First-principles study on the phase diagram and multiferroic properties of \((\text{SrCoO}_3)_{1/\text{(SrTiO}_3)}_{1}\) superlattices

Guang Song & Weiyi Zhang

National Laboratory of Solid State Microstructures and Department of Physics, Nanjing University, Nanjing 210093, China.

To design a multiferroic material at atomic scale, strong spin-lattice and charge-lattice couplings play crucial roles. Our first-principles calculation on \((\text{SrCoO}_3)_{1/(\text{SrTiO}_3)}_{1}\) superlattices, with above coupling properties, yields a rich physical phase diagram as a function of epitaxial strain. In particular, a robust ferroelectric ferromagnetic insulator of \(Pc\) symmetry is stabilized at tensile strain \(\Delta a/a_0 = 0.86\%–5.53\%\). The polarization can be as large as \(36\, \mu\text{C/cm}^2\) and magnetic moment can reach \(6\, \mu\text{B per unit cell}\). The magnetocrystalline anisotropy energy \((0.16\, \text{meV/Co in (001) plane, 0.6\, meV/Co in (100) plane})\) is comparable with that of \(\text{TbMnO}_3\) compound and the magnetoelectric constant \(\alpha (1.44 \times 10^{-3}\text{ Gaussian unit})\) is comparable with that of \(\text{Co}_2\text{B}_2\text{O}_6\text{Br}\) compound. Our study suggests that epitaxially strained \((\text{SrCoO}_3)_{1/(\text{SrTiO}_3)}_{1}\) superlattices not only offer an excellent candidate for multiferroic materials, but also demonstrate the half-metal and ferromagnetic insulator properties with potential application in spintronic devices.

An ferroelectric ferromagnetic insulator can be a good candidate for multiferroic materials if the cross control of polarization or magnetization by magnetic or electric field can be manipulated\(^{1,2}\). Thus, a satisfactory multiferroic compound not only possesses large polarization and magnetization, but also requires strong magnetoelectric coupling\(^{3,4}\). As device miniaturization demands integrating electronic and magnetic components together, searching for new multiferroic materials constitutes an important research direction\(^{5,6}\).

The perovskite family of compounds offers an excellent candidate for multiferroic materials because of the strong coupling among spin, charge, and orbital degrees of freedom\(^{7,8}\). In particular, the subtle balance between different competing interactions makes the structural tuning very effective so that novel phenomena appear in the presence of either compressive or tensile strain\(^{9–11}\). Among others, Lee \textit{et al.} demonstrated the feasibility of converting nonferroelectric and nonferromagnetic \(\text{EuTiO}_3\) films into multiferroics under epitaxial tensile strain imposed by substrates\(^{12,13}\). The critical temperature \(T_C = 4.24\, \text{K}\) was very low, if, nevertheless, provided a new direction to explore multiferroic materials. The substrate induced strain also helps to make the \(\text{LuFeO}_3\) thin films a room temperature multiferroic, a weak ferromagnetism was observed at \(130\, \text{K}\) resulting from spin reorientation phenomena\(^{14}\). Inspired by the experimental advances, the first-principles studies have also offered valuable information in this endeavor. The multiferroic property has been predicted by Lee \textit{et al.} in \(\text{SrMnO}_3\) thin films under epitaxial strain and \(T_C = 92\, \text{K}\) was estimated\(^{15}\). An interesting phase transition between a ferromagnetic metal and ferroelectric antiferromagnetic (AFM) insulator is also shown in strained \(\text{SrCoO}_3\) thin film\(^{16}\). There are also attempts to transform ferroelectric compounds into multiferroic compounds by doping. For instance, ferromagnetism was induced in \(V\)-doped ferroelectric \(\text{La}_2\text{Ti}_3\text{O}_7\) compound\(^{17}\), but the magnetoelectric coupling was too weak to function as a multiferroic. Although great processes have been made in the search of multiferroic materials, many important issues remain unresolved. The critical temperature is still low which hinders applications; compounds with both large polarization and magnetization are rare; even if large polarization and magnetization have been achieved, strong magnetoelectric coupling still needs to be dealt with.

Since epitaxial strain plays such an important role in tuning material properties, combining crystals with similar structures but complementary properties into superlattices can be a good option\(^{18–20}\). One expects that the resultant materials might combine the characteristics of their constituents. Furthermore, interface mediated strain effectively couples the physical properties of their constituents so that the cross controls of constituent properties can be realized. In the recent studies on superlattice structures, the improper ferroelectric effect was found in \(\text{PbTiO}_3/\text{SrTiO}_3\) superlattices\(^{16}\) and a large magnetoelectric coupling was also observed in nonferroelectric \(\text{NdMnO}_3/\text{SrMnO}_3/\text{LaMnO}_3\) superlattices\(^{19}\). To shed further insight of interface effect on material
properties, we have studied, in this Report, the electronic and magnetic properties of (SrCoO$_3$)$_x$(SrTiO$_3$)$_{1-x}$ superlattice (made of SrCoO$_3$ and SrTiO$_3$ layers of one cubic-cell thick, SCO/STO). As is well known, SrCoO$_3$ is a prototype spin-state transition compound and possesses strong Jahn-Teller effect while SrTiO$_3$ is near the ferroelectric instability. It is hoped that large ferroelectricity and ferromagnetism can arise from its constituent compounds while strong magnetoelastic coupling can be achieved by the interface mediated spin-lattice and charge-lattice couplings.

To explore the phase diagram of SCO/STO superlattices, possible crystal structures with different oxygen octahedra tilting (OOT) patterns are derived from the unstable phonon modes of high symmetry P4/mmm structure and their relative stabilities are analyzed. In Glazer’s notation, the considered metastable crystal structures include: P4/mmm (a’$a’c’$), P4mm ($\Gamma_3$), Amm2 ($\Gamma_5$), P4/mmb (a’$a’c$), C2/m (a’$a’c$), Pmma (a’$a’c’$), P21/c (a’$a’c’$), Pbam (P4/m with Jahn-Teller distortion), P4bn (P4/mmb + $\Gamma_3$), Cm (C2/m + $\Gamma_5$), Pnma2 (Pmma + $\Gamma_3$), Pc (P21/c + $\Gamma_3$ + $\Gamma_5$), and Pb2a(Pbam + $\Gamma_3$) symmetries. $\Gamma_3$ and $\Gamma_5$ refer to the polar distortion modes perpendicular and parallel to the (001) plane of superlattices (see Supplementary Information). In addition, both ferromagnetic (FM) and nearest neighbor antiferromagnetic (AFM) states are considered for cobalt moments. Although the Co-ion is well known for its varying spin-state depending on crystal properties, we have studied, in this Report, the electronic and magnetic properties of (SrCoO$_3$)$_x$(SrTiO$_3$)$_{1-x}$ superlattice (made of SrCoO$_3$ and SrTiO$_3$ layers of one cubic-cell thick, SCO/STO). As is well known, SrCoO$_3$ is a prototype spin-state transition compound and possesses strong Jahn-Teller effect while SrTiO$_3$ is near the ferroelectric instability. It is hoped that large ferroelectricity and ferromagnetism can arise from its constituent compounds while strong magnetoelastic coupling can be achieved by the interface mediated spin-lattice and charge-lattice couplings.

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**Results**

In Fig. 1, we plot the energies of those possible ground states for the strain range $e = -5.6% - 5.89%$. As strain varies from compression to tensile, the ground state of the superlattices changes consecutively from the antiferromagnetic metal of P4mm symmetry to the ferromagnetic half-metal, insulator, and again half-metal of Pbam symmetry, then to the ferromagnetic insulators with almost degenerate P21/c and C2/m symmetries, and is followed by the robust multiferroic insulator of Pc symmetry with large polarization and magnetization combined with strong magnetoelectric coupling. This state is finally replaced by the antiferromagnetic insulator of Pc structure. To correlate the electromagnetic properties of possible ground states with the specific crystal structures, the lattice constant $c$, OOT, band-gap, and exchange energy are presented in Fig. 2.

Below we discuss the electronic and magnetic properties of various possible ground states one by one. For $-5.6% < e \leq -4.33$%, the most stable state is an AFM metal with P4mm symmetry (see Supplementary Information). This state has no OOT and the band gaps for both spin-up and spin-down bands are zero. The projected electron occupation number and magnetic moment on Co-d orbitals are $n_{d_{x^2}} = 6.86$ and $m_{d_{x^2}} = 2.75\mu_B$. The Co ions take an intermediate-spin state and form an AFM order.

As strain $e$ approaches $-4.33\%$, above AFM state is replaced by a ferromagnetic state with Pbam symmetry. From the band-gap shown in Fig. 2c, this state is initially a half metal with perfect spin polarization. The half-metal state is further developed into a ferromagnetic insulator at $e = -3.45%$. The band-gaps for both spin-up and spin-down bands become nonzero though one decreases while another increases with epitaxial strain $e$. A half-metal state with reversed spin polarization could be recovered at $e = -0.01\%$ which is, however, beyond the border ($e = -0.57\%$) of stability for this
state. AAFD vector changes very slowly with epitaxial strain, the only nonzero tilting angle along z-axis changes from 1.38° to 1.02° in the strain range (−4.3%, −0.57%). The electron occupation number \( n_{d}^{Co} = 6.90 \) is almost unchanged while magnetic moment \( m_{d}^{Co} = 2.25 \mu_{B} \) is reduced. These half-metal and ferromagnetic insulator may find their applications in spintronic devices.

In the region \(-0.57% < e \leq 0.86%\) where strain is small, the two ferromagnetic insulators with separate P21/c and C2/m symmetries appear as the most stable states. These two states are almost degenerate in energy and their crystal structures are all of monoclinic crystal class. Similar case was also found previously in EuTiO\(_3\)\textsuperscript{24}. The lattice constants and exchange energies have similar values. The electron occupation numbers and magnetic moments are almost identical, \( n_{d}^{Co} = 6.90, m_{d}^{Co} = 2.26 \mu_{B} \) for both states. The band-gaps for spin-up bands are of the same sizes while the band-gaps for spin-down PDOS are plotted downwards. Other notations are described in the text.

Further increasing the tensile strain destabilizes the ferromagnetic state and the AFM insulator of Pc structure becomes stable for \( e > 5.53%\). The x and y components of the AAFD vector are reduced significantly while the z component increases considerably. In comparison with the FM state of Pc structure, this state has the similar electron occupation number \( n_{d}^{Co} = 6.91 \) and slightly reduced magnetic moment \( m_{d}^{Co} = 2.11 \mu_{B} \). This state is also a multiferroic state, the calculated polarization is \((27.9 \mu C/cm^2, 34.0 \mu C/cm^2, 32.9 \mu C/cm^2)\) at \( e = 5.89%\).

To shed further insight into the physical properties of the multiferroic state of Pc structure, the spin and orbital resolved partial densities of states (PDOS) are presented in Fig. 4. The epitaxial strain is set at \( e = 2.3%\) and Fermi energy is set as zero. The Co-d orbitals are decomposed into triplet \( t_{2g}(d_{xy}, d_{yz}, d_{zx}) \) and doublet \( e_{g}(d_{x^2−y^2}, d_{3z^2−r^2}) \) sets with respect to CoO\(_6\) octahedron. The two nearest neighbors Co-I and Co-II ions are included in order to illustrate charge and orbital ordering phenomena. It is seen that the multiferroic state is an insulator with a band-gap of 0.12 eV.
PDOMs are the same for the $d_{xy}$-orbitals of both Co-ions while those of $d_{yz}$-orbitals are almost the same if x and y-axes are interchanged for two Co-ions. To analyze the spin and orbital configurations, the projected electron occupation numbers are calculated for Co-ions within the muffin-tin radius of 1.25Å. For $d_{xy}$-orbitals, all spin-up states are occupied while only one of the spin-down states is occupied for each Co-type. The doubly occupied $d_{xz}$-orbital is $d_{yz}$ for Co-I and $d_{xy}$ for Co-II. Thus, the Co-ions form an antiferro-orbital ordering and take an intermediate spin state. Such orbital ordering is made possible by the spontaneous Jahn-Teller distortion similar to LaMnO$_3$ (see Supplementary Information). The periodic elongation of CoO$_6$ octahedra along x and y-axes is not only responsible for alternately doubly occupied $d_{xz}$ and $d_{yz}$-orbitals, but also responsible for the different tilting angles along x and y-axes. We would like to emphasize that the Jahn-Teller distortion induced orbital-ordering is a typical feature for all the ground states of SCO/STO superlattices.

So far, we have obtained a ferroelectric ferromagnetic insulator with large polarization and magnetization. To verify whether such state is a genuine multiferroic state or not, the issues concerning the hysteresis loops for ferroelectricity and ferromagnetism as well as magnetoelectric coupling have to be addressed. While the hysteresis loop for ferroelectricity shows itself automatically by the double well structure, the hysteresis loop for the ferromagnetism has to be demonstrated through the magnetocrystalline anisotropy energy (MAE). By using the algorithms adopted by Xiang et al.$^{27}$, we compute the MAE of Co-ions of SCO/STO superlattice and the results are presented in Fig. 5a–b. The magnetic anisotropy energies are 0.16 and 0.61 meV at $\epsilon = 2.3\%$ in the (001) and (100) planes, respectively, which have the same order of magnitude as those of Mn-ions in the good multiferroic compound TbMnO$_3$.$^{27}$ Because of the oxygen octahedral tilting, the minima of MAE in (001) plane are located at 35° with respect to a-axis. The minimum of MAE in (100) plane is slightly off the (001) plane and at 93° measuring from c-axis. These data are consistent with the AAFD vector shown in Fig. 2(b) where y component (3.65°) is very close to the easy axis. Magnetoelectric constant can be similarly estimated using the technique devised by Íñiguez.$^{28}$ The dependences of polarization and magnetization as functions of polar-mode distortion are shown in Fig. 5c–d. The polar-mode is chosen as a linear interpolation between the paraelectric P21/c structure and the ferroelectric Pc structure.$^{27}$

The dielectric polarity $P_n^q = 55.9|q|$ (q is electron charge) and the magnetic analogue of the dielectric polarity $P_n^m = 27.64 \times 10^{-7} \mu_H/\AA$ can be extracted from the linear part of P and M. The corresponding eigenvalue $C_n = 15.07 \text{ eV/Å}^2$ is obtained from the total energy shown in Fig. 1, and the volume of unit cell is 248.53Å$^3$. The estimated value of magnetoelectric constant is $\alpha = 1.44 \times 10^{-3}$ in Gaussian unit, which is comparable to that of Co$_3$B$_2$O$_7$Br$_2$. To have a reliable magnetoelectric constant, as usual, a high convergence criterion ($10^{-6}$ eV) is imposed throughout the computations. Thus, the tensile strained SCO/STO superlattices do show excellent multiferroic property with large polarization and magnetization as well as strong magnetoelectric coupling.

**Discussion**

The robustness of the multiferroic state is checked against the different exchange-correlation functionals and different values of Coulomb repulsion U. As shown in the phase diagram for LDA + U with $U_{\text{eff}} = 3.9\text{ eV}$ and GGA + U with $U_{\text{eff}} = 2.9\text{ eV}$ (see Supplementary Information), the strain values for transition points in Fig. 1 may shift somewhat, but the ordering of various ground states are never altered. Thus the overall shape of the phase diagram is independent of the specific exchange-correlation functionals and the specific value of U.

The physical mechanism underlying the multiferroic property of SCO/STO superlattices can be understood from the crystal structure and electron orbital occupation information (see Supplementary Information). The asymmetrical bond lengths around Co- and Ti-ions in the Pc structure demonstrate off-center polar distortion within the CoO$_6$ and TiO$_6$ octahedra. Thus, the electric polarization is contributed by both Co- and Ti-ions. The magnetism comes from the unpaired Co-d electrons. Since Co-ions are responsible for both electric polarization and magnetization, strong magnetoelectric coupling is, of course, expected. With regard to the origin of ferromagnetism in the Pc structure, to the zeroth order, the spin-up states of Co-ions are all occupied while only one of the spin-down states is occupied. The electron occupation is 6 electrons. If we switch to hole picture, the level scheme for holes is just the reverse of level scheme for electrons. In the hole picture, lowest two Co-$d_{xy}$-orbitals and

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**Figure 5** | The magnetocrystalline anisotropy energy, polarization, and magnetization. (a)–(b) MAE of Co-ions in the (001) and (100) planes, respectively; (c)–(d) polar-mode distortion dependence of polarization and magnetization. Solid lines refers to $P_x$, $M_z$, dotted lines to $P_y = P_z$, $\Delta M_x = \Delta M_y$. Other parameters are described in the text.
Co-$d_{xz}$ (xy)-orbital are singly occupied by spin-up holes. The nearest neighbor Co-$d_{yz}$ (yz) and $d_{xy}$ (xz) orbitals are alternatively occupied by a spin-down hole due to antiphase antiferrodistortive tilting of oxygen octahedra. The scenario here is quite similar to LaMnO₃ case except the exchange of electrons for holes. AFM state would be favored if the hole occupation is exactly four. Since the exact electron occupation number is larger than 6, CoO₂ plane is intrinsically electron doped which favors the FM state according to the double exchange mechanism.

We have also extended our study to the generalized (SrCoO₃)$_n$/SrTiO₃$_m$ superlattices ($n = 1, 2, m = 1, 2$). The numerical analysis suggests that extended superlattice structures do not improve the material properties as a candidate for multiferroic compound. A close proximity between the ferromagnetic SrCoO₃ atomic layer and near ferroelectric SrTiO₃ atomic layer is the best configuration ensuring the novel multiferroic property. Deviating from this setting will either destabilize the ferromagnetism or favor metallic ground state.

In summary, comprehensive first-principles calculations have been carried out for the electronic and magnetic structures of SCO/STO superlattices and complex phase diagram has been obtained as a function of epitaxial strain. Half-metal and ferromagnetic insulator were discovered in the Pbam structure under compressive strain while a robust multiferroic state was found in tensile strained Pc structure. This ferroelectric ferromagnetic insulator has large polarization and magnetization, and strong magnetoelectric coupling arises from the strong piezoelectric and piezomagnetic coefficients as well as the peculiar orbital ordered structure. The calculated magnetocrystalline anisotropy energy is comparable to that of TbMnO₃ while the estimated interface mediated magnetoelectric coupling is comparable to that of CoO₂B₂O₇Br. This robust multiferroic state offers an interesting alternative worthy of further experimental investigations.

**Methods**

**Details of numerical computation.** In this Report, the electronic structures were studied using a plane wave pseudopotential approach to the density-functional theory as implemented in the Vienna ab Initio Simulation Package (VASP). We adopt the generalized gradient approximation with Perdew-Burke-Ernzerhof parametrization and the Dudarev implementation for the on-site Coulomb repulsion $U$ and exchange interaction $J_H$. The projected augmented wave potentials explicitly include 10 valence electrons for Sr (4s$^2$4p$^6$5s$^2$), 9 for Co (3d$^7$4s$^2$), 12 for Ti (3s$^2$3p$^6$4s$^2$3d$^2$), and 6 for O (2s$^2$2p$^4$). The wave functions are expanded in a plane-waves basis with an energy cutoff of 600 eV. A 5×5×5 Monkhorst-Pack k-point sampling is used for a 5 unit cell is fixed while the out-of-plane (c) lattice constant is 3.94Å is also reaped. To simulate an epitaxial strain, the in-plane lattice constant is (a=b) of a $\sqrt{2} \times \sqrt{2} \times 1$ unit cell is fixed while the out-of-plane (c) lattice constant and atomic positions are allowed to relax. The ferroelectric polarization is computed using the Berry-phase approach.

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