Magnetic and electric properties in the distorted tetrahedral spin chain system \( \text{Cu}_3\text{Mo}_2\text{O}_9 \)

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Abstract. We study the multiferroic properties in the distorted tetrahedral quasi-one dimensional spin system \( \text{Cu}_3\text{Mo}_2\text{O}_9 \), in which the effects of the low dimensionality and the magnetic frustration are expected to appear simultaneously. We clarify that the antiferromagnetic order is formed together with ferroelectric properties at \( T_N = 7.9 \) K under zero magnetic field and obtain the magnetic-field-temperature phase diagram by measuring dielectric constant and spontaneous electric polarization. It is found that the antiferromagnetic phase possesses a spontaneous electric polarization parallel to the \( c \) axis when the magnetic field \( H \) is applied parallel to the \( a \) axis. On the other hand, there are three different ferroelectric phases in the antiferromagnetic phase for \( H \) parallel to the \( c \) axis.

1. Introduction

Recently, the discovery of the strong magnetoelectric effect in \( \text{TbMnO}_3 \) \(^1\) has rekindled significant interest in multiferroics displaying the interplay between ferromagnetic and ferroelectric properties. After that, the multiferroism has been extensively studied \(^2\) in transition metal oxides and a few microscopic mechanisms of this phenomenon have been proposed. The inverse Dzyaloshinskii-Moriya interaction and the inverse Kanamori-Goodenough interaction induce multiferroic properties in the spiral spin and collinear structures, respectively, where the magnetic superlattices are formed.\(^3\), \(^4\), \(^5\) The geometrical magnetic frustration also plays an important role as the origin of the nontrivial spin configuration which breaks the spatial inversion symmetry.\(^6\) Recently we reported a possibility that \( \text{Cu}_3\text{Mo}_2\text{O}_9 \) shows multiferroic behaviors without any magnetic superlattice formation.\(^7\) In ref.\(^7\), we focused on the dielectric properties and the electric polarization induced by an antiferromagnetic (AFM) spin order when the magnetic field \( H \) is applied along the \( c \) axis. In the present work, we report mainly the results for \( H \) parallel to the \( a \) axis.

\( \text{Cu}_3\text{Mo}_2\text{O}_9 \) has two distorted tetrahedral quasi-one dimensional quantum spin systems made from \( S = 1/2 \) spins along the \( b \) axis in its orthorhombic unit cell (see Figs. 1(a) and (b)).\(^8\), \(^9\) This compound has magnetic frustrations due to the tetrahedral spin alignment and the quasi-one dimensionality simultaneously. This compound undergoes an AFM phase transition at \( T_N = 7.9 \) K at zero magnetic field and shows a weak ferromagnetic order due to the spin canting at low
temperatures.[8, 9] The inelastic neutron scattering study shows the hybridization effects due to the $J_1$ and $J_2$ superexchange interactions between two elemental magnetic excitations, i.e., that of the quasi-one dimensional AFM spin system made from the $J_4 (= 4.0$ meV) superexchange interactions and that of the isolated AFM spin dimers made from the $J_3 (= 5.8$ meV) ones.[10, 11]

Figure 1. Schematics of the distorted tetrahedral chain in Cu$_3$Mo$_2$O$_9$ along the $b$ axis (a) and in the $ac$ plane (b). The circles indicate the $S = 1/2$ Cu$^{2+}$ ions and the symbols distinguish their coordinates along the $b$ axis from others. O$^{2-}$ and Mo$^{4+}$ ions are omitted. The dashed, solid, bold and dot-dashed lines distinguish the superexchange interactions $J_1 - J_4$ between Cu$^{2+}$ ions. The solid rectangle in (b) denotes the unit cell, which contains two tetrahedral chains.

2. Experiment
We measured the temperature $T$ and magnetic-field $H$ dependences of the dielectric constant $\epsilon_\alpha$ and $\epsilon_c$ in Cu$_3$Mo$_2$O$_9$ when $H$ is applied along the $a$ and $c$ axes. We prepared the plate-like single crystals of Cu$_3$Mo$_2$O$_9$ of which cross sections and thicknesses are typically about 60 mm$^2$ and 0.4 mm, respectively. To form a capacitor, the faces were coated with gold and attached using gold wires. The capacitance, of which the typical value was on the order of 10 pF, was measured using the impedance analyzer (Yokogawa-Hewlett-Packard 4192A). $\epsilon_\alpha$ ($\alpha = a$ or $c$) was obtained from the capacitance at 100 kHz with a peak voltage of 1 V. The magnetic field was applied using a superconducting magnet (Oxford Instruments, Teslatron S14/16), of which the maximum magnetic field was 16 T.

3. Results and Discussion
Figures 2(a) and (b) show the typical $T$ dependences of $\epsilon_\alpha$ ($\alpha = a$ or $c$) under a fixed $H$ along the $a$ axis ($H_a$), (the $\epsilon_\alpha$-$T$ curves), respectively, each of which has a (local) maximum value $\epsilon_\alpha^{\text{peak}}$ at $T_\alpha^{\text{peak}}$. $T_\alpha^{\text{peak}}$ increases at 6 T, but it decreases at 16 T. $\epsilon_a$ at 16 T shows two anomalies consisting of two peaks, as shown in Fig. 2(a). As shown in Fig. 2(c), the detailed $\epsilon_a$-$T$ curves under magnetic fields between 12 and 16 T, the $\epsilon_a$ above 15 T has two peaks indicated by arrows. The values of $T_\alpha^{\text{peak}}$ against $H$ are plotted in the $H$-$T$ phase diagram in Fig. 3(a) by the solid symbols. Figure 2(d) shows the typical $H$ dependences of $\epsilon_c$ from 8 to 12 K (the $\epsilon_c$-$H_a$ curves). The $\epsilon_c$-$H_a$ curves have a cusp between 8.3 and 9 K and two ones between 9.5 and 10 K, respectively. These are plotted in the phase diagram in Fig. 3(a) by the open symbols.

The inset of Fig. 3(a) shows the polarization-electric field ($P_c$-$E_c$) loops at 3 K under 0 and 13 T when the electric field $E$ and the magnetic field $H$ are applied along the $c$ and $a$ axes, respectively. Typical ferroelectric $P_c$-$E_c$ hysteresis loops were observed, indicating that the AFM phase is ferroelectric and has a spontaneous electric polarization parallel to the $c$ axis. This result is consistent with the fact that the peak height of $\epsilon_c$ is about ten times larger than that of $\epsilon_a$, as seen in Figs. 2(a) and (b). At 13 T, all of the saturated polarization, the spontaneous polarization and the coercive electric field are larger than the values at 0 T. These results indicate that the ferroelectric correlation increases with increasing $H$. These magnetic-field dependences
of electric polarization are different from the ones when the magnetic field is applied along the $c$ axis. The magnetic-field dependence of magnetization also depends on the direction of the magnetic field. We consider that the anisotropic electric property of Cu$_3$Mo$_2$O$_9$ is related to the anisotropic magnetization of this compound.\[8, 9\] And it suggests the ferroelectricity originating from the frustrating spin configuration as an origin of the multiferroic behavior.

Together with the phase boundary obtained from the $T$ dependence of the specific heat under $H$, we obtain the $(H-T)$ phase diagram in Fig. 3(a) when $H$ is applied parallel to the $a$ axis. The $T_N$ obtained by the specific heat is little bit lower than $T_{\text{peak}}$.

We compared Fig. 3(a) to the $H$- $T$ phase diagram from ref. \[7\] (Fig. 3(b)), which is obtained under $H$ along the $c$ axis. There are three different ferroelectric phases in the AFM phase of Fig. 3(b), indicating that the phase diagram for $H//a$ is simpler than that for $H//c$. When $H//c$, a change in direction of the spontaneous electric polarization occurs at the phase boundary running from $(H, T) = (8 \text{ T}, 2 \text{ K})$ to $(10 \text{ T}, 8 \text{ K})$. Around the tricritical point at $10 \text{ T}$ and $8 \text{ K}$, the change of the direction in the electric polarization causes a colossal magnetocapacitance effect.\[7\] When $H//a$, the $\epsilon_a$-$T$ curve shows two peaks under magnetic fields above $14 \text{ T}$, as shown in Fig. 2(c), suggesting that a new phase appears in the narrow region. Then, another tricritical point may exist around $(9 \text{ K}, 14 \text{ T})$. At this tricritical point, the strong magnetocapacitance effect has not been observed in the present work. This suggests that the strong magnetocapacitance effect originates from the change in the direction of the spontaneous electric polarization. We conclude that much different multiferroic behaviors occur when $H//a$ and $H//c$. At present we are interested in the multiferroic behaviors under high magnetic fields.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figures.png}
\caption{Typical temperature dependences of (a) the dielectric constant $\epsilon_a$, (c) its expansion between 12 and 16 T and (b) $\epsilon_c$ under fixed magnetic fields along the $a$ axis. For the visibility, the data were shifted. Arrows in (c) denote one and two peaks of dielectric constants. The magnetic-field dependence of the dielectric constant $\epsilon_a$ from 8 to 12 K is shown in (d).}
\end{figure}
Figure 3. The $H - T$ phase diagrams in Cu$_3$Mo$_2$O$_9$. The shape of symbols distinguish the physical quantities to be used to obtain the phase boundary. The triangles, squares and circles denote the dielectric constants along the $a$ and $c$ axes and specific heat, respectively. The solid (open) symbols denote the phase boundary obtained from the data of the $T (H)$ dependence. The inset of (a) shows typical polarization-electric field loops when the electric field is applied along the $c$ axis at 3 K under 0 and 13 T.

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