First-Principles Study of Magnetism and Electronic Structure in Eu\textsuperscript{2+} Perovskite Oxides

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The magnetism of Eu\textsuperscript{2+} compounds has been intensively investigated from both experimental and theoretical viewpoints since the discovery of ferromagnetism in EuO. Recently, EuTiO\textsubscript{3} has attracted much interest due to its stress\textsuperscript{1} or carrier-induced\textsuperscript{2} ferromagnetism. Bulk EuTiO\textsubscript{3} has a cubic perovskite structure [Fig. 1(a)], and the localized 4f\textsuperscript{sp} spins belonging to the A-site Eu\textsuperscript{2+} ions compose a simple cubic lattice with a G-type antiferromagnetic (AFM) ordering below $T_N=5.5$ K [Fig. 1(b)]. Fujita et al.\textsuperscript{1} have observed ferromagnetic (FM) behavior in an epitaxial (001)-oriented EuTiO\textsubscript{3} thin film with a 2 \% out-of-plane elongation. In addition, a previous first-principles study has predicted a critical balance between FM and AFM states in EuTiO\textsubscript{3}, leading to its cell-volume-dependent magnetism.\textsuperscript{3} The mechanism behind such magnetic behavior, however, remains to be clarified; elucidation of the magnetic interactions requires understanding of the exchange mechanism in terms of the electronic structure. In this study, we have systematically investigated the magnetic interactions, electronic structure, and their cell-volume dependence in Eu\textsuperscript{2+} perovskite oxides using first-principles calculations.

The calculations were performed using the projector augmented-wave method and the generalized gradient approximation (GGA) as implemented in the VASP code.\textsuperscript{4} The wave functions were expanded in a plane-wave basis set with an energy cutoff of 550 eV. Spin polarization was taken into account for all calculations. The strong on-site Coulomb interaction on the Eu 4f orbitals was considered by the $+U$ correction (GGA+$U$). The $\sqrt{2}\times\sqrt{2}\times2$ supercell was used in order to describe the four magnetic configurations, namely, $G$, $F$, $A$, and $C$ types shown in Fig. 1(b). The nearest-neighbor ($J_1$) and next-nearest-neighbor ($J_2$) exchange interactions [Fig. 1(a)] were evaluated as a function of cell volume ($V$), by mapping the total energies of the four magnetic configurations with varied lattice constants onto the Heisenberg Hamiltonian,

$$H = -2\sum_{i<j} J_{ij} S_i \cdot S_j.$$  

Figure 2 shows the dependence of $J_1$ and $J_2$ on $V$ for EuTiO\textsubscript{3} at $U_{\text{eff}}=4$ eV. With an increase in $V$, the sign of $J_1$ changes from the negative to the positive, accompanied by the switching of the magnetic ground state from the $G$-type AFM to FM state. This is qualitatively consistent with the ferromagnetism in the epitaxial thin film with lattice expansion.\textsuperscript{1} An analysis of the partial density of states (PDOS) reveals that the valence band is mainly composed of Eu 4f\textsuperscript{sp} and O 2p states, and the conduction band Ti 3d and Eu 5d states. Figure 3 depicts the PDOS in the energy region near the Eu 4f states for a series of $V$. As $V$ is decreased, Eu 4f and Ti 3d states interact with each other more strongly. These results are well explained by the scenario of AFM superexchange interactions between Eu 4f\textsuperscript{sp} spins via Ti 3d states. The cell-volume contraction facilitates...
mixing of Eu 4f and Ti 3d states, leading to the enhancement of the AFM superexchange interaction. Systematic calculations for EuM03 (M=Zr, Si, and Ge) and Eu2TiO4 support the importance of the interactions between the Eu 4f and B-site cation d states in the magnetism of EuTiO3 and related systems.

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References


FIG. 1. (a) Crystal structure of EuTiO3. The numbers 1 and 2 refer to the spin exchange paths of $J_1$ and $J_2$, respectively. (b) Schematic of the four magnetic configurations, A, C, F, and G.

FIG. 2. Cell-volume dependence of $J_1$ and $J_2$ for EuTiO3. The equilibrium volume is indicated by $V_{eq}$.

FIG. 3. Partial density of states for EuTiO3 with a G-type AFM ordering in the energy region near the valence Eu 4f states for $V = (a)\, 210$, (b)\, 245, and (c)\, 283 Å³.