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Theoretical study of magnetic phase transitions of cubic $SrMnO_3$ under physical and chemical pressures

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ABSTRACT

A magnetic configuration phase transition from antiferromagnetic (AFM) to ferromagnetic (FM) ordering is observed in cubic $SrMnO_3$ under negative pressure of −9 GPa by density functional calculations, while the ground state of G-type AFM ordering is maintained under the positive pressure. To realize the negative pressure, $SrMnO_3$ with chemical pressure by Sr site doping of Ba and La ions is further investigated, respectively. It is found that the required negative pressure is reduced by ~1 GPa for the cubic $SrMnO_3$ favoring FM configuration when doped with Ba, though it keeps C- or G-AFM under positive pressures. In addition, the stability of G-AFM configuration is destroyed in cubic $SrMnO_3$ when doped with La under various pressures.

1. Introduction

The perovskite $SrMnO_3$ is a polymorph with complicated magnetic ordering and polarizations and thus attracted much attention as a multiferroic material [1–3]. $SrMnO_3$ can be stabilized at orthorhombic, hexagonal, and cubic structures under various temperatures according to recent studies [4–7]. In particular, the cubic $SrMnO_3$ structure, with a high symmetry, has raised much interest for its rich magnetic property and potential applications [1–3,8–11]. The ground state of cubic $SrMnO_3$ synthesized by using a conventional cubic anvil-type high-pressure apparatus is regarded to be with a *G* type antiferromagnetic (G-AFM) ordering [3,8]. Here, G-AFM refers to the configuration with all nearest neighbor magnetic ions AFM coupling; C-AFM configuration implies that the AFM coupled *ab* planes stack ferromagnetically along the *c* direction; A-AFM configuration refers to the configuration that the FM coupled *ab* planes are coupled along the *c* axis antiferromagnetically. However, rich magnetic behaviors were reported in cubic $SrMnO_3$ with doping or strain approaches [3,12–14], while its ground state is still controversial theoretically [3]. It was reported experimentally that the G-AFM ordering may transfer to the C-AFM ordering in cubic $SrMnO_3$ by doping Ce or La [3]. Recently, bulk cubic $SrMnO_3$ with G-AFM and paraelectric orderings was reported to be stabilized by epitaxial strains [2], leading to an interesting ferroelectric–ferromagnetic state. As a result, epitaxial strains and doping carriers in cubic $SrMnO_3$ become the driving force for the magnetic phase transitions, among the various AFM phases and even between AFM and FM phases. As a matter of fact, pressures as three dimensional strains have great influence on the magnetic properties of perovskites [15–18].

In this article, we have investigated the physical and chemical (through A-site doping) pressures effects on the cubic $SrMnO_3$ by first-principles calculations. It is found that the ground state of G-AFM phase becomes more stable under positive pressures. $SrMnO_3$ under negative pressure shows transition between rich magnetic phases in a similar scenario under epitaxial strains as reported earlier [2]. In particular, FM phase is energetically favored when the pressure is more negative than −9.4 GPa. While negative pressure is hard to realize, we further investigated the impact of chemical pressure by doping ions with larger ionic radii at site A. It is found that the required negative pressure is reduced by ~1 GPa for the cubic $SrMnO_3$ favoring FM configuration when doped with Ba, though it keeps C- or G-AFM under positive pressures. The C-AFM configuration in cubic $SrMnO_3$ doped by La becomes the stable ground state under high positive pressures, largely in line with the experiment.

2. Computational details

In this work, the *ab initio* calculations were carried out by using density-functional theory within the generalized gradient approximation (GGA) and beyond (+*U*) approaches [19,20] with the Perdew–Becke–Erzenhof (PBE) [21] parameterization as implemented in the Vienna *ab initio* simulation package [22,23]. The GGA + *U* method is used to deal with the Mn 3*d* electrons for a

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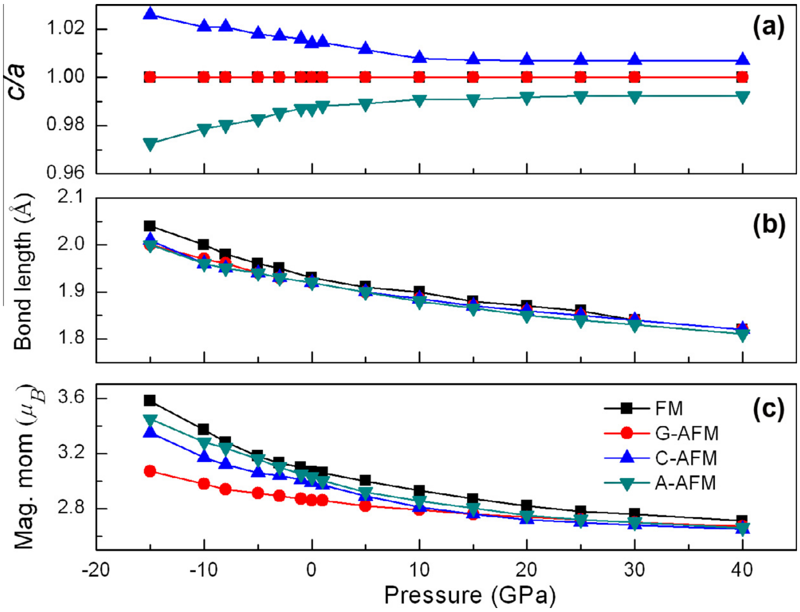

Fig. 1. The calculated *c/a* (a), bond lengths of Mn–O (b), and local magnetic moment of Mn ion (c) of $SrMnO_3$ with FM, G-AFM, C-AFM, and A-AFM configurations under various pressures.

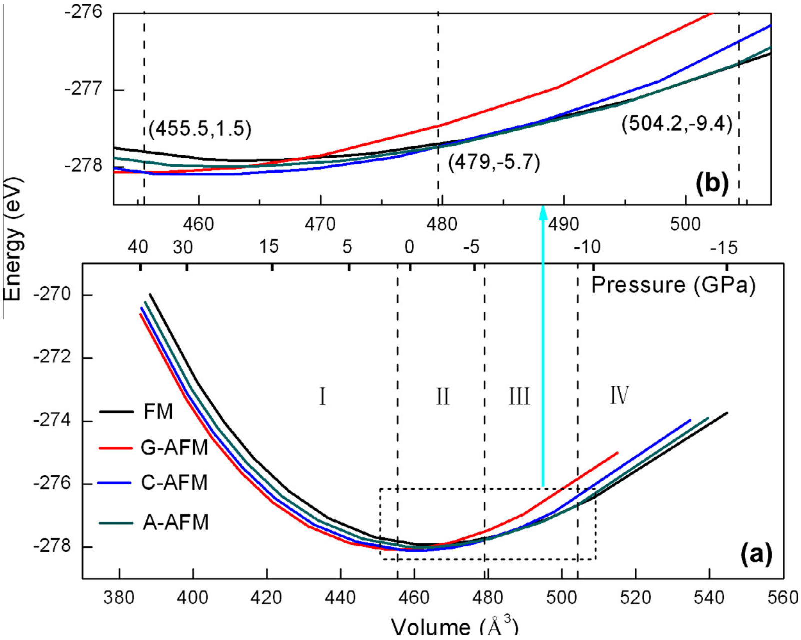

Fig. 2. The total energy of $SrMnO_3$ with FM, G-AFM, C-AFM, and A-AFM configurations under various pressures, with the details near the phase transitions enlarged for a clear view.

better description of the $SrMnO_3$ electronic structure, where $U = 3$ eV and $J = 0.3$ eV are adopted. Here the GGA + *U* calculated local magnetic moments (2.86 μ_B) of $SrMnO_3$ is in agreement with the experiment values($2.6 \pm 0.2\mu_B$) [2,8]. The energy cutoff is set to 500 eV and a 5 × 5 × 5 Monkhorst–Pack grid [24] is used for the 2 × 2 × 2 super cell model. The radii of Sr, Mn, and O are set to 1.635, 1.302, 0.802 Å (as default in the code package), respectively, for the calculations of local magnetic moments and projected density of states (DOS). The lattice vectors and the ionic positions are relaxed fully until the corresponding Hellman–Feynman forces are less than 0.01 eV/Å. The hydrostatic pressures within the range of −15 to 40 GPa have been studied in our simulations.

3. Results and discussion

An evident different magnetic behavior appears when $SrMnO_3$ is under positive and negative hydrostatic pressures. The Mn–O bond length is presented to change with varied pressures linearly. The range of Mn–O bond length is from 2.05 Å to 1.80 Å under pressures of −15–40 GPa. The local magnetic moment of Mn ions is changed with the positive pressure linearly, while the local magnetic moment of Mn ions becomes large under the negative pressure obviously. The cubic $SrMnO_3$ can be synthesized under high temperature and high pressure condition in the experiment, which is regarded to favor the G-AFM ordering [3,8]. Positive

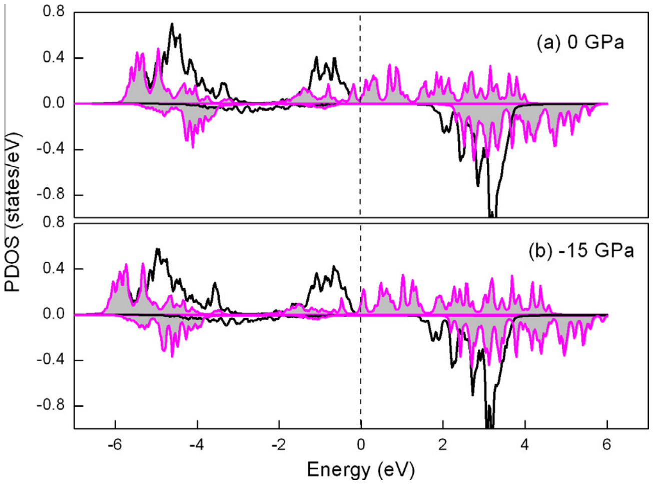

Fig. 3. The projected DOS of Mn 3*d* levels in FM ordered $SrMnO_3$ (a) without pressure and (b) with −15 GPa. Here the Fermi energy level is set to 0 and the spins up and down DOS are denoted by positive and negative values, respectively. The shaded plots correspond to the e_g levels, while the other lines correspond to the t_{2g} levels.

pressures keep $SrMnO_3$ more stable in G-AFM ordering. Relaxed $SrMnO_3$ with various magnetic orders is often stabilized at different lattice structures under certain pressure ranges. As shown in Fig. 1, $SrMnO_3$ with FM and G-AFM ordering maintains cubic lattice ($c/a = 1$) as its ground state under the studied pressures. However, it prefers to the tetragonal lattice distortions with C-AFM ($c/a = 1.014$) and A-AFM ($c/a = 0.987$) orderings, and changes gradually into a cubic lattice under increasing positive hydrostatic pressures. This indicates that the cubic lattice with high symmetry could be stable at the high positive pressure. Meanwhile, the bond length of Mn–O (Fig. 1) becomes shorter and the local magnetic moment of Mn decreases with the increasing positive pressure. This indicates that the shorter bond length of Mn–O and cubic lattice take advantages to keep the nearest Mn ions AFM (*G* type AFM) coupling. In fact, there are three phase transitions (Fig. 2) in the studied pressure range (40 to −15 GPa): G-AFM → C-AFM → A-AFM → FM, with corresponding transition pressures of 1.5, −5.7, −9.4 GPa, respectively. The three phase transitions in $SrMnO_3$ were also reported under epitaxial strain earlier [2]. Here, tetragonal lattice distortion of $SrMnO_3$ with C-AFM and A-AFM magnetic orders becomes large with increasing negative pressure. It seems that $SrMnO_3$ with C-AFM and A-AFM ordering are stable with quantitative tetragonal lattice distortion. FM ordering ultimately turns to be the ground state under a negative pressure, −9.4 GPa. Here the Mn^{4+} ion ($3\mu_B$) with increasing negative pressure is apt to become Mn^{3+}, in line with its increased local moment (3.58 μ_B). Mn ions of FM $SrMnO_3$ are located at the center of oxygen octahedral crystal field. Mn 3d orbitals split into two degenerate e_g levels and three degenerate t_{2g} levels. The Coulomb effect on the e_g levels is stronger than the t_{2g} levels since the distribution of e_g levels is opposite to the neighbor oxygen ions directly. As shown in Fig. 3, different from the zero pressure situation, the e_g levels of Mn ions near the Fermi level shift toward higher energy under −15 GPa, and are finally unoccupied and more localized. Meanwhile, the length of Mn–O becomes greater with the negative pressure to reduce the Coulomb effect on the e_g levels.

The lattice volume usually becomes smaller under the positive pressures, while it often expands under negative pressures. Thus, the negative pressure is hard to achieve physically in experiments. Here, we attempt to study the magnetic behavior of $SrMnO_3$ under chemical pressure through A site doping. The ionic radii of Sr^{2+}, Ba^{2+}, and La^{3+} are 1.13 Å, 1.35 Å, and 1.06 Å, respectively. Models of $Sr_7X_1Mn_8O_{24}$ (X = Ba, and La) were established to study the A site doping of ions with both larger and smaller radii. Three phase transitions (Fig. 4) were also observed in cubic $SrMnO_3$ with Ba substituting Sr under the range of positive pressure to negative pressure: G-AFM → C-AFM → A-AFM → FM. The transition pressures are −0.4,−5.2, −8.2 GPa, respectively, which indicates that Ba, with a larger ionic radius, substituted in cubic $SrMnO_3$ can realize certain negative pressure effect by expanding its volume to reduce the external negative transition pressures. However, cubic $SrMnO_3$ doped by La only contains two phase transitions under the range of studied pressure (Fig. 5): C-AFM → A-AFM → FM. The G-AFM magnetic configuration cannot be stabilized by the

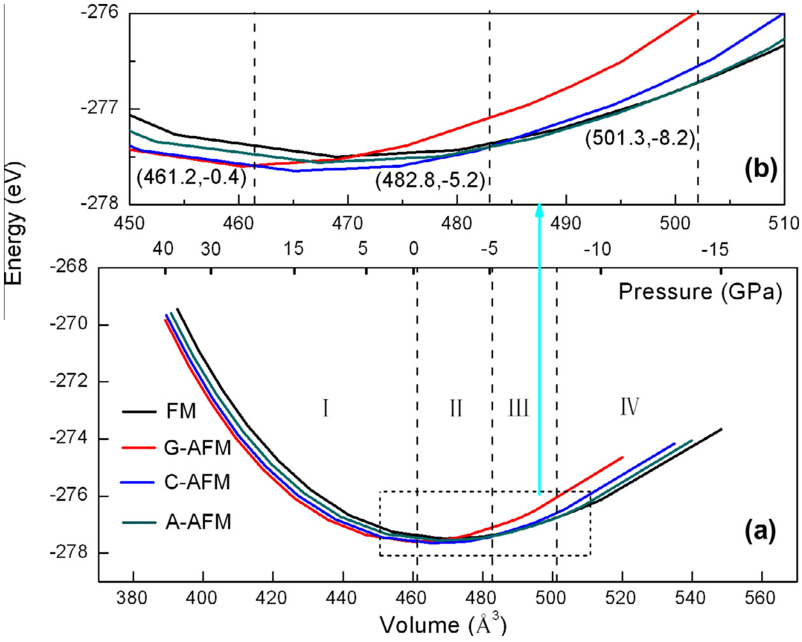

Fig. 4. (a) The energy of $Sr_7Ba_1Mn_8O_{24}$ and (b) the energy of $Sr_7Ba_1Mn_8O_{24}$ near the phase transition under different pressure with FM, G-AFM, C-AFM and A-AFM order.

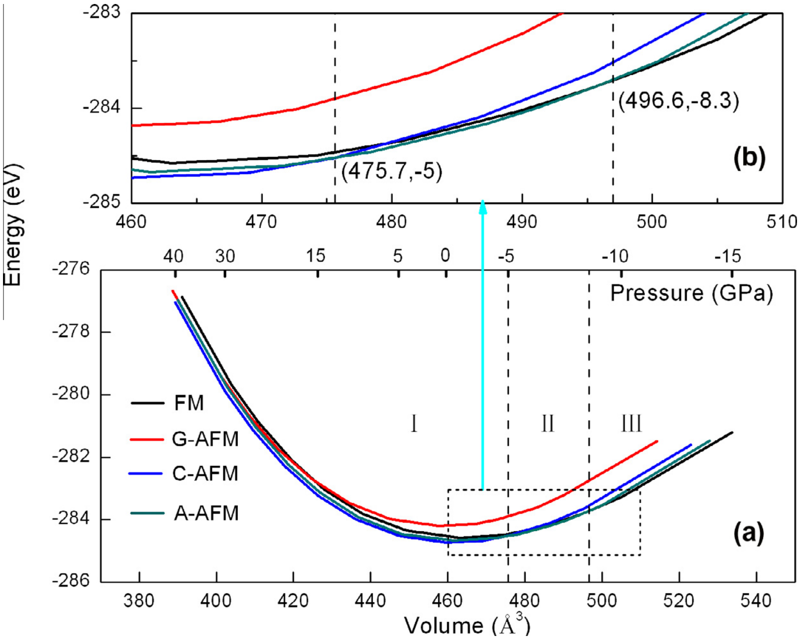

Fig. 5. (a) The energy of $Sr_7La_1Mn_8O_{24}$ and (b) the energy of $Sr_7La_1Mn_8O_{24}$ near the phase transition under different pressure with FM, G-AFM, C-AFM and A-AFM order.

pressure. In fact, La doped $SrMnO_3$ with more than 2% concentration is expected to be energetically favored to the C-AFM rather than the G-AFM configuration (the ground state of pure $SrMnO_3$) experimentally [3]. The experiment is explained that the mismatched valence electrons of A site impurity can afford electron-type carriers as electron doping in the La doped $SrMnO_3$, leading to a tetragonal lattice distortion and a transition of G-AFM to C-AFM [3]. The *c/a* is changed from 1.019 to 1.013 with an increased positive pressure to 40 GPa in $Sr_7La_1Mn_8O_{24}$ in its C-AFM configuration according to our calculations.

4. Conclusion

In summary, we have investigated the magnetic property of cubic $SrMnO_3$ under various pressures and found the cubic $SrMnO_3$ keeps the G-AFM magnetic order under the positive pressure and rich magnetic phase transitions were observed under negative pressures. The magnetic phase transitions G-AFM → C-AFM → A-AFM → FM can also be found in Ba doped $SrMnO_3$ with a reduced negative transition pressure, indicating the effect of negative chemical pressure by substitutions of ions with larger ionic radii. However, the original ground state of G-AFM could not be stabilized in the La doped $SrMnO_3$, in line with recent experimental reports.

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