

# Novel multiferroic phase of CsCuCl<sub>3</sub> in High Magnetic Fields

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**Abstract.** We measured the magnetization and the electric polarization under pulsed magnetic field up to 44 T. In magnetization measurements for  $H//b^*$  (perpendicular to the  $ca$ -plane), we found a new phase transition through the differential magnetization at 17 T, which is slightly higher than the field range of the magnetization plateau. This finding was supported by the electronic polarization measurements, with the observation of a bump structure in  $dP/dB$  signal. These results suggest the new phase transition.

## 1. Introduction

CsCuCl<sub>3</sub> is a family of a hexagonal perovskite, which belongs to the  $P6_122$  space group. The magnetic Cu<sup>2+</sup> ions ( $S = 1/2$ ) forms a stacked triangular-lattice and exhibits exotic magnetic ground states with and without an external magnetic field. In this material, a ferromagnetic interaction along the chain direction ( $c$ -axis) is dominant, and a frustrated antiferromagnetic interaction in the  $ab$ -plane is as small as one-sixth of the main ferromagnetic interaction.

In the absence of an external magnetic field, CsCuCl<sub>3</sub> undergoes a transition to a spin-helix structure at 10.65 K ( $T_N$ ), in which the spins are arranged into the well-known 120° structure in the  $ab$ -plane with an incommensurate (IC) modulation along the  $c$ -axis owing to the Dzyaloshinskii-Moriya interaction. [1] Nojiri *et al.* reported that when the magnetic field is applied parallel to the  $c$ -axis, the magnetization curves exhibit a jump at  $\mu_0 H_J \sim 12.5$  T and then saturate at  $\mu_0 H_{\text{sat}} \sim 30$  T. When an external magnetic field is applied within the  $ab$ -plane, a plateau-like anomaly was observed between  $\mu_0 H_{p1} \sim 11$  T and  $\mu_0 H_{p2} \sim 13$  T.



These field-induced anomalies were theoretically investigated by Nikumi and Shiba with taking into account a quantum effect [2,3]. They proposed that the magnetization jump at  $\mu_0 H_J$  can be attributed to the transition from an in-plane  $120^\circ$  structure to a coplanar structure. In a high-field phase (coplanar structure), the spins gradually tilt to the field orientation by further increasing the magnetic field towards  $\mu_0 H_{\text{sat}}$ . On the other hand, application of  $H \perp c$  is expected to change the in-plane IC solution to the out-of-plane one at a certain field, and then cause a transition to the commensurate (C) state at larger fields. This model is widely believed to explain these field-induced phenomena.

In this paper, we report the experimental observation of an additional field-induced phase transition in  $\text{CsCuCl}_3$  through magnetization measurements in magnetic fields applied normal to the  $c$ -axis. Owing to the low crystallographic symmetry, some kinds of symmetry breaking caused by magnetic order result in the emergence of polarization as observed in a related material of  $\text{TlCoCl}_3$  [4]. Measurement of electric polarization in pulsed high magnetic field on  $\text{CsCuCl}_3$  revealed that this novel phase has spontaneous electric polarization.

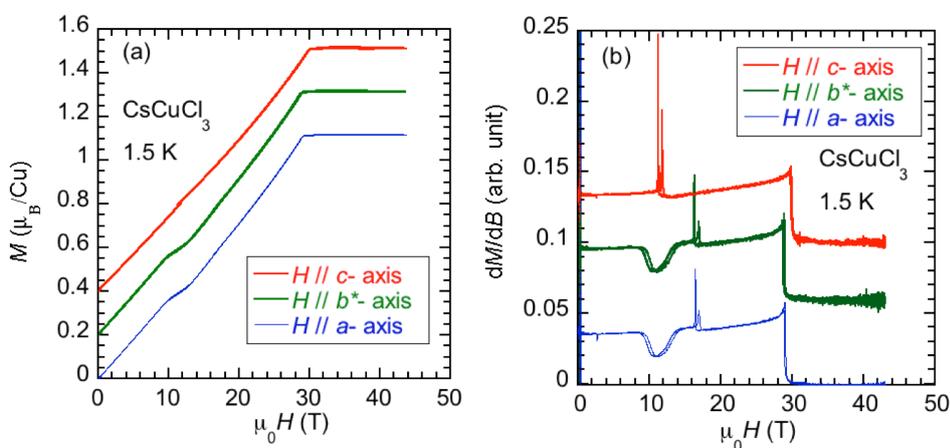
## 2. Experiment

In this study, we investigated magnetic and dielectric properties in single crystals of  $\text{CsCuCl}_3$  in high magnetic fields. Measurements in high magnetic fields were performed using non-destructive pulse magnets installed at The Institute for Solid State Physics at The University of Tokyo. For magnetization and electric polarization measurements, magnetic fields up to 44 T (pulse duration of 8 ms), were generated using unipolar and bipolar pulse magnets, respectively.

Single crystals of  $\text{CsCuCl}_3$  were synthesized by dissolving stoichiometric amounts of  $\text{CsCl}$  and  $\text{CuCl}_2 \cdot \text{H}_2\text{O}$  in water. And the solution evaporates slowly. The single crystals grew as hexagonal bipyramids and were about 4 cm long along the  $c$ -axis. By the back Laue method, we determined the principal axes of the sample and cut them along perpendicular or parallel to the  $c$ -axis with using a wiresaw.

Magnetization ( $M$ ) measurements were performed by the induction method using two pickup coils placed coaxially. In electric polarization ( $P$ ) measurement, we measured polarization currents caused by the field-induced changes in electric polarization. To eliminate the effect of induced voltage in wiring, the data in positive and negative field scans were averaged [5], and then integrated.

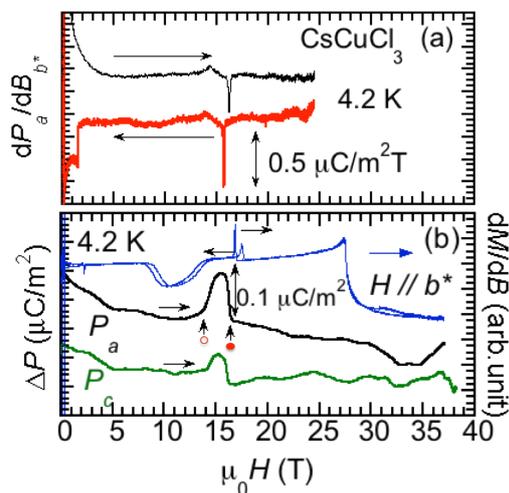
## 3. Results and discussion



**Figure 1.** (colors online) (a) The field dependence of magnetization up to 44 T at 1.5 K for fields along  $c$  (red),  $b^*$  (green),  $a$  (blue), respectively. The data were vertically offset for clarity. (b) The field dependence of differential magnetization for each field direction.

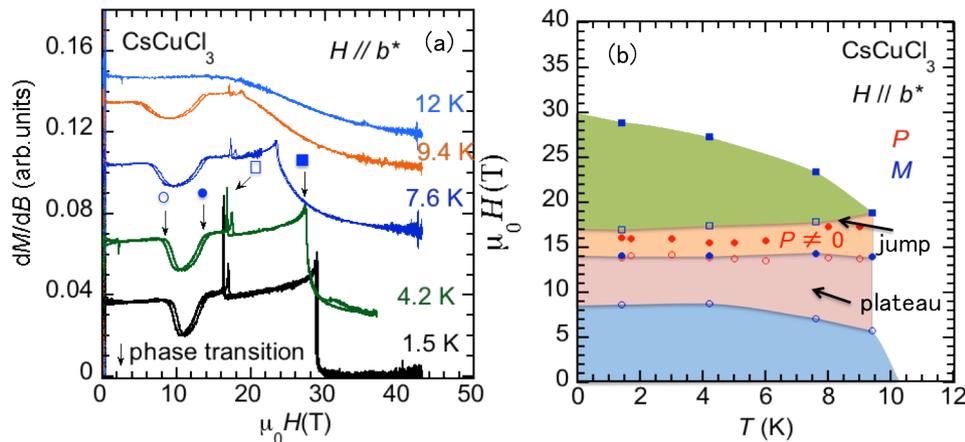
Figure 1(a) shows the field dependence of magnetization. We applied the magnetic fields along  $c$ ,  $a$ , and  $b^*$ -axis (perpendicular to the  $ca$ -plane). The overall features of the magnetization curves are

consistent with the results in the previous report [1]. However, close look into the present data reveals the existence of novel features as exhibited in the differential magnetization curves in Fig. 1(b). For  $H // c$ , a sharp peak was observed at around 11 T corresponding to the magnetization jump. On the other hand, the differential magnetization for  $H // b^*$ , which is nearly identical with that for  $H // a$ , decreases between 9 T and 14 T, corresponding to the plateau-like structure. In addition to these features reported earlier, the present data show clear peaks at  $\sim 17$  T indicating abrupt jumps in magnetization. Since we observed difference in the peak fields between up- and down-sweeps, we regard these anomalies as the transition of first order.



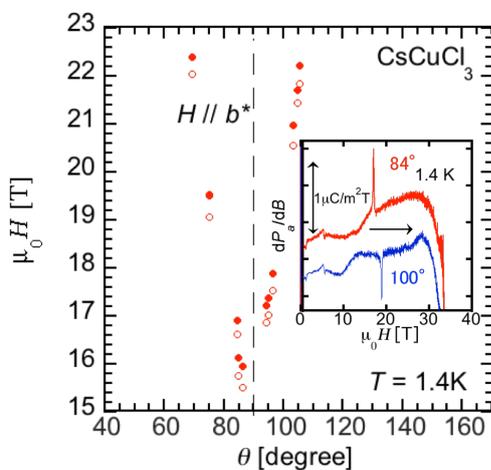
**Figure 2.** (colors online) (a) Differential electric polarization parallel to the  $a$ -axis as a function of applied magnetic fields along the  $b^*$ -axis in the field increasing (black) and decreasing (red) processes. The data were vertically offset for clarity. (b) The field dependence of differential magnetization (blue) and electric polarization along the  $a$  ( $P_a$ ) and  $c$  ( $P_c$ ) -axes for  $H // b^*$ .

Figure 2(a) shows differential electric polarization ( $dP/dB$ ) parallel to the  $a$ -axis as a function of applied magnetic fields along the  $b^*$ -axis. A bump and successive opposite sharp peak structures are observed at about 14 T and 17 T, respectively. The profiles in both up- and down-sweeps show negative peaks in  $dP/dB_{b^*}$  at the fields of 16.5 T and 15.5 T, respectively. The integrated field dependence of the electric polarization is shown in Fig. 2(b) together with the differential magnetization at the same temperature. Significant  $\Delta P$  along the  $a$ - and  $c$ -axes are observed between 14 T and 16 T. The  $\Delta P$  along the  $a$ -axis is roughly two times larger than that along the  $c$ -axis. The observed  $\Delta P \sim 0.5 \mu\text{C}/\text{m}^2$  is less than  $10^{-3}$  of  $P$  in the related material,  $\text{TlCoCl}_3$ , and can be discernible only in highly sensitive measurements in pulsed-fields.



**Figure 3.** (colors online) (a) The field dependence of differential magnetization at various temperatures for  $H // b$ -axis. The data were vertically offset for clarity. (b) Magnetoelectric phase diagram in the  $H_{b^*}$ - $T$  plane. Red (Blue) circles represent transition fields determined by the inflection points of the  $P$ - $H$  ( $M$ - $H$ ) curves.

Figure 3(a) shows the field dependence of differential magnetization at various temperatures between 1.5 K and 12 K. For  $H // b^*$ , a sharp jump is observed at  $\sim 17$  T below  $T_N (= 10.65$  K). The cusp-like structure that emerges at the saturation field moves to lower field with increasing temperature, whereas the other features for plateau-like anomalies and peaks are less sensitive to the temperature. The arrows in Fig. 3(a) represent our definition of the transition fields. Figure 3(b) shows magnetoelectric phase diagrams in the  $H_{b^*}$ - $T$  plane determined from these results. The novel polar phase emerges in the orange area between 14 T and 17 T. Multiple phase transitions of  $\text{CsCuCl}_3$  for in-plane fields have been reported through specific heat measurements and neutron diffraction [6,7,8]. Our present results revealed the emergence of a novel multiferroic phase in between the IC3 and commensurate phases shown in Fig. 8 of Ref. 7. Careful reader might notice the discrepancy of the transition field at  $\sim 17$  T determined by magnetization and electric polarization, which can be ascribed to the finite misalignment of the field angle as shown in the following.



**Figure 4.** (colors online) Angular dependence of the transition field determined by polarization measurements at 1.4 K. The  $\theta$  denotes polar angle from the  $c$  to  $b^*$  axis. The insets show differential polarization along the  $a$ -axis as a function of magnetic field at  $\theta = 84^\circ$  and  $100^\circ$ .

Figure 4 shows angular dependence of the transition fields determined by measurements of electric polarization along the  $a$ -axis. The  $\theta$  denotes the polar angle of the applied field from the  $c$ - to the  $b^*$ -axis. The inset shows field dependence of differential polarization along the  $a$ -axis at  $\theta = 84^\circ$  and  $100^\circ$ . The transition field steeply increases with tilting away from the  $b^*$  axis. The  $dP_a/dB$  signal changed its sign between  $\theta < 90^\circ$  and  $\theta > 90^\circ$ , and was hardly discernible at  $\theta = 90^\circ$ .

Here, we will discuss the possible origin of the phase transitions at  $\sim 17$  T for  $H \perp c$ -axis. Early neutron experiments reported deformation of the helical structure up to the plateau-like region [8], at which field dependence of the index  $\delta$  of the incommensurate magnetic peak at  $(1/3, 1/3, \delta)$  also shows a plateau at  $\delta \sim 0.047$  [9]. With further increasing the field, the  $\delta$  started to decrease again toward zero at  $\sim 17.5$  T [9]. The present polar phase emerges in the region with this small  $\delta$ , and hence, the period of the incommensurate spin modulation becomes sufficiently long in this field region.

According to the theoretical study by Nikuni and Jacobs [3], application of the transverse fields realizes "out-of-plane" incommensurate spin order in the intermediate field region. Although the details of the "out-of-plane" state was not well described, simple cycloidal structure cannot explain the coexistence of  $P_a$  and  $P_c$  in the polar state within the framework of the spin-current model [10] while the modulation vector pointing to the  $c$ -axis. On the other hand, the same authors also mentioned the solitonic phase as one of the in-plane solutions at large fields. Recently, a solitonic lattice state was found in a chiral heli-magnet  $\text{Cr}_{1/3}\text{NbS}_2$  in fields applied normal to the ferromagnetic spin chains [11]. Although it is not clear whether such solitonic state can accommodate with electric polarization in  $\text{CsCuCl}_3$  even if it exists, the observed polar phase will be of interest as a novel phase of chiral magnets in the transverse fields.

Recent X-ray study on  $\text{CsCuCl}_3$  revealed that usual crystals of this material contain mixed crystallographic domains with right- and left-hand chirality [12], which may diminish the net electric polarization detectable in the whole sample. Future experiments on crystals having single chirality will clarify the intrinsic nature of the novel multiferroic phase in this material.

#### 4. Conclusion

We measured magnetization and electric polarization of single crystals of  $\text{CsCuCl}_3$  in pulsed magnetic field up to 44 T. For fields applied normal to the  $c$ -axis, we found novel multiferroic phase between 14 – 17 T.

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