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Density functional studies of $LaMnO_3$ under uniaxial strain

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ABSTRACT

We study the electronic and magnetic properties of tetragonal $LaMnO_3$ (LMO) under uniaxial strain, appropriate for epitaxially grown LMO heterostructures, from density functional calculations. The optimized tetragonal structure without strain has volume, magnetic order, and Jahn–Teller distortions similar to the bulk LMO, which forms in the orthorhombic structure. Strain affects the relative magnitudes of these distortions and changes the magnetic and conduction properties. While unstrained LMO is a type A antiferromagnet and insulating, we find that it changes to a ferromagnetic metal under tensile strain condition (*c*-axis stretched). The latter is the result of a diminishing magnitude of the Jahn–Teller distortion with strain, which in turn reduces the splitting of the Mn-e_g orbitals, eventually leading to a metallic state, and finally to a ferromagnet due to the double exchange interaction. The calculated Poisson's ratio from geometry optimization agrees with the experimental values for the bulk.

1. Introduction

Currently there is a considerable interest on the epitaxially grown oxide interfaces because of potential new physics and promising device applications. One such interface being studied is the epitaxially grown LMO heterostructure on various substrates such as $SrTiO_3$. The heterostructure is often pseudomorphic, assuming the planar lattice constants of the substrate on which it is grown. While bulk LMO forms in the orthorhombic structure, it has the tetragonal structure when grown on a substrate, with the *ab* plane in registry with the substrate. It also becomes uniaxially strained, with the magnitude of the strain being different for different substrates. A wide range of electronic and magnetic properties varying from metallic ferromagnetic (FM) state to insulating antiferromagnetic (AFM) state or an intermediate canted magnetic state [1–9] has been observed in these heterostructures. In this paper, we study the effect of uniaxial strain on the electronic and magnetic properties of tetragonal LMO by performing density-functional calculations using the linear augmented plane wave method.

Our main results can be summarized as follows: (i) The unstrained structure is an insulating type A antiferromagnet with Jahn–Teller (JT) distortions similar to the experimental orthorhombic structure. (ii) With tensile strain, it becomes a ferromagnetic metal, while with compressive strain it becomes a type G antiferromagnetic insulator. (iii) As the tensile strain is increased, the strength of the JT distortions diminishes, which results in a reduced splitting between the Mn-e_g states leading to a ferromagnetic metal.

2. Method

The density-functional calculations were performed using the linear augmented plane wave (LAPW) method [10] with the general gradient approximation (GGA) [11] for the exchange-correlation functional. We considered a tetragonal unit cell of LMO and constructed a supercell of four formula units by doubling it both along the *ab* plane and along the *c*-axis to accommodate the relevant magnetic ordering, viz., the antiferromagnetic type G, type A, and type C, as well as the ferromagnetic structure. For each strain condition, all four magnetic structures were considered. For each case, the in-plane lattice constant 'a' was held fixed and full structural optimization was performed to obtain the out-of-plane lattice constant 'c' as well as the internal atomic positions within the cell.

For all strain conditions, the atomic sphere radii were taken as 2.5, 1.75, and 1.55 a.u. for La, Mn, and O, respectively. Generally the spin densities are well confined within a radius of about 1.5 a.u. [12]; therefore the resulting magnetic moments as well as the relative magnetic energies do not depend strongly on the variation of the atomic sphere radii. The basis set for solving the Hamiltonian included 4s, 4p, and 3d valence and 3s and 3p semicore functions at the Mn site, 6s, 6p, and 5d valence and 5s and 5p semicore functions for the La site, and 2s and 2p functions for the O sites. Thirty two irreducible k points in the full Brillouin zone were used for the self-consistent calculations.

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3. Results

Unstrained crystal structure: As mentioned already, the crystal structure of LMO is orthorhombic in the bulk [13], but assumes a tetragonal structure when grown epitaxially on oxide substrates. In view of this, we first study the equilibrium crystal structure of LMO in the tetragonal structure. For this, we took a series of in-plane lattice constants 'a' and for each case optimized both the out-of-plane lattice constant 'c' and the internal atomic positions. The minimum energies for each lattice constant and for two different magnetic structures are shown in Fig. 1. The global minimum occurs at the lattice constant $a_0=3.99$ Å with the corresponding value $c_0=3.76$ Å; The corresponding volume is 3% smaller than the experimental value for the bulk orthorhombic structure, which is reasonable. We considered all four magnetic structures (only two are shown in the figure) and found the type A AFM structure to have the lowest energy in agreement with the experiment.

The three important octahedral bond-stretching modes for the MnO_6 octahedron are indicated in Fig. 2. For the unstrained tetragonal crystal, consistent with the experiments [13], the calculated ground-state has the type A magnetic configuration. The tetragonal structure allows a checkerboard JT distortion on the *ab* plane of the type (Q_2, Q_3) alternating with $(-Q_2, Q_3)$, while the distortions repeat along the *c* direction. The strength of the checkerboard JT distortion is related to the lattice constants: $a=\sqrt{2/3}\,Q_1-Q_3/\sqrt{3}$ and $c=a+\sqrt{3}\,Q_3$ [14]. From the computed atomic positions, we calculated the magnitudes of the JT modes for the global minimum structure, which yielded the values $Q_{20}=0.14$ Å and $Q_{30}=-0.12$ Å, respectively, for the in-plane distortion and the octahedral stretching modes. The corresponding experimental values are 0.28 and −0.10 Å, respectively [13].

Effect of strain on structure: For the strained structure, the in-plane lattice constant was held fixed at a particular value and full structural optimization was made with the four magnetic configurations, viz., type C, type A, type G, and type F, with all but the last one being antiferromagnetic. The type G phase represents the Neél order AFM phase, while the type C corresponds to inter-layer FM ordering and intra-layer AFM ordering, while type A represents FM *ab* planes stacked antiferromagnetically.

The strain parameters in this paper are measured with respect to the calculated lattice constants a_0 and c_0 for the global minimum structure, where the two strain parameters $\varepsilon_{xx}=(a-a_0)/a_0$ and $\varepsilon_{zz}=(c-c_0)/c_0$ characterize the strain state in the tetragonal structure. The magnitudes of the JT distortions Q_1 and Q_3 for each strain condition are computed from the expressions for the lattice constant given in the last subsection, while the magnitude of Q_2 for each strain condition is obtained from the computed positions of the oxygen atoms from energy optimization.

In Fig. 3, we have plotted the total energies for different magnetic structures as a function of the uniaxial strain ε_{zz}. From the figure we see that for the unstrained LMO ($\varepsilon_{zz}=0$), the type A AFM phase is the stable configuration, which is consistent with Fig. 1. With tensile strain, LMO becomes ferromagnetic, while our results show that it becomes type G AFM with compressive strain. The reason for these magnetic transitions lies in a complex interplay between the JT interaction and the magnetic double and super exchange interactions, which we will return to in Section 4.

From the computed lattice constants, we can estimate Poisson's ratio. In the tetragonal structure, there are two different Poisson's ratios, ν_{21} and ν_{31}, where the first index denotes the direction of the longitudinal extension, and the second, the direction of the corresponding lateral contraction [15]. The strain parameters are related by the expression $\varepsilon_{xx}=\varepsilon_{zz}(2\nu_{31})^{-1}(\nu_{21}-1)$. Within the pseudo cubic approximation, the magnitudes of ν_{21} and ν_{31} are taken as equal, yielding a single value ν for Poisson's ratio, which we can determine from the computed optimized lattice constants *a* and *c*.

In Fig. 4 we have plotted the strain parameters and the calculated Poisson's ratio, which is about 0.40 in agreement with the measured value of 0.37 [16]. The volume of the lattice is

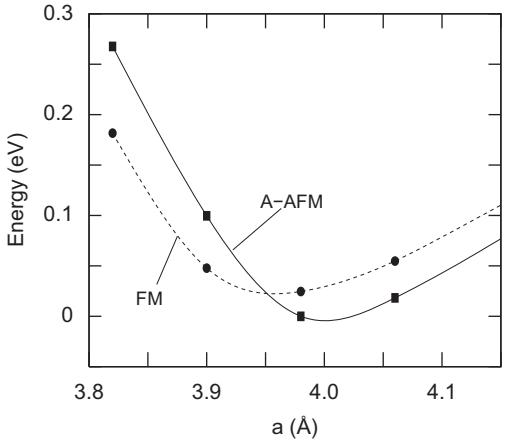

Fig. 1. Total energy per formula unit as a function of the in-plane lattice constant 'a' in the tetragonal structure for the FM and type A AFM magnetic ordering.

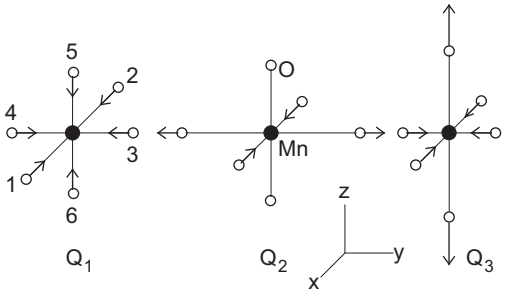

Fig. 2. Octahedral distortion modes for the MnO_6 octahedron with the eigenvectors: $|Q_1\rangle=(-X_1+X_2-Y_3+Y_4-Z_5+Z_6)/\sqrt{6}$, $|Q_2\rangle=(-X_1+X_2+Y_3-Y_4)/2$, and $|Q_3\rangle=(-X_1+X_2-Y_3+Y_4+2Z_5-2Z_6)/\sqrt{12}$, where X_1 denotes the *x* coordinate of the first oxygen atom, etc. Of these, Q_2 and Q_3 are Jahn–Teller active.

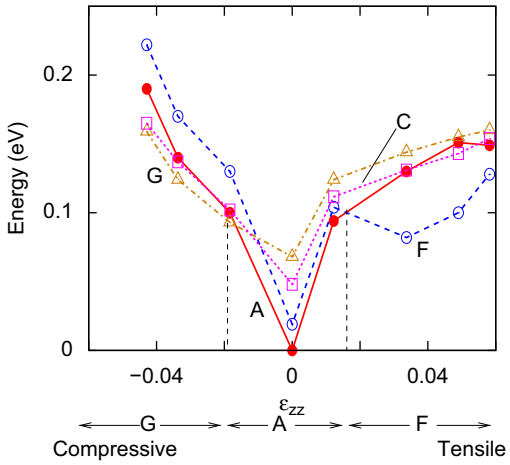

Fig. 3. Total energies for different magnetic phases of tetragonal LMO as a function of strain. The ground state magnetic ordering is insulating type A AFM, which is predicted to change to a metallic ferromagnet (F) under tensile strain condition.