Project Title:

Numerical study on new functionality of spin-heat cross effect

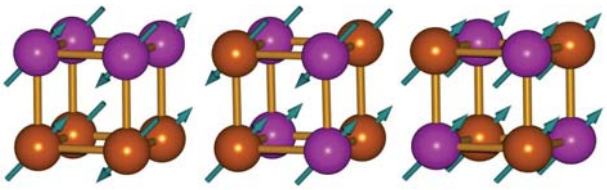
Name: Qinfang Zhang
Laboratory at RIKEN: Computational Condensed Matter Physics Lab.

1. Introduction

One of the major progresses in condensed matter physics nowadays is the discovery of various transition metal oxides in the perovskite structure, which exhibit a broad range of properties such as high-T_C superconductivity, multiferroics and colossal magnetoresistance. A recent advance in epitaxial growth techniques has made it even possible to fabricate oxide heterostructures. For example, a quasi two-dimensional electron gas with high mobility has been observed at the interface of the heterostructure made of two insulators, $LaAlO_3$ and $SrTiO_3$, demonstrating a potential of oxide heterostructures with emergent states and new functionalities.

Using laser-ablation technique, Ueda et al. have succeeded in fabricating the ordered perovskite La_2FeCrO_6, a superlattice of $[LaFeO_3]_n/[LaCrO_3]_m$ with p = (n,m) = (1,1) growing along [111] crystallographic direction, and found a ferromagnetic (FM) ordering at low temperatures. Furthermore, Ueda et al. have studied the magnetic properties of $LaFeO_3/LaCrO_3$ superlattices stacking along [001] and [110] directions, and found that, although the numbers of Fe and Cr ions are the same in both superlattices, their magnetic structures are different, i.e., C-type and A-type antiferromagnetic (AFM) for the superlattices stacking along [100] and [110] directions, respectively.

It was Pickett who has first studied theoretically the electronic structure of La_2FeCrO_6 using density functional theory (DFT) within the local spin density approximation (LSDA), and found that the ground state is ferrimagnetic. Thus, his results are not consistent with the experimental observation. This is partly because LSDA is often less reliable for strongly correlated transition metal oxides. Indeed, a later calculation using LDA+U method has found that the local electron correlations stabilize the ferromagnetic ground state for La_2FeCrO_6.



(a) (b) (c)

Fig. 1 Schematic figures indicating Fe (red spheres) and Cr (purple spheres) locations in $LaFeO_3/LaCrO_3$ superlattices stacking along (a) [001], (b) [110], and (c) [111] directions. The ground state spin alignments are indicated by arrows.

While earlier theoretical reports focus only on ordered perovskite La_2FeCrO_6, a little effort has been devoted to studying the electronic and magnetic structures of $LaFeO_3/LaCrO_3$ growing along [001] and [110] directions. It is also interested to study other superlattices $[LaFeO_3]_n/[LaCrO_3]_m$ with different p = (n,m) and stacking directions. This is simply because such a systematic theoretical study certainly helps to understand what determines their magnetic structures and offers to experiments guidelines on how to tailor complex magnetic structures in transition metal oxide superlattices. Therefore, in this paper, we perform first principles DFT calculations to analyze the magnetic properties of $[LaFeO_3]_n/[LaCrO_3]_m$ with p = (1,1), (1,2), and (2,2) in different stacking directions. We show that a variety of magnetic structures, some of them being not observed in bulk systems, can be stabilized as the ground states of these superlattices. We also find that these magnetic structures are understood based

on Kanamori-Goodenough (KG) rule, i.e., FM $Fe^{3+}(d^5)$-$Fe^{3+}(d^5)$ and $Cr^{3+}(d^3)$-$Cr^{3+}(d^3)$.

2. Computational Method

The calculations are performed using the projected augmented wave method and a plane wave basis as implemented in the Vienna Ab initio Simulation Package (*VASP*). The valence states included are (2p, 3d, 4s), (2p, 3d, 4s), and (2s, 2p) for Fe, Cr, and O, respectively. The electronic interactions are described by the GGA and GGA+U methods. We use the rotationally invariant GGA+U method with U_{eff} = U - J = 5 eV for *d* electron states. For simplicity, we use the same vales of U and J for both Fe and Cr atoms. The atomic positions are fully optimized until the Hellman-Feynman forces are converged to less than 0.01eV/ Å. The structure optimizations as well as the electronic self-consistency calculations are performed using the plane-wave cutoff of 500 eV and a 8x8x8 Monkhorst-Pack k-point grid in combination with the tetrahedron method. We consider only collinear magnetic structures, and the superlattices studied in this paper are all in the perovskite structure.

3. Results and Discussions

Let us first consider the simplest superlattices $[LaFeO_3]_n[LaCrO_3]_m$ with p = (n,m) = (1,1) stacking along three different directions, i.e., [001], [110], and [111] directions (Fig. 1). We find that the magnetic structures are all different for three superlattices depending on the stacking directions. As shown schematically in Fig. 1, the ground state magnetic

coupling for $Fe^{3+}(d^5)$-$Cr^{3+}(d^3)$ and AFM coupling for

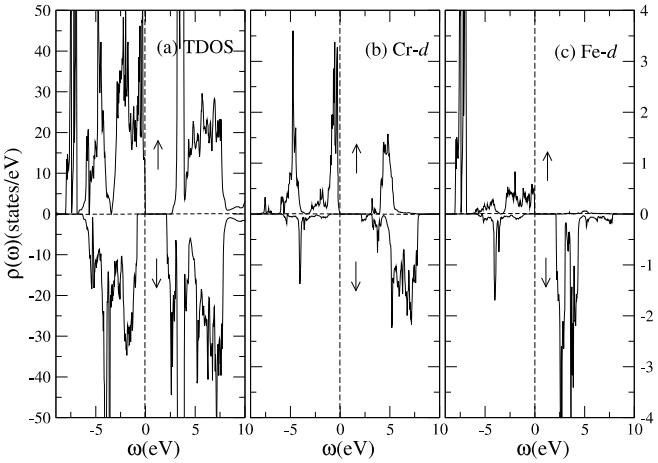


Fig. 2. The density of states for the ground states of $LaFeO_3/LaCrO_3$ superlattice stacking along [111] direction: (a) total DOS, (b) [(c)] atomically resolved partial DOS projected onto Cr (Fe) *3d* orbitals. The contributions from majority and minority spins are indicated by the positive and negative vertical values, respectively. Fermi energy is indicated by vertical dashed lines.

structures of the superlattices stacking along [001], [110], and [111] directions are C-type AFM, A-type AFM, and FM, respectively. These results are in fact in good agreement with experiments observations.

p	stacking directions		
(n,m)	[001]	[110]	[111]
(1,1)	C	A	B
(1,2)	$C_{4/6}G_{2/6}$	$A_{2/6}E_{4/6}$	$F_{2/6}J_{4/6}$
(2,2)	CG	E	FH

Tab. 1. Magnetic structures of $[LaFeO_3]_n[LaCrO_3]_m$ superlattices. To classify the complex magnetic structures, we use notation A-G. H and J are depicted in Fig. 3.

The magnetic moments obtained for Fe and Cr ions are 4.19 μ_B and 2.99 μ_B for the superlattice stacking along [001] direction, 4.24 μ_B and 3.04 μ_B for the one stacking along [110] direction, and 4.27 μ_B and 3.09 μ_B for the one stacking along [111] direction. Fig. 2 shows the results for density of states (DOS) of the superlattice with p = (1,1) stacking along [111]

direction. It is clearly seen in Fig. 2 (a) that the ground state is insulating. We find that states near the Fermi level are mostly contributed by transition metal 3d orbitals. Figs. 2 (b) and (c) show the projected DOS for Cr and Fe irons, respectively. It is observed in Figs. 2 (b) and (c) that (i) 3d orbitals with the minority spin are mostly empty for both Fe and Cr and (ii) 3d orbitals with the majority spin are instead almost fully occupied for Fe. By projecting Bloch functions onto atomic-like orbitals, we find that the 3d electron occupancies with majority spin for Cr are 0.967 ($\mathbf{d}_{xy}$), 0.966 ($\mathbf{d}_{yz}$), 0.966($\mathbf{d}_{zx}$), 0.292($\mathbf{d}_{x^2-y^2}$), and 0.317($\mathbf{d}_{3z^2-r^2}$), whereas the ones for Fe are close to one. Therefore, it is safely concluded that Fe and Cr ions are both in the high spin configuration. Qualitatively the same results are obtained for the other superlattices with **p** = (1,1) stacking along [001] and [110] directions, which will

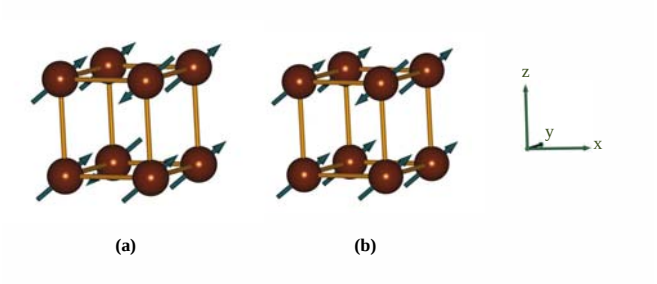


Fig. 3. Schematic figures of spin structure units: (a) H and (b) J.

be presented elsewhere. Next, we study the $[LaFeO_3]_n[LaCrO_3]_m$ superlattices with p = (1, 2) and (2,2) in different stacking directions. The magnetic structures of the ground states, together with the ones for p = (1,1), are summarized in Table 1. We find rather complex magnetic structures, including ones which are not even observed in bulk systems. To classify the complex magnetic structures, we adopt in Table 1 the notation introduced by Wollan and Koehler with several additional ones introduced in Fig. 3. Although they seem very complex, we find that all these magnetic structures are understood using KG rules, namely, FM coupling for neighboring Fe^{3+} (d^5 high spin state) and Cr^{3+} (d^3 high spin state), and AFM coupling for neighboring Fe^{3+} (Cr^{3+}) and Fe^{3+} (Cr^{3+}). It is especially intriguing that even E-type AFM ground state appears for the superlattice with p = (2, 2) growing along [110] direction, for which the spin alignment is up-up-down-down-like ordering, naturally expected to induce a finite ferroelectric polarization.

4. Conclusion

We have performed first-principles calculations based on DFT for various $[LaFeO_3]_n[LaCrO_3]_m$ superlattices to demonstrate that the magnetic structures of these superlattices can be controlled by changing the stacking direction and/or periodicity p = (n, m). We have shown that complex magnetic structures, including ones which are not even observed in bulk systems, can be stabilized in these superlattices. We have found that these magnetic structures are understood based on KG rule. Finally, it is interesting to note that we have also found the E-type magnetic structure for p = (2, 2) stacking along [110] direction, where, following extensive studies for multiferroics in manganite, a finite ferroelectric polarization is naturally expected. This line of study is now in progress and will be presented elsewhere. Our results demonstrate a great potential of artificially fabricated superlattices made of different transition metal oxides to tailor much complex magnetic structures.

In the following year, we will continue to study the Multiferroic behavior on $[LaFeO_3]_n[LaCrO_3]_m$ superlattice.