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Magnetoelectric coupling driven dielectric anomaly in non-polar system $SeCuO_3$

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ABSTRACT

The non-polar material $SeCuO_3$, which contains Cu^{2+} with $S=1/2$ spin and Se^{4+}, has a highly distorted perovskite structure due to the small radii of Se^{4+} cations. The dielectric constant displays a critical decrease at 25 K, at which temperature the ferromagnetic ordering of the Cu^{2+} spin appears, suggesting a strong coupling between the magnetic and dielectric properties. Studies on $SeCuO_3$ show that the magnetic and electrical subsystems reciprocally correlate via the hybridization of sp and pd. We conclude that the spin–pair correlation along the *b*-axis plays a significant role in the decrease of the dielectric constant around the magnetic transition temperature via the magnetoelectric coupling, and successfully explain the dielectric anomaly. The obtained dielectric constant and the magnetocapacitance for $SeCuO_3$ are quantitative agreement with experimental results.

1. Introduction

The behavior of systems with strongly coupled magnetic and dielectric properties has attracted attention for the wide range of potential applications in device technology [1,2]. After the first experimental realization of magnetoelectric (ME) coupling in Cr_2O_3 [3] and the measurement of ME coupling via the dielectric anomaly in $YMnO_3$ [4], similar phenomena have been observed in many other materials such as $BiMnO_3$ [5], $EuTiO_3$ [6], $TbMnO_3$ [7] and $CdCr_2S_4$ [8]. Many theoretical works have also been reported to explain the interesting phenomena [9,10]. In order to investigate the ME coupling between the magnetic and dielectric properties in the non-polar system, we use $SeCuO_3$ as a model system. $SeCuO_3$, a representative member of $A^{4+}B^{2+}O_3$ (A=Se, Te, and B=Mg, Mn, Co, Ni, Cu, Zn) family, has been reported recently that the dielectric constant shows an evident anomaly at its magnetic transition temperature, indicating the ME coupling between the magnetic and dielectric properties [11–13].

As shown in Fig. 1, $SeCuO_3$ has a highly distorted perovskite (ABO_3) structure, in which the Se^{4+} cation occupies the larger A site and Cu^{2+} at the B site. The rotation and tilting of the CuO_6 octahedron compose the distorted structure and form a three dimensional network, and Se^{4+} cation resides in the cavity of this network. Unlike the ideal perovskite structure, the distorted perovskite structure of $SeCuO_3$ arises from the mismatch in the size of the Se^{4+} and Cu^{2+} cations. Ref. [14] provides the detailed structure description. In this structure the small Se^{4+} cation, with a strong covalent character, attracts 3 out of the 12 oxygens so that a structural unit of the $[SeO_3]^{2-}$ trigonal pyramid forms. Such a trigonal pyramid unit $[SeO_3]^{2-}$ lacks a center of symmetry, which can be interpreted because of an off-center displacement of Se^{4+}. Besides, the Se^{4+} cation carries a non-bonded s-electron pair which points to the apex of each trigonal pyramid [15]. The stereochemical activity of the non-bonded s-electron, which plays an important role because of its peculiar stereochemistry and high polarizability, can decide the nature of polarization. On the other hand, the rotation and tilting of oxygen octahedra due to the Jahn–Teller(JT) effect in $Cu^{2+}(d^9)$ promote the antiparallel alignment of neighboring local dipolar moments. Then the resulting local dipole moments cancel out to give zero net polarization. As a result, $SeCuO_3$ can be regarded as a non-polar system [16,17]. Such systems, of which $EuTiO_3$ [6], $SiTiO_3$ [18], $CaTiO_3$ [19] are the prototype, are often analogous to the incipient ferroelectrics. On the other hand, the transverse-field Ising model has been extended to the systems of the dipolar moments interaction [20] and the incipient ferroelectrics [18,21], and successfully deduced the Barret formula [22] which described the temperature dependence of the dielectric susceptibility of the incipient ferroelectrics. Therefore, the transverse-field Ising model can be proposed to describe the interaction of the dipolar moments for $SeCuO_3$.

The previous researches on $SeCuO_3$ reveal that the magnetic properties arise entirely from the Cu^{2+} with $S=1/2$ spin. Electronic structure calculation [23–25] shows that the ferromagnetic (FM) and A-type antiferromagnetic (AFM) state are the most stable for $SeCuO_3$ and its isostructural compound $TeCuO_3$, respectively. In Fig. 1(a) and (b), it is shown that the compound has two

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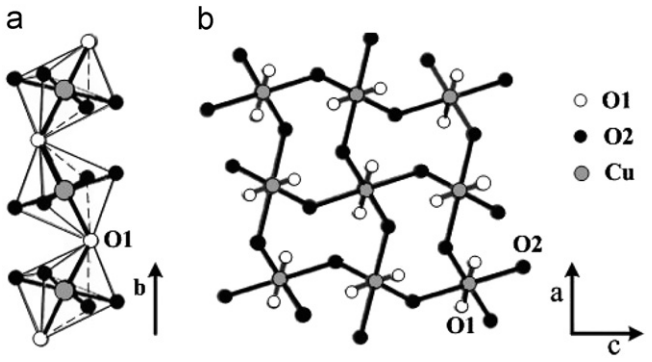

Fig. 1. Projection of the crystal structure of orthorhombic $SeCuO_3$ showing the octahedral arrangement (a) along the *b*-axis, and (b) in the ac plane. The O_1 and O_2 atoms are marked.

nonequivalent oxygen atom, O_1 and O_2. Then there are two distinct nearest-neighbor magnetic interactions for a given Cu atom. One that is described by J_b is along the *b*-axis via Cu-O_1-Cu path, the other that is described by J_{ac} is in the ac plane via Cu-O_2-Cu path. Besides, the next-nearest-neighbor magnetic interaction that is described by J' is also considered to understand the magnetic properties [24]. The magnetic interaction J, for simplicity, includes two contributions: an AFM superexchange (SE) J_{SE} and an FM direct-exchange (DE) J_{DE}, so that $J=J_{SE}+J_{DE}$. In general, the FM component, J_{DE}, is a small constant so that the trend in the J_{SE} value reflects that in the corresponding J value. Based on the extended Huckel tight-binding (EHTB) calculation [25], we know the hybridization between Se-4 s and O-2p orbital plays an important role in J_{SE}. The sp hybridization affects the magnitude of the Cu-3d-O-2p hopping, and the change of J_b and J_{ac} ensue. As expected, it is feasible that the sp hybridization somehow modifies the SE interaction and renders an FM J_b in $SeCuO_3$ and an AFM J_b in $TeCuO_3$ via the pd hybridization [26]. We describe the magnetic properties with a Hamiltonian, in which we include the magnetic interaction J_b, J_{ac}, and J' mentioned in above part.

On the other hand, the pd hybridization inevitably affects the dielectric properties of Se^{4+} cations via the sp hybridization. To check this conjecture, we analyse the structural feature of $SeCuO_3$ and find the distance of the neighboring Se-O_1 is 1.75 Å. In general, shorter distance of the Se-O_1 induces stronger sp hybridization and leads to stronger the correlation between the hybridization of sp and pd. One may thus hypothesize that the strength of correlation directly reflects the ME coupling coefficient [26]. As for the ME coupling, many theoretical and experimental researches have processed on the interaction between the magnetic and electric subsystems. A Monte Carlo simulation on the basis of Ising model and the discrete model with fourth order anharmonicity (DIFFOUR) [27] has investigated the magnetic transition in the two-dimensional magnetic ferroelectrics, where the spin moment and polarization interact [28]. In $CdCr_2S_4$, we coupled the dimensionless order parameter field with the Heisenberg spin [29]. Based on the transverse-field Ising model and the Heisenberg model, the interaction between the z component pseudospin and the magnetic spin is suitable for $SeCuO_3$ [30].

In this paper, we concentrate on the ME coupling dependence of dielectric anomaly in $SeCuO_3$. We attribute the dielectric anomaly around the magnetic transition temperature to the spin–pair correlation along the *b*-axis, likely via the sp hybridization, and the occurrence of magnetocapacitance (MC) response to the fluctuation of spin–pair correlation. Briefly the article is organized as follows: models and methods which describe the temperature and magnetic field dependence of the dielectric constant are given in Section 2, The numerical results and discussion are given in Section 3, and finally the conclusions are given in Section 4.

2. Model and calculation

The particularity of $SeCuO_3$ lies in the tight correlation between the magnetic and dielectric properties. In order to describe the dielectric properties, we introduce $\vec{S}_i$ and δ_m to represent the Heisenberg spin at Cu^{2+} site and the pseudospin for the electrical subsystem, respectively. In addition, the ME coupling interaction between the electrical and magnetic subsystems is taken into account. So the Hamiltonian for this system can be presented as

$$H=H^m+H^e+H^{me}, \tag{1}$$

where H^m is the Hamiltonian of the magnetic subsystem, H^e is the Hamiltonian of the electric subsystem, and H^{me} is the ME coupling interaction between the two subsystems.

The magnetic properties of Cu^{2+} in the distorted perovskite can be expressed as [6,11]

$$H^m=-\sum_{\langle i,j\rangle}J_b\vec{S_i}\cdot\vec{S_j}-\sum_{\langle i,k\rangle}J_{ac}\vec{S_i}\cdot\vec{S_k}-\sum_{[i,l]}J'\vec{S_i}\cdot\vec{S_l}-\sum_i\vec{B}\cdot\vec{S_i}, \tag{2}$$

where $\vec{S_i}$ is the magnetic spin of Cu^{2+} at site i. J_b, J_{ac} represent the nearest-neighbor magnetic interaction along the *b*-axis and in the ac plane, respectively, J' is the next-nearest-neighbor magnetic interaction. $\vec{B}$ is the external magnetic field. $\langle\cdots\rangle$ and $[\cdots]$ denote that over the nearest and the next nearest-neighbors sum once, respectively.

To describe the dielectric properties, we have utilized the transverse-field Ising model. Thus H^e in the presence of electrical field can be written as [6]

$$H^e=-\Omega\sum_m\delta_m^x-\frac{1}{2}\sum_{m,n}A_{mn}\delta_m^z\delta_n^z-2\mu E\sum_m\delta_m^z, \tag{3}$$

where δ_m^z denotes the fictitious spin-$\frac{1}{2}$ operator, E is the external electrical field. Ω is the tunneling frequency between the two spin positions, A_{mn} represents the nearest-neighbor pseudospin interaction, the summation $\sum_n A_{mn}=A_0$ covers the nearest neighbors of site m, and μ is the effective dipole moment of each spin, caused by the off-centered Se^{4+} cation. In this system, the mean electrical polarization is proportional to the z component of the pseudospin introduced in the transverse-field Ising model.

In the previous proposal, the ME coupling terms were denoted as $g\sum_{k,\langle i,j\rangle}u_k^2S_iS_j$ in Ising-DIFFOUR model [28] and $g\sum_{\langle i,j\rangle}\sum_{(k,l)}\overrightarrow{\sigma_k}\cdot\overrightarrow{\sigma_l}\vec{S_i}\cdot\vec{S_j}$ in the spherical random-bond-random-field (SRBRF) model [29]. For these coupling terms, the order parameters of electrical subsystem, which couple with the magnetic spin, are both proportional to the polarization. On grounds of the Janssen model, the ME coupling term between the magnetic and electrical subsystems in $SeCuO_3$ takes the following term [30]:

$$H^{me}=g\sum_{\langle i,j\rangle}\sum_{m,n}\delta_m^z\delta_n^z\vec{S_i}\cdot\vec{S_j}, \tag{4}$$

where g is the ME coupling coefficient indicating the strength of the ME coupling.

We deal with the electrical subsystem including the ME coupling interaction, the Hamiltonian can be written as

$$\begin{aligned}H^E&=H^e+H^{me}\\&=-\Omega\sum_m\delta_m^x-\frac{1}{2}\sum_{m,n}\left(A_{mn}-2\,g\sum_{\langle i,j\rangle}\vec{S_i}\cdot\vec{S_j}\right)\delta_m^z\delta_n^z-2\mu E\sum_m\delta_m^z.\end{aligned} \tag{5}$$

We find the modified pseudospin interaction embodies the magnetic effect on the electrical subsystem. Studies show the