Observation of ferroelastic domains in layered magnetic compounds using birefringence imaging

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Abstract. The two-dimensional Heisenberg antiferromagnet (C2H5NH3)2CuCl4 is a candidate compound for the coexistence of ferroelectricity and ferroelasticity; however, the microscopic observations of multiferroic domains may still be unclear. In-plane birefringence imaging measurements were performed to observe the manner in which the ferroelectric and the ferroelastic domains change during phase transitions between 15 K and 300 K. It was found that 90° ferroelastic domains appeared in the ab-plane at 300 K. As the temperature decreased toward 15 K, each domain inverted at a certain temperature (T_a) without structural or magnetic phase transitions. The value of T_a was found to be significantly influenced by external stresses; therefore, birefringence imaging techniques are useful for investigating variations in ferroelastic domains with temperature. Furthermore, a structural phase transition from orthorhombic to monoclinic or triclinic occurred at 230 ∼ 240 K; however, no spontaneous polarization appeared in the ab-plane over the entire investigated range.

1. Introduction
The layered magnetic compound (C2H5NH3)2CuCl4 (abbreviated as EACuCl) is known as a representative two-dimensional Heisenberg magnet[1]. This compound essentially comprises CuCl4 layers that are well separated from one another by a bilayer of alkylammonium chains (C2H5NH3). The intralayer exchange interaction is ferromagnetic owing to the antiferrodistortive arrangement of the Jahn-Teller distorted CuCl6 octahedra. The antiferromagnetic interlayer exchange interaction is very weak, and the antiferromagnetic phase transition occurs at T_N = 10.3 K[1, 2]. In contrast, the structural phase transition occurs at T_d = 234 K wherein the crystal symmetry changes from orthorhombic (Pbca) to monoclinic with the a- or the b-axis as the unique axis or triclinic when the temperature decreases[3-5]. Even though the space group Pbca is known to be a non-polar point group, the ferroelectric phase transition has been reported to occur at T_5 = 247 K[6, 7, 8]. Below T_5, a large remnant polarization (37 μC/cm²) appears when electric fields are applied parallel to c-axis. There are two types of domains above T_5; one of these vanishes below T_5, while all other domains disappear below T_4. Under such circumstances, the intermediate phase between T_4 and T_5 would be considered to be an improper ferroelectric state. It is likely to be important to observe the manner in which the ferroelastic and the ferroelectric domains in EACuCl change during the structural and ferroelectric phase transitions at T_4 and T_5 should be essentially observed.
Birefringence imaging microscopy is suited for comprehensively investigating various structural phase transitions. In ferroelastic systems, the temperature dependence of birefringence is directly proportional to the order parameter[9]. As demonstrated in our previous studies[10, 11], retardance (δ) and fast-axis direction (ψ) images created using birefringence imaging techniques are useful for investigating domain structures because δ levels are proportional to the degree of distortion and ψ indicates not only optical anisotropy but also uniaxial stress in crystals. In this study, birefringence imaging measurements were performed on EACuCl to observe the ferroelastic domains with ferroelectric properties.

When the indices of refraction along the orthogonal optical principal axes are defined as n1 (for the slow axis) and n2 (for the fast axis) with n1 ≥ n2 > 1, the birefringence Δn is expressed as

\[ \Delta n \equiv n_1 - n_2. \] (1)

In a material with n1 ≠ n2, the transmitted light becomes elliptically polarized because the electric-field component of the light along the fast axis travels faster than that along the slow axis, leading to a phase shift between the two components[12]. The effect can be described as a retardation between the electric-field wave components along the fast and slow axes. The relation between Δn and δ is given by following equation:

\[ \delta \equiv \Delta n \cdot t, \] (2)

where t is the optical-path length. If a ferroelectric phase transition occurs, δ is expected to be very large and ψ gives information about the polarization direction. In our previous study, a converted retardance method using different λ values was developed to exceed the inherent upper limit of birefringence[11]. In this study, we discuss the birefringence imaging data using the converted retardance (δ543Cv) and the fast-axis direction (ψ543Cv) at λ = 543 nm.

2. Materials and Methods
We used an ellipsometer (Photonic Lattice, Inc. WPA-100) to accurately characterize the polarization via the Stokes parameters \((S_0, S_1, S_2, S_3)\). In addition, we used a polarimeter with a 6-W LED white-light source with an irradiation area of 100 × 136 mm² that exhibited circular polarization at \(S_3/S_0 \simeq -1\). Thus, the energy density of the light was very low, resulting in negligible increases in the sample temperature due to irradiation. The wavelength was monochromated using three different wavelength filters (λ = 523, 543, and 575 nm). Sample temperatures were varied using a GM refrigerator with a range of 12 ∼ 315 K. The samples were mounted with grease on a copper plate with a thermometer to achieve good thermal contact but prevent stress-induced birefringence. A high-accuracy temperature controller with a silicon diode thermometer was used to ramp the temperature at a rate of ±0.1 K/min over the entire investigated range of 12 ∼ 315 K.

Single crystals of EACuCl were prepared via the slow evaporation of water solutions of CuCl₂·2H₂O and C₂H₅NH₃·HCl at 30°C. The samples appeared yellow. To measure a “transmission-type” birefringence imaging system, thin plates had be prepared. The cleavage plane corresponding to (001) at room temperature was peeled off in the form of flakes because cutting, beating, or polishing causes internal damage of the sample and internal strain must be avoided due to ferroelastic compound. The incident light was perpendicular to (001) and, as in previous studies, we define the fast-axis direction in (001) as the a-axis at room temperature[3, 4].

3. Experimental Results and Discussion
In ferroelastic materials, 90° domains are expected to appear and can be controlled by applying external uniaxial stress. Thus, we used two different sample setup configurations with the sample
laid (A) perpendicularly and (B) diagonally across the gap between opposite copper plates (see Fig. 1). In setup A [Fig. 1(a)], the $a$-axis (the fast axis at room temperature) is at 45° to the copper plates. Conversely, in setup B [Fig. 1(b)], the $a$-axis is rotated by 45° with respect to setup A. Figure 1(c) shows a side view of the sample stage. As the temperature decreases and the copper sample stage shrinks, it is likely that external stresses are generated. The resulting stress may be applied along both the $a$-axis and $b$-axis directions in setup A, but only along one or other of the two axes directions in setup B.

Figure 2 shows birefringence images of EACuCl for setup A. Although the $\delta^{543}_{Cv}$ distributions are uniform over the entire temperature range, the 90° domains, which indicate a ferroelastic state, appear at 300 K[13]. The $\psi^{543}_{Cv}$ direction in each domain is inverted between 300 K and 15.0 K. As can be seen in Figs. 2(c) and 2(f), the transmittance is inhomogeneous because the peeled sample contains many defects, cracks, and grooves[14]. To avoid complications due to crystal quality, the sample analysis area (10×10 pixels) was selected not only in the single $\psi^{543}_{Cv}$ domain area but also in the highly homogeneous transmittance area, as shown by the small square in Fig. 2(b). Figure 3 shows the temperature dependence of $|\Delta n_{001}|$ and $\psi^{543}_{Cv}$, where $n_a$ and $n_b$ are refractive indices along the $a$- and $b$-axis, respectively. When the minimum value of $|\Delta n_{001}(T)|$ is defined as $T_a$, switching between the fast- and slow-axis occurs at $T_a = 196.0 \sim 198.9$ K. This result agrees well with previous results observed using the rotating analyzer method[3, 4]. Because the 90°-jump of $\psi^{543}_{Cv}$ at $T_a$ may become unclear regardless of the ferroelastic 90° domains, birefringence imaging techniques are very useful for the ferroelastic materials.

Furthermore, the birefringence experiments for setup B were performed using another sample. Figure 4 shows the temperature dependence of $|\Delta n_{001}|$ and $\psi^{543}_{Cv}$ in setup B. The value of $|\Delta n_{001}|$ at 300 K is larger than that at 15 K in setup A, and the opposite is true for setup B. In a transmission birefringence imaging system, the value of $\Delta n_{001}$ is averaged along [001], i.e., the beam axis. When the 90° domains stack along the beam axis in our samples, the value of $\Delta n_{001}$ becomes small because the opposite components cancel out. The $|\Delta n_{001}(T)|$ curves during cooling and heating coincide with each other in setup A but show thermal hysteresis in setup B. The $T_a$ values differ by over 30 K in setups A and B although they show small thermal hysteresis. Because of the ferroelastic state in EACuCl, its physical properties are strongly affected by the arrangement of the $(C_2H_5NH_3)$ chains, but the weak N-H⋯Cl hydrogen bonds are affected by sample quality and internal strain. Thus, the structural phase transition temperatures observed by different methods frequently differ by over 20 K[15]. To confirm the dependence of $T_a$ on sample quality, all the samples were measured in both setups. The results shown in Fig. 5 indicate that the sample quality dependence is negligible, but the values of $T_a$

![Figure 1. Schematic of the sample setup configurations. (a) The $a$-axis is a 45° to the copper plate (b) The $a$-axis is rotated by 45° with respect to the copper plate (c) Side view of the sample stage.](image-url)
converted $(\delta_{\text{CV}}^{543})$ retardance images at (a) 300 K and (d) 15.0 K for a \((\text{C}_2\text{H}_5\text{NH}_3)_2\text{CuCl}_4(001)\) plate in setup A. Converted \((\psi_{\text{CV}}^{543})\) fast-axis images at (b) 300 K and (e) 15.0 K. Transmittance images at (c) 300 K and (f) 15.0 K. The square in (b) indicates the sample analysis area. The thickness \(t\) is 0.086 mm.

Figure 3. Temperature dependence of (a) $|\Delta \nu_{001}|$ and (b) $\psi_{\text{CV}}^{543}$ for a \((\text{C}_2\text{H}_5\text{NH}_3)_2\text{CuCl}_4(001)\) plate in setup A. Inset to (a) is a zoomed-in view of the $|\Delta \nu_{001}(T)|$ curve around $T_a$. Inset to (b) is a zoomed-in view of the $|\Delta \nu_{001}(T)|$ and $\psi_{\text{CV}}^{543}(T)$ curves around $T_4$ and $T_5$.

Can be classified by setup configuration. The average value of $T_a$ is 197(3) K in setup A but 226(3) K in setup B. The hysteresis of $T_a$ seems to be opposite in the two setups (i.e., inverted in setup A and normal in setup B). This result indicates that the value of $T_a$ is suppressed by the external stress because the 90°-jump in $\psi_{\text{CV}}^{543}$ is caused by the tilt of the $c$-axis in the $ab$-plane below $T_4$[3-5].
Figure 4. Temperature dependence of (a) $|\Delta n_{001}|$ and (b) $\psi_{543}^{Cv}$ for a $(C_2H_5NH_3)_2CuCl_4(001)$ plate in setup B. Inset to (a) is a zoomed-in view of the $|\Delta n_{001}(T)|$ curve around $T_a$. Inset to (b) is a zoomed-in view of the $|\Delta n_{001}(T)|$ and $\psi_{543}^{Cv}(T)$ curves around $T_4$ and $T_5$.

Figure 5. Variation of $T_a$ across all the $(C_2H_5NH_3)_2CuCl_4(001)$ plates in the two-setup configurations.

As can be seen in the inset of Fig. 3(b), a kink in the $|\Delta n_{001}(T)|$ curve and a large anomaly in the $\psi_{543}^{Cv}$ direction appear at 230~240 K in setup A. In setup B, by contrast, it can be seen in the inset of Fig. 4(b) that no anomaly appears in the $|\Delta n_{001}(T)|$ curve and the change in $\psi_{543}^{Cv}$ direction is less than 2°. From our previous studies on isomorphous compounds[11], the $\psi_{543}^{Cv}$ directions are closely related to the arrangements of the alkylammonium chains $(C_nH_{2n+1}NH_3)$. Thus, the fluctuations in $\psi_{543}^{Cv}$ are probably due to rotation of the $(C_2H_5NH_3)$ chains accompanied by the structural phase transition around $T_4$. As a result, the gradual change in the $|\Delta n_{001}(T)|$ curve indicates a second-order structural phase transition at 230~240 K corresponding to $T_4$. The crystal symmetry below $T_4$ can be characterized as monoclinic with the $a$- or the $b$-axis as the unique axis[3] or triclinic with $\gamma$ close to 90° because a large change in $\Delta n_{001}$ should occur at $T_4$ if $\gamma$ is far from 90°. In addition, the 90°-jump in $\psi_{543}^{Cv}$ at $T_a$ may be due to $\gamma = 90°$. If spontaneous polarization appears along the $c$-axis below $T_5$, ferroelectric polarization should appear in the $ab$-plane because the $c$-axis tilts toward the $ab$-plane below $T_4$. However, no anomalies in the in-plane birefringence, which could indicate the existence of ferroelectric polarization, appeared between 15 K and 300 K. To directly observe spontaneous polarization along the $c$-axis, it would be necessary to measure the birefringence in the plane that included the $c$-axis. In ref.
3, the temperature dependence of birefringence in (111) was observed by the rotating analyzer method and the $\Delta n_{111}(T)$ curve was found to be almost the same as that of the $\Delta n_{001}(T)$ curve; however, no $\psi_{543}^{Cv}(T)$ data were obtained. In future our study, an observation method using oblique incident light will be developed to obtain birefringence images in (111) with 90° ferroelastic domains in the $ab$-plane.

4. Conclusion
We successfully observed 90° ferroelastic domains in the $ab$-plane using the birefringence imaging techniques. From the temperature dependence of $|\Delta n_{001}|$ and $\psi_{543}^{Cv}$, the 90°-jump in $\psi_{543}^{Cv}$ appears at $T_a = 197(3)$ K in setup A and $T_a = 226(3)$ K in setup B without structural or magnetic phase transitions because the c-axis tilts toward the $ab$-plane below $T_4$. Furthermore, the structural phase transition from orthorhombic to monoclinic or triclinic was observed at $T_4$, but no ferroelectric phase transition was observed at $\sim T_5$. Because the value of $T_a$ is significantly influenced by external stresses, we found that it was important to carefully observe the changes in the ferroelastic domains with temperature in stress-free conditions. Conversely, if large uniaxial stress is applied in the $ab$-plane, stress-induced ferroelectric phase transitions are expected to occur around $T_4$ and $T_5$. In future studies, we will endeavor to measure stress-induced birefringence.

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