If pressurization gives rise to enhancement of the Ising-type anisotropy for the other ABX_3 compounds, it would be very interesting to investigate the pressure effects on the phase transition for TL-AF with XY-type anisotropy such as $CsMnCl_3$ [17]. One would observe a crossover of the anisotropy from XY-type to Ising-type, which changes the nature of the phase transitions, upon pressurization.

In conclusion, we have studied the heat capacity of a typical triangular lattice Heisenberg antiferromagnet $CsNiCl_3$ under pressure up to 6.6 kbar. We found that the successive phase transition temperatures T_{N1} and T_{N2}, which arise from a small Ising-type anisotropy of the $S = 1$ moments, shift to higher temperatures in proportion to pressure at the rates of 1.91×10^{-4}

and 0.87×10^{-4} K bar^{-1}, respectively. In other words, the intermediate phase AF$_1$ and the low temperature phase AF$_2$ expand upon pressurization. We also showed that the entropy of the Ising component in the spin moments S_{I} increases with increasing pressure, while that of the XY component S_{XY} decreases linearly. These results are explained by the AF$_1$ phase becoming stable with increasing pressure due to the pressure-induced enhancement of the Ising component in the $S = 1$ spin moments.

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