Role of *d* States of B-Site Cations for Spin-Lattice Coupling in Eu^{2+} Perovskite Oxides

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From technological and scientific viewpoints, increasing attention has been attracted by multiferroic materials, which exhibit multiple 'ferroic' order such as ferromagnetism, ferroelectricity, and ferroelasticity, and their strong cross correlation. Since Fennie and Rabe have predicted that cubic perovskite $EuTiO_3$ can be switched from a paraelectric (PE) and antiferromagnetic (AFM) state into a ferroelectric (FE) and ferromagnetic (FM) state by biaxial strain [1], the physical properties of divalent europium perovskites have been extensively investigated through both experimental and theoretical approaches [2-6]. For instance, FM behavior has been reported for an epitaxial $EuTiO_3$ film with 2%–3% out-of-plane elongation [2]. Very recently, an FM and FE phase has been realized in an epitaxial film on a $DyScO_3$ substrate by means of 1.1% biaxial tensile strain [3], which corroborates the prediction by Fennie *et al.* experimentally [1]. Thus, $EuTiO_3$ is of great interest in that it has a strong spin-lattice coupling and that it is multicritically balanced between the AFM and FM states and between the PE and FE states. However, the microscopic origin of its strong spin-lattice coupling has not been clarified yet. In this study, in order to get insight into the origin, its magnetism and electronic structure and their relationship have been investigated by first-principles calculations.

The first-principles calculations were performed using the projector augmented wave (PAW) method and the HSE06 hybrid functional as implemented in the VASP code [7]. $\sqrt{2}\times\sqrt{2}\times2$ tetragonal supercells with 20 atoms were used in order to describe three magnetic configurations, namely, AFM *A*-, *G*-, and FM *F*-types. The ratio of the tetragonal lattice constants *a* to *c* remains 1 to $\sqrt{2}$ after a full structural optimization. The lattice constant of $(a^2c/4)^{1/3}$ is 3.903 Å at the equilibrium volume for the *G*-type magnetic configuration, which is consistent with an experimental value measured at room temperature [4]. We calculated total energies for the magnetic configurations as a function of elongation along the *c* axis and biaxial strain in the *c* plane. In the former case, *a* was fixed to the value at the equilibrium volume. In the latter case, *c* was relaxed for the varied values of *a*.

Figure 1(a) shows the total energies of the *A*- and *F*-type magnetic configurations relative to the *G*-type magnetic configuration as a function of *c* axis elongation. The magnetic ground state is *G*-type AFM at the equilibrium cell volume, which is in good agreement with a experimental result that $EuTiO_3$ shows an AFM transition at 5.3 K [4]. As $EuTiO_3$ is elongated along the *c* axis, the total energy of the FM state relative to the *G*-type AFM state is decreased, and then the magnetic ground state is changed into FM at 5 % elongation. Thus, the experimental observation of an FM behavior in the epitaxial $EuTiO_3$ thin film on a $SrTiO_3$ substrate with *c* axis elongation is qualitatively reproduced [2].

Variation of the total energies of the *A*- and *F*-type magnetic configurations relative to the *G*-type magnetic configuration with biaxial strain in the *c* plane is illustrated in Fig. 1(b). The FM state becomes more stable compered to the *G*-type AFM above 2 % tensile strain. On the other hand, compressive strain does not make the FM state more stable. These results are consistent with the experimental results that FM behavior was observed in the $EuTiO_3$ thin film with 1.1 % tensile strain on a $DyScO_3$

substrate and not in the $EuTiO_3$ thin film with 0.9 % compressive strain on a $(LaAlO_3)_{0.29}$–$(SrAl_{1/2}Ta_{1/2}O_3)_{0.71}$ substrate [3].

Our previous calculations have revealed that AFM superexchange interaction via Ti 3*d* states plays an important role for AFM coupling between the nearest-neighbor Eu^{2+} 4*f* spins in $EuTiO_3$ [5]. This AFM superexchange competes with an FM indirect exchange via Eu 5*d* states, resulting in an AFM-FM switching by an isotropic cell-volume expansion. The strong spin-lattice coupling seen in the present calculations also can be explained in terms of such competition because interactions between the Eu 4*f* and Ti 3*d* states and between the Eu 4*f* and Eu 5*d* states are possibly changed by the *c* axis elongation and biaxial strain in the *c* plane.

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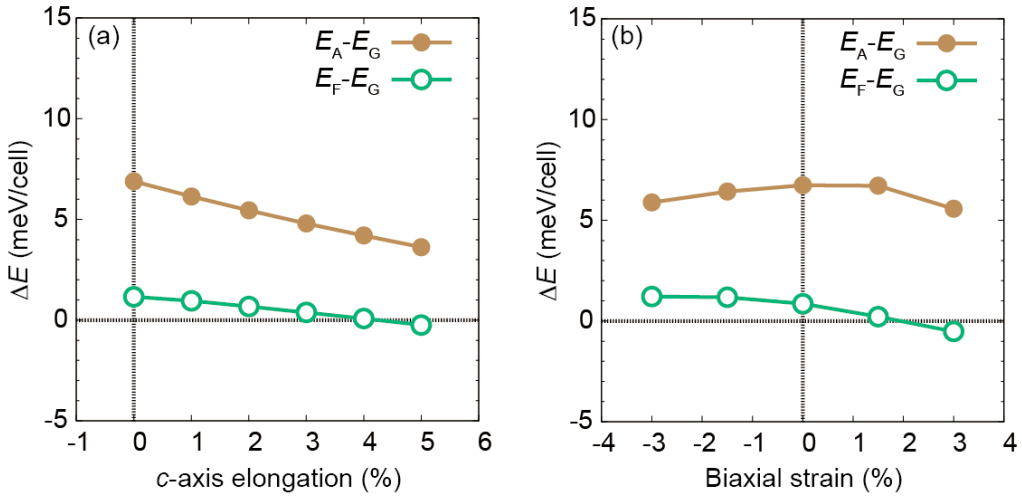

Fig. 1. Total energies of the *A*- and *F*-type magnetic configurations relative to the *G*-type magnetic configuration as a function of (a) *c* axis elongation and (b) biaxial strain in the *c* plane. In (a), the lattice constant *a* was fixed to the value at the equilibrium volume. In (b), the lattice constant *c* was relaxed under given values of *a*.