Theoretical study of magnetic phase transitions of cubic SrMnO$_3$ under physical and chemical pressures

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A magnetic configuration phase transition from antiferromagnetic (AFM) to ferromagnetic (FM) ordering is observed in cubic SrMnO$_3$ under negative pressure of $\sim9$ 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 $\sim1$ 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.

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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 $\sim9.4$ 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 $\sim1$ 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 3d electrons for a
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 $\mu_B$) of SrMnO$_3$ is in agreement with the experiment values (2.6 ± 0.2 $\mu_B$) [2,8]. The energy cutoff is set to 500 eV and a 5 x 5 x 5 Monkhorst-Pack grid [24] is used for the 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
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 $\rightarrow$ C-AFM $\rightarrow$ A-AFM $\rightarrow$ 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 $\mu_B$). Mn ions of FM SrMnO$_3$ are located at the center of oxygen octahedral crystal field. Mn 3d orbitals split into two degenerate eg levels and three degenerate t$_{2g}$ levels. The Coulomb effect on the eg levels is stronger than the t$_{2g}$ levels since the distribution of eg levels is opposite to the neighbor oxygen ions directly. As shown in Fig. 3, different from the zero pressure situation, the eg 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 eg 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 models of Sr$_7$X$_1$Mn$_8$O$_{24}$ ($X =$ 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 $\rightarrow$ C-AFM $\rightarrow$ A-AFM $\rightarrow$ 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 $\rightarrow$ A-AFM $\rightarrow$ FM. The G-AFM magnetic configuration cannot be stabilized by the...
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$_7$La$_1$Mn$_8$O$_{24}$ 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 $\rightarrow$ C-AFM $\rightarrow$ A-AFM $\rightarrow$ 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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