Multiple magnetoelectric coupling effect in BaTiO$_3$/Sr$_2$CoMoO$_6$ heterostructures

Chang Liu$^{1,2}$, Wenhui Wan$^1$, Sai Gong$^1$, Hongbin Zhang$^3$ & Wei Guo$^1$

Due to the demand of controlling magnetism by electric fields for future storage devices, materials with magnetoelectric coupling are of great interests. Based on first-principles calculations, we study the electronic and magnetic properties of a double perovskite Sr$_2$CoMoO$_6$ (SCMO) in a hybrid heterostructure combined with BaTiO$_3$ (BTO) in different polarization states. The calculations show that by introducing ferroelectric state in BTO, SCMO transforms from an antiferromagnetic semiconductor to a half-metal. Specially, altering the polarization direction not only controls the interfacial magnetic moment, but also changes the orbital occupancy of the Co-3$d$ state. This novel multiple magnetoelectric coupling opens possibilities for designing new type of spintronic and microelectronic devices with controllable degree of freedom of interfacial electrons in the heterostructures.

Multiferroics has attracted extensive research interests because magnetoelectric (ME) coupling effect enables control of magnetic properties via electric fields, and vice versa$^{1-3}$. These superior characteristics possess wide range of possible novel applications, such as ME actuators, sensors, and high density nonvolatile memory devices$^{4-7}$. Because of the relatively high ME operation temperatures and remarkable performance among the multiferroic family, composite multiferroic heterostructures, which are composed of magnetic materials and ferroelectric oxides, have been widely studied$^{8-11}$. In general, three types of physical mechanism of ME coupling in such structures have been proposed$^{9,12}$, including strain mediated$^{13-17}$, charge mediated$^{18-20}$, and exchange interaction mediated mechanisms$^{21,22}$. Under such theoretical guidance, many efforts have been focused on searching new multiferroic systems with novel properties and high performance$^{11,23-25}$.

The orbital degree of freedom plays an important role in electronic structure and magnetic ordering and hence has a significant effect on physical properties$^{26,27}$. Usually, the orbital occupancy and shape can be modulated through introducing strain, but it is hardly controllable and inevitably introduces defects to materials. Very recently, Song et al. found in their experiment that the interfacial orbital occupancy can be partially changed under electric field in BaTiO$_3$/La$_{2/3}$Sr$_{1/3}$MnO$_3$ multiferroic heterostructures$^{28,29}$, providing an orbital mediated new ME coupling mechanism. However, theoretical study on this new type of ME coupling is rare, and new materials with better performance are vital for future applications.

In this paper, by means of first-principles calculations, we have studied three types of multiferroic heterostructures composed by ferroelectric material BaTiO$_3$ (BTO) and antiferromagnetic (AFM) double perovskite Sr$_2$CoMoO$_6$ (SCMO) with different BTO polarization states. SCMO has a conventional double perovskite structure: the alternated CoO$_6$ and MoO$_6$ octahedrons with opposite rotations along [001] are arranged as a checkerboard configuration. Its antiferromagnetic order is along [101] direction and the Neel temperature is about 34 K$^{30,31}$. When introducing electric polarization in the BTO-SCMO heterostructure, SCMO transforms from AFM semiconductor to a ferromagnetic (FM) half-metal. Via changing the direction of the dipole moments in BTO, a considerable variation of interfacial magnetization has been achieved, corresponding to a strong ME coupling. Particularly, we find that the orbital occupancy of interfacial Co$^{2+}$ ions can also be controlled by the polarization. This new degree of freedom of interfacial electrons together with magnetism, conductivity and spin polarization, are all coupled with the electric polarization, leading to a multiple ME coupling effect. We believe that such coupling opens new perspectives in applications of composite multiferroic heterostructures for magnetic storage, microelectronic and spintronic devices.

$^1$School of Physics, Beijing Institute of Technology, Beijing, 100081, China. $^2$Kunming Institute of Physics, Kunming, 650223, China. $^3$Department of Materials and Geosciences, TU Darmstadt, Darmstadt, 64287, Germany. Correspondence and requests for materials should be addressed to H.Z. (email: hzhang@tmn.tu-darmstadt.de) or W.G. (email: weigu07@bit.edu.cn)
Results

As shown in Fig. 1, three types of BTO-SCMO-BTO slab structures have been built along the c-direction with different BTO polarization states: Nonpolar system (NP) (Fig. 1 (b)); Type 1 polar system (P1) (Fig. 1 (c)) and Type 2 polar system (P2) (Fig. 1 (d)). More details for the heterostructures building can be found in the supplementary material (SM). We have calculated the total energy of ferromagnetic (FM) and antiferromagnetic (AFM) solutions in bulk SCMO and the configurations in Fig. 1. The energy difference between the two magnetic states $\Delta E_{AFM-FM}$ and the magnetic moments of Co and Mo atoms in the ground states are shown in Table 1. $\Delta E_{AFM-FM}$ is negative in bulk SCMO, indicating that AFM state is more stable than FM state. The magnetic moment $M_{Co} = 2.73 \mu_B$ and $M_{Mo} = 0.04 \mu_B$ for Co and Mo atoms, respectively, agreeing with previous experimental and theoretical studies.

For NP heterostructure in Fig. 1(b), the $\Delta E_{AFM-FM}$ and atomic magnetic moments on Co and Mo atoms are almost the same as in bulk SCMO, indicating that the SCMO slab is almost undisturbed and keeps the AFM state even in very thin film (~7.9 Å) and nonpolar BTO shows negligible effect on SCMO’s magnetic state. An interesting phenomenon arises when BTO generates ferroelectric instability in the P1 and P2 configurations, in which both of them turn into FM states from the bulk AFM solution. A considerable change in the atomic magnetic moment is observed (See Table 1), resulting in a large magnetoelectric coupling. For P1 configuration, the magnetic moment of Co is slightly decreased (from 2.73 $\mu_B$ to 2.69 $\mu_B$), while $M_{Mo}$ varied from 0.05 $\mu_B$ to $-0.42 \mu_B$, corresponding to a large change of about 0.47 $\mu_B$. On the contrary, in P2, $M_{Co}$ has a big change from 2.73 $\mu_B$ to 3.10 $\mu_B$, while $M_{Mo}$ remains nearly zero as in NP system.

To understand the nature of the polarization induced magnetism change, we have calculated the electronic structure and provide the densities of states (DOS) of bulk SCMO and heterostructures of BTO-SCMO-BTO in Fig. 2 (a) and Fig. 2 (b)–(d) in their ground states, respectively. BTO is a large gapped (about 3.3 eV) semiconductor, it has little contribution to the electronic states near $E_F$, so we only show the local DOS of atoms in SCMO; the local DOS from Sr atom is not shown in Fig. 2 for the same reason. For bulk SCMO in the AFM state (Fig. 2(a)), we find that it is a semiconductor with a small gap of about 0.4 eV, the valence band maximum (VBM) is composed of Co-3d and O-2p electron states while the conduction band minimum (CBM) mainly contains Mo-4d and O-2p states. There is no big difference in the DOS between the NP configuration (Fig. 2(b)) and bulk SCMO, except that the band gap becomes ~0.1 eV larger in NP system. This is probably due to the quantum confinement in ultrathin films. When polarization is induced in the P1 (Fig. 2(c)) and P2 (Fig. 2(d)), interestingly, both systems show half-metallic character where one spin channel (majority-spin) behaves like an insulator with a finite gap, while the other spin channel (minority-spin) has non-zero DOS at $E_F$. The magnetic moment variation in

![Figure 1. Atomic structure of three types of BTO-SCMO-BTO [001] multilayer configurations. Polarizations are induced by varying the Ti-O displacement in BTO. (a) Top view of the system. All three structures have been relaxed and the polarization orientation is marked by arrows. (b) Nonpolar system (NP), the BTO composition is pseudocubic with no polarization. (c) Type 1 polar system (P1), the polarization direction of BTO is towards SCMO. (d) Type 2 polar system (P2), the polarization direction is away from SCMO.](image-url)
Mo and Co atom between different polar states can again be understood by comparing their DOS. As mentioned before, the CBM is mainly composed of Mo 4d electron states and system is semiconducting in NP. However, in P1, the minority spin of Mo CBM state is partially filled just below the \( E_F \), while the orbitals with majority spin are still unoccupied. Hence Mo produces a negative moment of \(-0.42 \mu_B\). While in P2, the Mo CBM state is still unoccupied, therefore results in a nearly zero \( M_{Mo} \) like in NP.

For both P1 and P2 structures, the majority spin of Co is fully occupied while the minority spin only partially filled below the \( E_F \) such difference contributes to a net magnetic moment of \(-0.42 \mu_B\). While in P2, the Mo CBM state is still unoccupied, therefore results in a nearly zero \( M_{Mo} \) like in NP.

Figure 2. Local densities of states (DOS) of Co (blue line), Mo (dark yellow line), O (red line) atoms and Total DOS (black line) in (a) AFM bulk SCMO, (b) AFM NP, (c) FM P1 and (d) FM P2 configurations. Up- and down-spin DOS are shown in positive and negative values, respectively. The dotted lines correspond to Fermi level (\( E_F \)).
dxz/dyz orbitals. On the other hand, the in-plane Co-O-Mo bond angle gets larger in P2 than in P1. This octahedral rotation makes $d_{xy}$ orbital closer to the in-plane O anions while $d_{xy}$ is away from them. Therefore, the energy of $-d_{xy}$ will rise up and the $d_{xy}$ orbital energy will get lower at the same time. In brief, changes of the Co-O bond lengths raise the $dxz/dyz$ orbital energy while changes of the Co-O bond angle lower $d_{xy}$ state energy, resulting in the different orbital occupancy in P2. The second reason for this effect is the influence of an electric field caused by different signs of bound charges at the interfaces. In the P1 case, the electric dipole moment is pointing to the central SCMO (Fig. 4b), hence there are positive bound charges at the interfaces which attract electrons in $dxz/dyz$ states and reduce the orbital energy. On the contrary, in the P2 case, negative bound charges will raise the energy of $d_{xy}$ states. The $d_{xy}$ orbital does not get much influence in this mechanism because it is located in the $xy$ plane, away from the bound charges. As a result, the change in the Co-O octahedron structure and different interface bound charges together change the orbital occupation in P2.

The polarization induced half-metallic property may be responsible for the magnetism transition between the AFM and FM states. When SCMO turns into the half-metallic state due to the polarization from BTO, hopping interactions between the localized electrons and the conduction electrons cause a large spin splitting of the effective Mo $d$ band, resulting in a strong FM coupling between Co ions via the induced spin-polarized mobile electrons.

Figure 3. Projected Densities of states (PDOS) per atom of Co minority spin states in NP (a), P1 (b) and P2 (c). $d_{xy}$, $d_{xz}/d_{yz}$, $d_{z^2}$, $d_{xy}$ orbitals are shown as black line, red line, blue line and dark cyan line, respectively. The $d_{xz}$ and $d_{yz}$ orbital are degenerated due to the in-plane symmetry, so we only show one of them. The dotted lines correspond to Fermi level ($E_F$).

Figure 4. (a) Bond length and bond angle of Co-O octahedron in P1 and P2. The red small balls denote O ions and black lines denote Co-O bonds while the dotted lines are Mo-O and Ti-O bonds. (b) Schematic of different bound charges distribution in P1 and P2. Distribution of Co $d_{xz}$ electron is shown in the SCMO region.

$d_{xz}/d_{yz}$ orbitals. On the other hand, the in-plane Co-O-Mo bond angle gets larger in P2 than in P1. This octahedral rotation makes $d_{z^2}$ orbital closer to the in-plane O anions while $d_{xy}$ is away from them. Therefore, the energy of $d_{z^2}$ orbital will rise up and the $d_{xy}$ orbital energy will get lower at the same time. In brief, changes of the Co-O bond lengths raise the $d_{xz}/d_{yz}$ orbital energy while changes of the Co-O bond angle lower $d_{xy}$ state energy, resulting in the different orbital occupancy in P2. The second reason for this effect is the influence of an electric field caused by different signs of bound charges at the interfaces. In the P1 case, the electric dipole moment is pointing to the central SCMO (Fig. 4b), hence there are positive bound charges at the interfaces which attract electrons in $d_{xz}/d_{yz}$ states and reduce the orbital energy. On the contrary, in the P2 case, negative bound charges will raise the energy of $d_{xz}/d_{yz}$ states. The $d_{xy}$ orbital does not get much influence in this mechanism because it is located in the $xy$ plane, away from the bound charges. As a result, the change in the Co-O octahedron structure and different interface bound charges together change the orbital occupation in P2.

The polarization induced half-metallic property may be responsible for the magnetism transition between the AFM and FM states. When SCMO turns into the half-metallic state due to the polarization from BTO, hopping interactions between the localized electrons and the conduction electrons cause a large spin splitting of the effective Mo $d$ band, resulting in a strong FM coupling between Co ions via the induced spin-polarized mobile electrons.
electrons. It has been proposed that the oxygen-deficient SCMO has a strong FM state (\(T_c = 350 \text{ K to } 370 \text{ K}\)) with a dramatic increase of conductivity. This is also clear evidence that conducting electrons may induce FM magnetic coupling between Co\(^{2+}\) ions via the double-exchange mechanism in SCMO. Unfortunately, as the Neel temperature of SCMO is only about 34 K, it is therefore difficult to achieve the AFM–FM transition at room temperature. However, it is possible that double perovskites that have higher Neel temperature can be found through rational material design, and our approach provides a possible way to realize controllable AFM–FM transition through magnetoelectric coupling.

We have also tested a structure with thicker SCMO layers (1.5 u.c. SCMO + SrO) in P2 type of BTO polarization. We find that \(M_{Co}\) equals to 3.06 \(\mu_B\) near the interface; while for the Co atom in the center of SCMO, \(M_{Co}\) is reduced to 2.96 \(\mu_B\), indicating that the moment near the interface is mostly affected. Furthermore, we perform a calculation of a new BTO-SCMO polar state where both BTO polarizations point to the same direction (see Fig S5 in Supplementary material). The magnetic response near the interface resembles the characters in P1 and P2 depending on whether the BTO polarization pointing to or away from SCMO (more details can be found in Supplementary material). By switching electric fields between SCMO and BTO, one can change the polarization state between P1, P2 and this new polar state and thereby control the system magnetization. The resulting surface ME coefficient \(\alpha_s\) can be estimated by formula \(\alpha_s E = \mu_0 \Delta M = \alpha_s E\), where \(\Delta M\) is the range of magnetization change, \(E\) is the strength of applied electric field and \(\mu_0\) is the vacuum permeability. Taking \(\Delta M = 0.84 \mu_0 \Delta a^2\) (\(a\) is the lattice constant of SCMO) and assuming the coercive field of BTO \(E_c = 100 \text{kV/cm}\), we obtain a ME coefficient \(\alpha_s \approx 3.1 \times 10^{-10} \text{Gm^2/V}\) which is comparable to that in Fe/PbTiO\(_3\) system as reported by Lee et al.\(^{37}\).

In summary, we have demonstrated multiple magnetoelectric effects in the BTO/SCMO/BTO heterostructures based on first-principles calculations. It is shown that the polarization state in BTO can be used to tailor the magnetic ground state, interfacial magnetic moments and conductive state of SCMO. More importantly, switching polarization direction changes the magnetic coupling of the Co-3d states drastically, which is originated from the distortion of the CoO\(_6\) octahedron in addition to the bound charges at the interface. Our results not only provide a novel ME system with tunable multiple magnetoelectric effects, but also present a broad opportunity to realize applications of orbital degree of freedom in spintronic and microelectronic devices.

**Methods**

We have performed first-principles calculations of the electronic structures for three different BaTiO\(_3\)/Sr\(_x\)CoMoO\(_y\) [001] multilayer heterostructures (Fig. 1) using the Vienna Ab initio Simulation Package (VASP)\(^{40,41}\) with the projector augmented wave (PAW) method generated pseudopotentials. For all types of multilayers, a vacuum layer of 15 Å were used with a BaO surface termination as shown in Fig. 1. BTO layers close to the vacuum are fixed to their bulk positions and are more than 1 nm away from the BTO-SCMO interface. We have tested that the effects from such artificial surface states are negligible. The in-plane lattice constants are fixed to the experimental value of the bulk SCMO (5.565 Å) which is slightly smaller than \(\sqrt{2}\) times of BaTiO\(_3\)’s lattice (3.991 Å in experiment)\(^{38}\), the induced compressive strain in BTO can therefore suppress the in-plane ferroelectricity instability. Several optimizing processes have been made to eliminate possible artificial strains along c-direction. Details about the BTO-SCMO interface construction are shown in the supplementary material (SM). The convergence criterion was set to \(10^{-3}\) eV for the self-consistent electronic minimization and 0.03 eV/Å for forces during the ionitic relaxations. Since Co has 3d valence electrons, the on-site Coulomb interaction has been taken into account by using the LSDA++ approach. We have used U = 5.0 eV and J = 0.89 eV for Co atom because they well reproduced the AFM semiconductor state in SCMO\(^{35}\). After careful convergence tests, we have chosen a cutoff energy of 530 eV for the plane wave basis and a \(k\)-mesh grid of 13 \(\times\) 13 \(\times\) 1 for Brillouin zone sampling. The tetrahedron method was used for the Brillouin zone integration. More calculation details can be found in the supplementary material (SM).

**References**

1. Eerenstein, W., Mathur, N. D. & Scott, J. F. Multiferroic and magnetoelectric materials. *Nature* 442, 759–765 (2006).
2. Nan, C.-W., Bichurin, M. L., Dong, S., Viehland, D. & Sinhrivasa, G. Multiferroic magnetoelectric composites: Historical perspective, status, and future directions. *J. Appl. Phys.* 103, 031101 (2008).
3. Wang, K. F., Liu, J. M. & Ren, Z. F. Multiferroicity: the coupling between magnetic and polarization orders. *Adv. Phys.* 58, 321–448 (2009).
4. Bauer, U., Przybylski, M., Kirschnner, J. & Beach, G. S. Magnetoelectric charge trap memory. *Nanoscale* 4, 4761–4764 (2012).
5. Wang, Y., Li, J. & Viehland, D. Magnetoelectric for magnetic sensor applications: status, challenges and perspectives. *Mater. Today* 17, 269–275 (2014).
6. Ma, J., Hu, J., Li, Z. & Nan, C. W. Recent progress in multiferroic magnetoelectric composites: from bulk to thin films. *Adv. Mater.* 23, 1062–1087 (2011).
7. Vaz, C. A. Electric field control of magnetism in multiferroic heterostructures. *Journal of physics. Condensed matter: an Institute of Physics journal* 24, 333201 (2012).
8. Elbert, R. O. et al. Electric-field control of magnetic order above room temperature. *Nature materials* 13, 345–351 (2014).
9. Lu, C., Hu, W., Tian, Y. & Wu, T. Multiferroic oxide thin films and heterostructures. *Applied Physics Reviews* 2, 021304 (2015).
10. Vaz, C. A., Hoffman, J., Ahn, C. H. & Ramesh, R. Magnetoelectric coupling effects in multiferroic complex oxide composite structures. *Adv. Mater.* 22, 2990–2998 (2010).
11. Thiele, C., Dörk, K., Bilani, O., Rödel, J. & Schultz, L. Influence of strain on magnetization and magnetoelectric effect in \(\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3/\text{PMN-PT}(001)\) (\(A=\text{Sr; Ca}\)). *Phys. Rev. B* 75, 054408 (2007).
12. Zavaliche, F. et al. Electrically assisted magnetic recording in multiferroic nanostructures. *Nano Lett.* 7, 1586–1590 (2007).
16. Liu, M. et al. Voltage Tuning of Ferromagnetic Resonance with Bistable Magnetization Switching in Energy-Efficient Magnetoelastic Composites. Adv. Mater. 25, 1435–1445 (2013).

17. Zhang, S. et al. Electric-field control of nonvolatile magnetization in Co40Fe40B20/Pb(Mg1/3Nb2/3)O3(0.7)/Ti(0.3)O3 structure at room temperature. Phys. Rev. Lett. 108, 137203 (2012).

18. Rondinelli, J. M., Stengel, M. & Spaldin, N. A. Carrier-mediated magnetoelectricity in complex oxide heterostructures. Nature nanotechnology 3, 46–50 (2008).

19. Molegraaf, H. et al. Magnetoelastic Effects in Complex Oxides with Competing Ground States. Adv. Mater. 21, 3470–3474 (2009).

20. Duan, C. G., Jaswal, S. S. & Tsybml, E. Y. Predicted magnetoelastic effect in Fe/BaTiO3 multilayers: ferroelectric control of magnetism. Phys. Rev. Lett. 97, 047201 (2006).

21. Hochstrat, A., Bink, C., Chen, X. & Kleemann, W. Extrinsic control of the exchange bias. J. Magn. Magn. Mater. 272–276, Part 1, 325–336 (2004).

22. Fechner, M., Zahn, P., Ostanin, S., Bibes, M. & Mertig, I. Switching magnetization by 180 degrees with an electric field. Phys. Rev. Lett. 108, 197206 (2012).

23. Fusil, S., Garcia, V., Barthélémy, A. & Bibes, M. Magnetoelastic Devices for Spintronics. Annual Review of Materials Research 44, 91–116 (2014).

24. Tian, G. et al. Magnetoelastic Coupling in Well-Ordered Epitaxial BiFeO3/CoFe2O4/SrRuO3 Heterostructured Nanodot Array. ACS nano 10, 1025–1032 (2016).

25. Hu, J.-M., Nan, T., Sun, N. X. & Chen, L.-Q. Multiferroic magnetoelectric nanostructures for novel device applications. MRS Bull. 40, 728–733 (2015).

26. Tokura, Y. & Nagaosa, N. Orbital physics in transition-metal oxides. Science 288, 462–468 (2000).

27. Wang, G., Li, Z., Zheng, L. & Yang, Z. First-principles study on the orbital ordering of KCrF3. Phys. Rev. B 84, 045111 (2011).

28. Cui, B. et al. Magnetoelastic Coupling Induced by Interface Orbital Reconstruction. Adv. Mater. 27, 6651–6656 (2015).

29. Cui, B. et al. Manipulation of Electric Field Effect by Orbital Switch. Adv. Funct. Mater. 26, 753–759 (2016).

30. Itoh, M., Ohta, I. & Inaguma, Y. Valency pair and properties of 1:1 ordered perovskite-type compounds Sr2MMoO6 (M=Mn,Fe,Co). Materials Science and Engineering: B 41, 35–38 (1996).

31. Ivanov, S. A., Eriksson, S. G., Telgren, R., Rundlof, H. & Tegge, M. The magnetoelectric perovskite Sr2CoMoO6: An insight from neutron powder diffraction. Mater. Res. Bull. 40, 840–849 (2005).

32. Voita, M. C. et al. Induction of colossal magnetoresistance in the double perovskite Sr2CoMoO6. Chem. Mater. 14, 812–818 (2002).

33. Etz, C. & Steffler, D. First principle study of the magnetism of Sr2CoMoO6-δ (δ = 0, 1/2) double perovskites. The European Physical Journal B 54, 429–434 (2007).

34. Tringides, M. C., Jalochowski, M. & Bauer, E. T. Quantum size effects in metallic nanostructures. Phys. Today 60, 50–54 (2007).

35. Maruyama, T. et al. Large voltage-induced magnetic anisotropy change in a few atomic layers of iron. Nature nanotechnology 4, 158–161 (2009).

36. Sarma, D. D., Mahadevan, P., Saha-Dasgupta, T., Ray, S. & Kumar, A. Electronic structure of Sr2FeMoO6. Phys. Rev. Lett. 85, 2549–2552 (2000).

37. Sarma, D. D. A new class of magnetic materials: Sr2FeMoO6 and related compounds.Curr. Opin. Solid State Mater. Sci. 5, 261–268 (2001).

38. Duan, C. G. et al. Surface magnetoelectric effect in ferromagnetic metal films. Phys. Rev. Lett. 101, 137201 (2008).

39. Lee, J., Sai, N., Cai, T., Niu, Q. & Demkov, A. A. Interface magnetoelectric coupling in tricomponent superlattices. Phys. Rev. B 81, 144425 (2010).

40. Kresse, G. & Hafner, J. Ab initio molecular dynamics for open-shell transition metals. Phys. Rev. B 48, 13115–13118 (1993).

41. Kresse, G. & Furthmüller, J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. Computational Materials Science 6, 15–50 (1996).

42. Blöchl, P. E. Projector augmented-wave method. Phys. Rev. B 50, 17953–17979 (1994).

43. Kresse, G. & Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. Phys. Rev. B 59, 1758–1775 (1999).

44. Sai, N., Kolpak, A. M. & Rappe, A. M. Ferroelectricity in ultrathin perovskite films. Phys. Rev. B 72, 020101 (2005).

45. Díezquez, O., Rabe, K. M. & Vanderbilt, D. First-principles study of epitaxial strain in perovskites. Phys. Rev. B 72, 144101 (2005).

46. Anisimov, V. I., Zaanen, J. & Andersen, O. K. Band theory and Mott insulators: Hubbard U instead of Stoner. I. Phys. Rev. B 44, 943–954 (1991).

Acknowledgements
This work was financially supported by the National Natural Science Foundation of China (Grant No. 21503014) and Beijing Institute of Technology Research Fund Program for Young Scholars (Grant No. 2015CXM0434 and 20151842001). Hongbin Zhang acknowledges the financial support from the LOEWE project RESPONSE funded by the Ministry of Higher Education, Research and the Arts (HMWK) of the Hessen state (Germany).

Author Contributions
C.L. performed DFT calculations. C.L., W.H.W., S.G., H.B.Z. and W.G. analyzed the data and wrote the paper. H.B.Z. and W.G. supervised the project and the paper. All authors reviewed the manuscript.

Additional Information
Supplementary information accompanies this paper at doi:10.1038/s41598-017-03876-6

Competing Interests: The authors declare that they have no competing interests.

Publisher’s note: Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. The images or other third party material in this article are included in the article’s Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this license, visit http://creativecommons.org/licenses/by/4.0/.

© The Author(s) 2017