Probing Spin Chirality of the Equilateral Triangular-Lattice Antiferromagnet RbFe(MoO$_4$)$_2$ through Multiferroicity

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Abstract. Ferroelectricity was studied in magnetic fields up to 14 T on the XY-like perfect-triangular-lattice antiferromagnet RbFe(MoO$_4$)$_2$, which exhibits a magnetically induced ferroelectric polarization along the $c$ axis in the low-field 120°structure phases P1 and P2. We have experimentally confirmed that the high-field P4$\parallel$P5 phases of RbFe(MoO$_4$)$_2$ for $B \parallel a$ are nonferroelectric. The results favor the scenario that the ferroelectricity in the low-field phases of this system is driven by the in-plane spin chirality.

1. Introduction
Magnetically driven ferroelectricity (MFE) has attracted much interest. Most of the phenomena have successfully been explained by the spin current mechanism in which the local electric polarization is expressed as $P_{ij} \propto r_{ij} \times (S_i \times S_j)$ [1]. It has also been pointed out that MFE can be a probe for spin helicity [2]. Recently, ferroelectricity with $P \parallel c$ has been found to emerge concomitantly with an antiferromagnetic transition at $T_N = 3.9$ K in the triangular lattice compound RbFe(MoO$_4$)$_2$ (hereafter referred to as RFMO) [3], in which Fe$^{3+}$ ions carrying spin $S = 5/2$ form a perfect triangular lattice [4]. According to the neutron diffraction measurements, the zero-field ordering wave vector of this compound is $(1/3, 1/3, 0.468)$, where the in-plane spin configuration is a so-called 120°structure phases P1 and P2. We have experimentally confirmed that the high-field P4$\parallel$P5 phases of RbFe(MoO$_4$)$_2$ for $B \parallel a$ are nonferroelectric. The results favor the scenario that the ferroelectricity in the low-field phases of this system is driven by the in-plane spin chirality.
Adopting their calculations, P1 and P2 have finite in-plane spin chirality but P3~P5 do not. Considering the c-axis incommensurability of the magnetic structure of RFMO, on the other hand, inter-plane helicity may exist in all the phases except for P3 (collinear up-up-down state). The experiment by Kenzelmann et al. [3] has revealed that P1 and P2 are ferroelectric but P3 is nonferroelectric. Their results are, however, not sufficient to discriminate which chirality/helicity is most relevant for the MFE. If the in-plane spin chirality is responsible for MFE, then the high-field P4 and P5 phases must be nonferroelectric. Conversely, if P4 or P5 phase is ferroelectric, then one can conclude that the in-plane spin chirality is irrelevant for the MFE. We measured the dielectric properties of RFMO in much higher fields up to the P5 phase region and discuss the possible origin of MFE.

2. Experimental

Single crystals of RbFe(MoO$_3$)$_2$ with thin plate shape were prepared by a flux technique. Specific heat $C$, magnetization $M$ and dielectricity are measured in fields up to 14 T applied along the $a$ axis in a temperature range down to 0.25 K.

3. Results and Discussion

In order to give an overview of the dielectric and magnetic properties of RFMO, we first show in Fig. 1 the magnetic phase diagram for $B \parallel a$ determined by $C(T)$ (open diamonds), $M(T)$ (open squares), $M(H)$ (open circles), $\epsilon(T)$ (solid squares) and $\epsilon(H)$ (solid circles) measurements. Apart from the P4-P5 boundary, which is not clearly resolved in the present experiment, our phase diagram is in good agreement with the previous results [8].

Figure 2 shows the $\epsilon(T)$ data in various magnetic fields. For $B = 0$, a small but distinct peak of $\epsilon(T)$ is observed at $T_N = 3.9$ K. At this temperature, a remarkable change is observed in the $P - E$ loop as shown in the inset; a clear hysteresis as well as an S-shape feature appear. Thus, we consider that the peak in $\epsilon(T)$ reflects the ferroelectric transition. Increasing $B$ from zero, this peak in $\epsilon(T)$ moves to the low temperature side along the P1 or P2 boundary showing a significant increase in the amplitude. This confirms that P1 and P2 are both ferroelectric. On the other hand, no dielectric anomaly is observed upon the transitions from paramagnetic to P3, P5 phases nor at the P4-P5 transition. This result indicates that not only P3 but also P4/P5 phases are nonferroelectric.

We first discuss why MFE is allowed in the P1/P2 phases of RFMO. The appearance of $P \parallel c$ implies that any symmetry with respect to the c-axis inversion is broken. For a triangular lattice with the highest symmetry of $P6/mmm$, there are six symmetry operations that make the c-axis inversion. These are $m_z$, $i$, $S_3$, $S_6$, $C_{2x}$ and $C_{2y}$. How the lattice and the zero-field spin structures in RFMO transform under these symmetry operations is illustrated in Fig. 3. For instance, the lattice structure ($P\bar{6}$) below $T_S$ is invariant under $i$ and $S_6$ (Table 1). This fact ensures that no ferroelectricity with $P \parallel c$ appears in the paramagnetic state. When the magnetic order sets in, transformations of the spin structures should also be considered. As can be seen from Table 1, the in-plane spin chirality changes sign by $i$ and $S_6$. Similarly, the helical spin alignment along the c axis also breaks the symmetry with respect to $i$ and $S_6$ as given in Table 1. These symmetry properties also hold in a magnetic field applied along the c plane, in which case the relevant symmetry operation becomes only the inversion $i$. Thus, both of the in-plane and the inter-plane spin configurations can drive MFE in the P1/P2 phases in RFMO [3, 10]. For the P3 phase, the spin configuration becomes the up-up-down state without spin chirality/helicity. Then, the inversion symmetry is recovered and MFE vanishes in agreement with the experiment. Thus, the ferroelectric properties in P1~P3 phases can equally be explained by the in-plane spin chirality as well as the spin helicity along the c axis in the antiferromagnetically ordered phase.

Our experiment has shown that MFE is absent both in the P4 and P5 phases. This observation is consistent with the scenario that MFE is caused by the in-plane spin chirality of the triangular lattice, since the in-plane spin chirality is considered to vanish in the P4/P5 phases. If the inter-plane spin helicity still exists in these phases, then we can conclude that the MFE in RFMO is driven exclusively...
Magnetic phase diagram of RbFe(MoO$_4$)$_2$ for $B \parallel a$.

by the in-plane triangular spin chirality. It is therefore highly desired to determine the spin configuration in the P4/P5 phases.

Transformations of the lattice and the triangular spins in the low temperature phase of RbFe(MoO$_4$)$_2$ at zero magnetic field. Only those involving the $c$-axis inversion are shown. Original position of the lattice and spins (a) changes into (b) ~ (f) by the symmetry operations $m_z$, $i$, $S_3$, $S_6$, $C_{2x}$ and $C_{2y}$, respectively. The lattice (spin chirality) is invariant under $i$ and $S_6$ ($m_z$, $S_3$ and $C_{2x}$).

| symmetry operations | $m_z$ | $i$ | $S_3$ | $S_6$ | $C_{2x}$ | $C_{2y}$ |
|---------------------|------|----|------|------|--------|--------|
| lattice             | ×    | ×  | ×    | √    | √      | ×      |
| in-plane spin chirality | √  | ×  | √    | ×    | ×      | √      |
| inter-plane spin helicity | ×  | ×  | ×    | ×    | √      | √      |
4. Summary
Whether or not a perfect triangular lattice XY antiferromagnet with the 120° spin structure exhibits macroscopic ferroelectricity perpendicular to the plane is a question which has not yet been resolved. RbFe(MoO$_4$)$_2$ with the $P\bar{3}$ structure is one of the candidate compounds to study the magnetically induced ferroelectricity driven by the in-plane spin chirality of the 120° structure. In this compound, however, the ordered spin structure possesses inter-layer spin helicity which also breaks $c$-axis inversion symmetry. We measured the dielectric polarization of RbFe(MoO$_4$)$_2$ in the high-field non-collinear P4/$P\bar{5}$ phases and confirmed that they are non-ferroelectric. Unless the spin alignment in the P4/$P\bar{5}$ phases takes a fan type structure, our results imply that the magnetically induced ferroelectricity in RbFe(MoO$_4$)$_2$ is driven by the in-plane spin chirality.

5. References
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