Dielectric relaxation in a nonferroelectric phase of magneto-electric multiferroic CuFeO$_2$

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Abstract. Magnetic oxide CuFeO$_2$ is a rare magneto-electric multiferroic where magnetic field-induced or nonmagnetic impurity-induced proper helical magnetic ordering generates a spontaneous electric polarization. We have measured the complex permittivity in various magnetic phases under an applied magnetic field up to 15 T, and found distinct Debye-type-like dielectric dispersion with low relaxation frequency in only 4-sublattice (4SL) magnetic phase among various (4SL, ferroelectric incommensurate, 5-sublattice, partially disordered and paramagnetic) magnetic phases. The relaxation frequency of dielectric dispersion shows interesting anisotropic magnetic field dependence. As one possible explanation of this phenomenon, we will discuss the dielectric dispersion in terms of 4SL-specific magnetic domain wall motion and corresponding displacement of oxygen near magnetic domain wall, instead of so-called Maxwell-Wagner effect in the dielectric system with heterogeneous nature.

1. Introduction

Recently, ferroelectricity induced by magnetic ordering has been extensively studied as a hot topic of material science, since giant magnetoelectric effects were discovered in TbMnO$_3$ [1]. The magnetic oxide CuFeO$_2$ to be investigated here is a triangular lattice antiferromagnet with delafossite crystal structure, in which each Fe$^{3+}$ triangular layer is well separated by one Cu$^{1+}$ and two O$^{2-}$ layers, and stacks along the hexagonal c axis, as is illustrated in figure 1(a). Because of the geometrical spin frustration, various magnetic phases with either collinear or non-collinear/either highly commensurate or incommensurate magnetic ordering appear in the magnetic field (H) along the c axis versus temperature (T) phase diagram, as shown figure 1(b) [2]. Furthermore, through the magneto-elastic coupling originating from the ferromagnetic direct exchange interaction between Fe spins and the super exchange interaction between Fe spins mediated by an oxygen ion, CuFeO$_2$ shows the successive lattice deformations [3] corresponding to field-induced magnetic structures.

Since Kimura et al. [4] discovered a spontaneous electric polarization in the first-field-induced phase (7 T < H < 13 T), multiferroic nature of CuFeO$_2$ has been extensively studied. Among multiferrosics, delafossite compound CuFeO$_2$ is a rare magneto-electric multiferroic, where magnetic field-induced [4] or nonmagnetic impurity-induced [5] proper helical magnetic ordering generates a spontaneous electric polarization parallel to the helical axis. Our recent polarized neutron diffraction [6] and synchrotron radiation x-ray [7] studies suggested that the microscopic origin of the ferroelectricity in CuFeO$_2$ is neither due to so-called spin current [8] nor magnetostriction mechanism,
but the variation in the metal ligand hybridization with spin-orbit coupling [9]. Apart from the aspect that magnetic ordering generates spontaneous electric polarization, another type of cross-correlation between electricity and magnetism can be also expected in multiferroics with spin frustration; magnetic fluctuation due to spin frustration would generate fluctuation of electric dipole moment. With such an aspect in hand, in present study, we have measured the complex permittivity over various magnetic phases (4-sublattice (4SL), ferroelectric incommensurate magnetic (FE-ICM), 5-sublattice (5SL), partially disordered (PD) and paramagnetic (PM)) appearing in the \( H-T \) phase diagram shown in figure 1(b). A single crystal of \( \text{CuFeO}_2 \) was prepared by the floating zone technique and was cut into disk-shape specimen (area~13 mm\(^2\), thickness~0.28mm) with largest surface, normal to the \( c \) axis, on which silver paste was pasted to make the electrodes. Complex dielectric permittivity was obtained by measuring the ac-impedance of the sample by LCR meter (Agilent E4980A) from 100 Hz to 1M Hz.

![Figure 1](https://example.com/fig1.png)

**Figure 1.** (a) Crystal structure of \( \text{CuFeO}_2 \) with the hexagonal unit cell, (b) the \( H-T \) phase diagram of \( \text{CuFeO}_2 \) taken from ref. [2], magnetic field dependence of (c-1) magnetization, (c-2) real part \( \varepsilon' \) and (c-3) imaginary part \( \varepsilon'' \) of complex permittivity, \( \varepsilon=\varepsilon'-i\varepsilon'' \), at \( T \approx 1.8 \) K.

### 2. Results and Discussion

The figure 1 (c-2 and c-3) show magnetic field dependence up to 15 T of the complex permittivity at several frequencies at \( T \approx 1.8 \) K. Corresponding to successive field-induced phase transitions seen in the magnetization curve shown in figure 1 (c-1), the permittivity shows the discontinuous change at the transition fields. Furthermore, distinct frequency dependence of the permittivity can be seen in 4SL phase, indicating dielectric relaxation. Actually, as is clearly seen in figure 2 (a-1 and a-2), the frequency dependence of imaginary part of complex permittivity \( \varepsilon''(\omega) \) in 4SL phase has peak shape and shows interesting anisotropic magnetic field variation; while under magnetic field applied along the [110] direction the peak moves to lower frequency side, the peak splits into two under magnetic field applied along the [001] direction. Note that the 4SL magnetic structure remains unchanged under [110] magnetic field up to 15 T. The complex permittivity can be well fitted by Cole-Cole relaxation model function [10],

\[
\varepsilon(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (i\omega\tau)^\alpha},
\]

where \( \omega \) is the angular frequency, \( \varepsilon_s \) and \( \varepsilon_\infty \) are the static- and high-frequency limits of the dielectric constant, respectively. \( \tau \) is the most probable relaxation time, and \( \alpha \) is an empirical constant accounting for a distribution of relaxation time. Note that as for the \( \varepsilon''(\omega) \) with two peak structure above \( H \approx 3 \) T along the [001] axis, we introduced Cole-Cole relaxation model function with two
contribution as the fitting is shown in figure 2 (b). As is clearly seen in figure 2 (c), relaxation time $\tau$ shows strongly anisotropic magnetic field dependence, whereas other fitting parameters are very weakly magnetic field dependent: $\varepsilon_\infty \sim 6$, total dispersion strength $\varepsilon_\infty - \varepsilon_\infty \sim 5$. Here we emphasize that distinct Debye-type-like dielectric relaxation found in 4SL phase is not seen in any other (FE-ICM, 5SL, PD and PM) magnetic phases.

Figure 2. (a) Magnetic field dependences of imaginary part of complex permittivity $\varepsilon''(\omega)$ (a-1) along the [110] direction and (a-2) along the [001] direction at $T \sim 1.8$ K. Solid lines are fitted curves (b) Typical fitting of real and imaginary parts of complex permittivity at $H=5$ T to Cole-Cole relaxation model with two contributions. (c) Magnetic field dependences of relaxation time obtained from the fittings.

So-called Maxwell-Wagner (MW) effect [11], which gives a relaxation spectrum similar to the Debye relaxation even without any dipole relaxation, often occurs in the heterogeneous system in which the component dielectrics have different conductivities, and therefore one may assert that a detected Debye-like relaxation response is due to not the electric dipole relaxation in the system but MW-effect. However, MW-effect can hardly explain the strongly anisotropic magnetic field dependences of detected Debye-like relaxation response, because electric conductivities in the 4SL phase shows very weak magnetic field dependences both along [001] and [110] directions according to our preliminary results of electric conductivity measurements.

As one possible explanation of this phenomenon, we discuss the dielectric dispersion in terms of 4SL-specific magnetic domain wall motion and corresponding displacement of oxygen near magnetic domain wall, instead of MW-effect. As Terada et al. discussed in their study of lattice modulation in CuFeO$_2$ [12], the oxygen ion placed at the center of triangular lattice moves from parallel-spins side toward antiparallel-spin corner so as to gain the superexchange energy. Consequently, as shown in figure 3, the antiferroelectic displacement of oxygen ions is induced by the 4SL magnetic ordering with ($\uparrow\downarrow\downarrow\downarrow$) spin-modulation along the hexagonal [110] axis. Note that the displacement is three-dimensional, not two-dimensional. Invoking 4SL-specific magnetic domain wall moving back and forth, which is essentially the same as AD-type domain wall discussed in domain growth kinetics in the isosceles triangular Ising antiferromagnet CoNb$_2$O$_6$ [13], the movable electric dipole moment originating from displacement of oxygen near magnetic domain wall can respond to the oscillating electric field in the measurements of complex dielectric permittivity, which must be responsible for
the dielectric relaxation. The experimental fact that distinct dielectric relaxation is not seen in 5SL magnetic phase is also consistent with this magnetic domain scenario, because the AD-type domain wall moving back and forth does not exist in 5SL (↑↑↑↓) magnetic structure. Although at present stage we do not have any explanation for the anisotropic strongly magnetic field dependent relaxation time on the basis of this naive magnetic domain scenario, we are convinced that the dielectric relaxation response in 4SL phase might be an typical cross-correlation between magnetic fluctuation due to spin frustration and electric dipole fluctuation. To clarify the origin of the dielectric relaxation, further systematic study is required.

To conclude, we have found distinct dielectric relaxation response with anisotropic strongly magnetic field dependent relaxation time in 4SL magnetic state of CuFeO$_2$. As one of the possibility, we suggest that 4SL-specific magnetic domain wall motion accompanied by the movable electric dipole moment near magnetic domain wall generates the dielectric relaxation response, instead of so-called Maxwell-Wagner effect in the dielectric system with heterogeneous nature.

![Figure 3. Schematic drawings of the 4SL magnetic structure and the displacement of oxygen ions due to the magneto-elastic coupling. Arrows show the Fe magnetic moments along the hexagonal [001] axis. Green and yellow circles show oxygen ions above and below Fe triangular lattice layer, respectively. Open circle shows the original position of oxygen ions. Vertical dashed line denotes magnetic domain wall.](image)

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