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Spin-state Transition in Unstrained & Strained Ultra-thin BiCoO₃ Films

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Using first principles density functional theory (DFT) based calculations supplemented with Hubbard U term (DFT+ U), we theoretically study the structural, electronic and magnetic properties of ultra-thin films of perovskite compound BiCoO₃, constructed along [001] direction at ambient condition. Our study shows that significant structural change occurs in thin-film geometry compared to bulk, which modifies the local oxygen coordination around the Co ion from a square pyramidal environment in the bulk phase to an octahedral environment in the thin-film structure. This changes high-spin state of Co³⁺ in bulk to low-spin state of Co³⁺ ions in the thin-film geometry. The influence of both tensile and compressive strain on the structural and electronic properties of the thin-film is studied. Our study shows a layer selective transition of Co³⁺ spin state when subject to tensile strain, which is found to be driven by the change in Bi environment. Our theoretical study should motivate experimental investigation of thin film of BiCoO₃.

1 Introduction

In search of lead-free multiferroic compounds, the Bi-based cobaltate compound BiCoO₃ was synthesized through high pressure route.¹ The ferroelectricity in this compound was found to be primarily driven by the lone-pair activity of the Bi³⁺ ion, magnetism being driven the high-spin (HS) state of Co³⁺ which orders in a C-type antiferromagnetic (C-AFM) structure below a Néel temperature of 420 K. The compound was predicted to exhibit a large polarization (calculated value of 120 $\mu\text{C}/\text{cm}^2$) and extremely high transition temperature.²

The well known flexibility of the Co spin-state, depending on external conditions, adds on another dimension to the problem. The ordered Co moment in BiCoO₃ at 5K was found to be 3.24 μ_B , indicating the high-spin state of Co³⁺, in marked contrast to similar compound LaCoO₃, where Co³⁺ is in the low-spin (LS) state at the lowest temperature and changes its spin state at higher temperature. In the situation contrary to LaCoO₃, the HS state of Co³⁺ in BiCoO₃ was found to be retained down to the lowest temperature, avoiding the temperature assisted spin-state transition.³ In an alternative route, the pressure induced spin-state transition in BiCoO₃ was investigated both theoretically as well as experimentally. The two DFT based studies predicted pressure induced structural phase transition from tetragonal ambient pressure phase to cubic⁴ and isosymmetric tetragonal⁵ high pressure phase accompanied by HS to LS transition of Co³⁺

and insulator to metal/semi-metal transition. Subsequent synchrotron X-ray and neutron power diffraction experiment revealed the structural transition from polar tetragonal symmetry to centro-symmetric GdFeO₃ type orthorhombic symmetry beyond a hydrostatic pressure of 3 GPa, accompanied by a drop of electrical resistivity and spin state transition from HS to LS.⁶ The less resistive high pressure phase is found to be insulating with narrow gap. The stabilization of the orthorhombic symmetry instead of theoretically predicted cubic or tetragonal symmetry and narrow gap insulating state instead of predicted metallic or semi-metallic state was argued to be driven by the Bi-O covalency effect.⁷ In very recent time the effect of uniaxial pressure has been investigated theoretically which shows stabilization of the LS state beyond a pressure of 9 GPa.⁸

Another possibility of inducing spin state transition is through thin-film geometry with specific aim of controlling properties, via tuning external parameters like strain, electric field etc. Such exercise has been carried out for the LaCoO₃, in which LaCoO₃ thin films have been grown on piezoelectric substrate and electric field is applied to tune the substrate lattice constant generating strain and consequently the magnetism in LaCoO₃ overlayers.⁹ To the best of our knowledge, such study has not been carried out for BiCoO₃. In view of difference in intrinsic behavior of LaCoO₃ and BiCoO₃ in terms of the ambient condition spin state of Co as well as in their temperature dependence, such a study is a worth while exercise. In the present study, we theoretically investigate the structural, electronic and magnetic properties of ultra-thin BiCoO₃ films employing density functional

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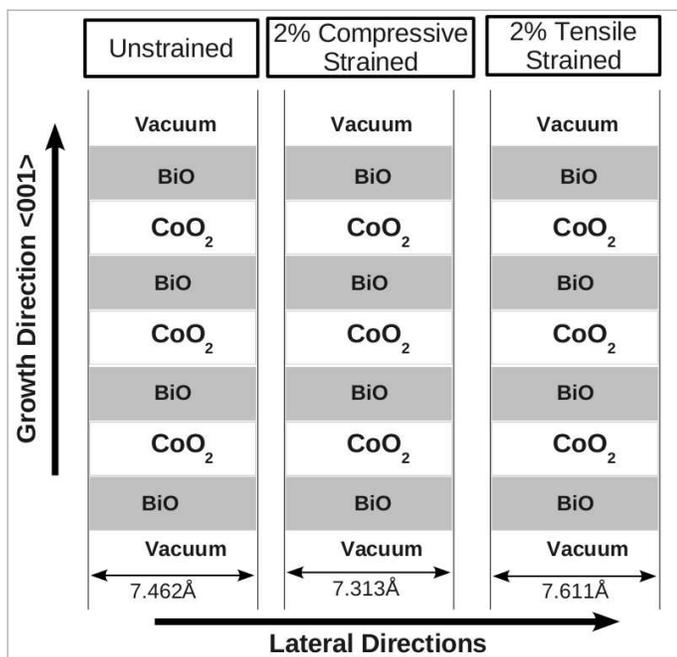


Fig. 1 The schematics of studied films with a growth direction of $\langle 001 \rangle$. Each film consists of BiO-CoO₂-BiO-CoO₂-BiO-CoO₂-BiO layers.

theory supplemented with Hubbard U . Our study shows dramatic changes in local structure in moving from the bulk to thin-film geometry, bearing important consequences in the spin-state of Co ions. We further study the effect of applied compressive and tensile strain on the thin-film geometry. The application of strain is found to have a profound effect on the magnetism with tensile strain being more effective in terms of producing a layer selective spin-state transition. We hope that our study will motivate future experimental studies to explore the validity of our theoretical predictions.

2 Computational Details

The DFT calculations have been carried out with choice of two basis sets, (a) linear augmented plane wave (LAPW) basis with no shape approximation to the potential and charge density as implemented in Wien2K¹⁰ and (b) plane wave based pseudo-potential method with the projector augmented wave potential¹¹ as implemented in VASP.¹² The consistency of the results between the two sets of calculations in LAPW basis and plane wave basis has been checked. We used a spin polarized generalized gradient approximation (GGA)¹³ to the exchange correlation functional. The missing correlation effect beyond GGA was taken into account through supplemented

Hubbard U correction.¹⁴ To simulate the thin-film geometry, a supercell of the bulk unit cell in ambient condition of dimension $2 \times 2 \times 8$ was constructed, and layers along $\langle 001 \rangle$ direction were removed to create the thin film geometry. Thus, the thin film was modeled through a repeated slab configuration, the slab consisting of atomic layers with the following sequence: BiO-CoO₂-BiO-CoO₂-BiO-CoO₂-BiO. This resulted in a unrelaxed film of thickness 15.12 Å and a vacuum layer of 22.68 Å in the cell.¹⁵ The thickness of vacuum layer was sufficient to keep the separation between the two slabs in periodic set-up of calculation large enough, allowing for structural relaxation. The defined supercell was held fixed, while the positions of the atoms were allowed to move along the vertical direction. This led to relaxation of the width of the thin-film along the vertical dimension, keeping the lateral dimension fixed as should be the case for films grown on substrates. The structural optimization was carried out until the forces on each atom became less than 5×10^{-3} eV/Å. All the Co, O and Bi atoms were considered to be inequivalent with no symmetry restriction, so that a situation like mixed spin-state solutions are allowed.

For the calculations in plane-wave basis set, a plane wave cut off of 800 eV was used. For calculations with LAPW basis, the number of plane waves was chosen following the criterion muffin-tin radius multiplied by K_{max} (for the plane wave) yielding a value of 7.0.

3 Results

3.1 Systems

We considered ultra-thin film of BiCoO₃ with a growth direction of $\langle 001 \rangle$ terminated on both sides by BiO (cf Fig 1). Our choice was motivated by creation of symmetric environment of all the CoO₂ layers in the films. The films, thus containing an extra layer of BiO are non-stoichiometric. With the remarkable advancement in layer-by-layer growth technique either by molecular beam epitaxy (MBE) or pulsed laser deposition (PLD), any kind of termination of surface layers is possible.¹⁶ We thus believe that our studied system could be synthesized experimentally. The studied film was subjected to both tensile and compressive strains which can be achieved by choice of different substrates, or using piezoelectric technology.

3.2 Structure

The structural relaxation of all three films under study, unstrained as well as that under compressive and tensile strain resulted into large compression in the width of the thin films, compared to initial unrelaxed width (see Fig 2.) constructed

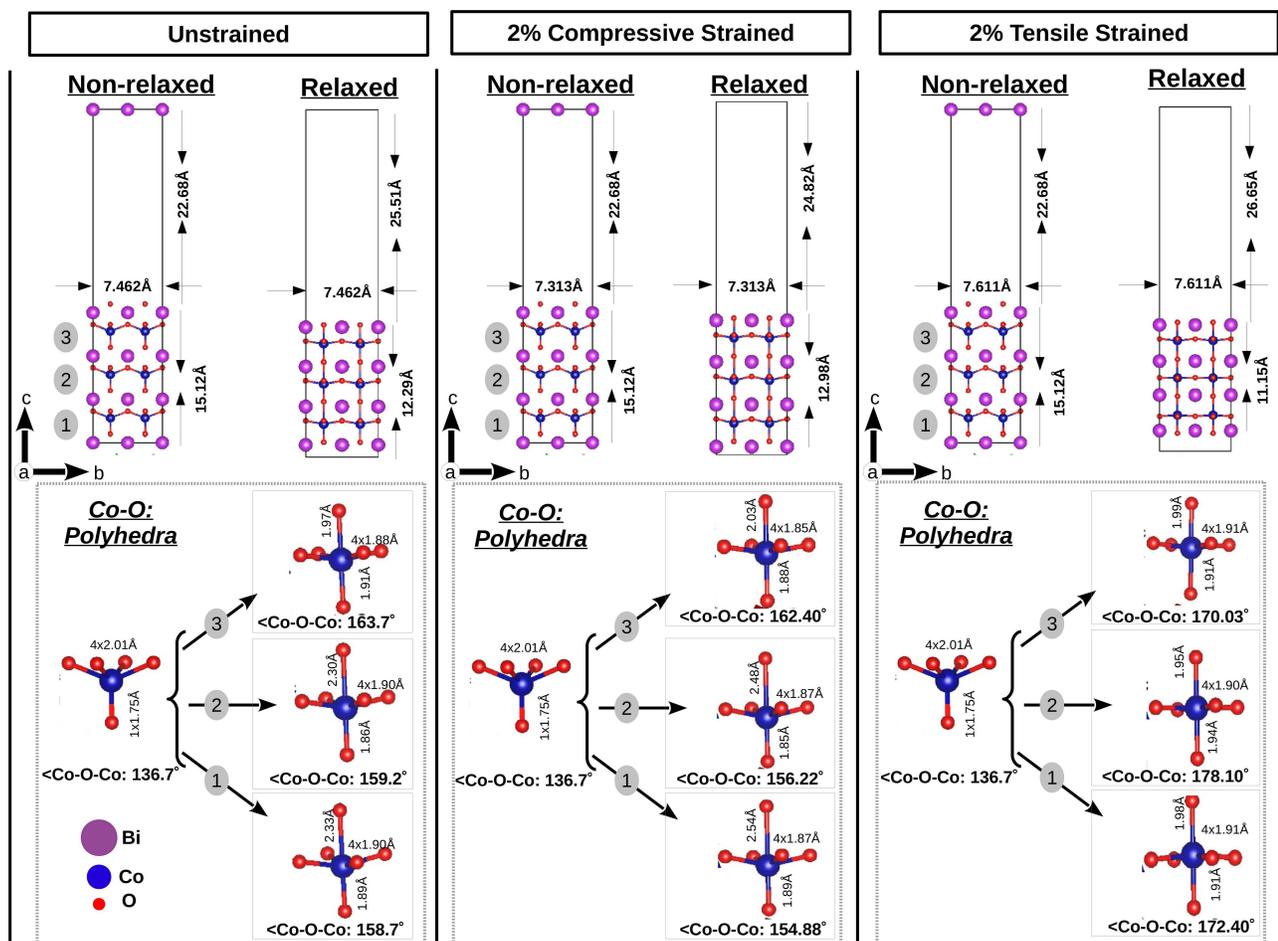


Fig. 2 The structure of the unstrained (left panels), 2% compressive strained (middle panels) and 2% tensile strained (right panels) BiCoO_3 in comparison to the initial guess structure, constructed from the bulk structure. Marked are the inplane lattice constants of the films, the thickness of the film and the width of the vacuum layer in the unit cell for each structure. The upper panels show the the geometry of the optimized films, while the bottom panels show the local oxygen coordination around Co ions, belonging to 1st, 2nd and 3rd CoO_2 layers in the film. Marked are the Co-O bondlengths as well Co-O-Co inplane bondangles.

from the bulk geometry in ambient condition. This generates an effective uniaxial pressure along the growth direction.

The compression in the film width is found to be as large as 18.7 % for the unstrained film compared to the initial unrelaxed structure. The structural relaxation produced significant changes in the Co-O-Co inplane bond angle as well as in the local environment of Co. The neighboring oxygens surrounding each Co ion in the three layers in the thin-film geometry formed octahedral coordination instead of polar, pyramidal coordination of oxygens around Co ions in bulk. The significant compression of the film width upon optimization also resulted into changes in Co-O-Co inplane bond angle from a value $\approx 137^\circ$ to values around 160° or so.

Application of 2% tensile strain resulted into further com-

pression of the film width by additional $\sim 9.3\%$ compared to the unstrained film, whereas application of 2% compressive strain resulted into expansion of the film width by $\sim 5.6\%$ compared to the unstrained film width. The octahedral coordination of oxygen environment in the unstrained film is maintained for both the tensile and compressive strained films. For tensile strained film CoO_6 octahedra are found to be almost regular with nearly equal Co-O bond lengths and Co-O-Co in-plane bond angle of $170\text{--}180^\circ$. Compressive strained films on the other hand shows distorted CoO_6 octahedra as in case of unstrained film with little change Co-O-Co in-plane bond angle compared to unstrained film.

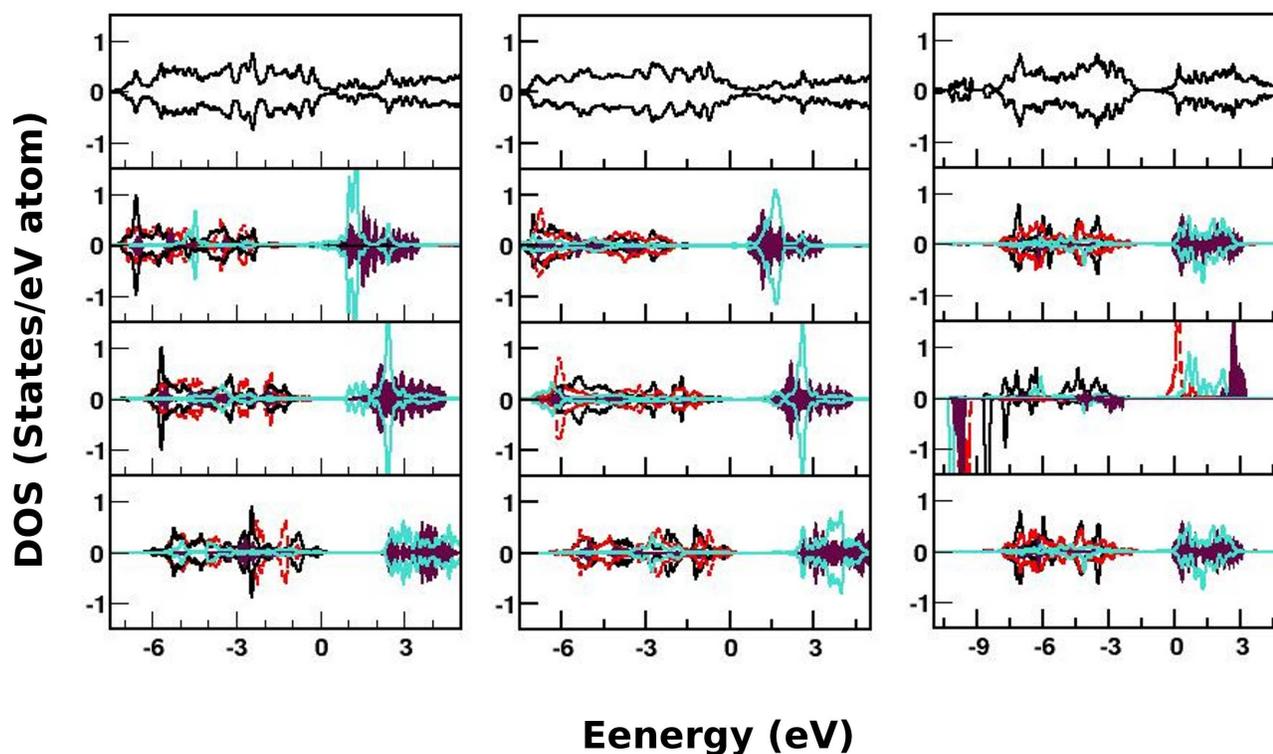


Fig. 3 (Color online) The GGA+ U density of the states for unstrained (left panels), 2% compressive strained (middle panels) and 2% tensile strained (right panels) BiCoO₃ films. The zero of the energy is set at GGA+ U Fermi energy. The upper panels show the total density of states, while the three following panels show the density of states projected to Co d states in layers 3, 2 and 1 (from top to bottom). The black solid, red dashed, cyan solid lines, and shaded magenta area represent Co d density of states projected on to d_{xy} , d_{yz}/d_{xz} , $d_{3z^2-r^2}$ and $d_{x^2-y^2}$ respectively.

3.3 Electronic and Magnetic Properties

Spin-polarized calculations have been carried out considering the optimized structure of the three films. As mentioned, all the calculations have been carried out with choice of GGA+ U as exchange-correlation functional. The choice of U is found to be an issue specially in deciding the spin-state of Co in LaCoO₃.¹⁷ In this context self-consistent determination of Hubbard U has been carried out for different spin-state of Co in thin-film geometry of LaCoO₃,¹⁸ which found a U value of 7eV for LS and intermediate spin-state (IS) and U value of about 5eV for HS state. We have thus carried out calculations considering two different choices of U values 7eV and 5eV. The consistency between the two sets of calculation provide confidence in our obtained results/conclusions. The results shown in the following are for the choice of $U = 7$ eV. We have checked the validity our calculations by starting with different initial guesses of the magnetic moments at Co sites corresponding to the HS, LS, IS, in order to avoid any bias on the choice of initial configuration.

Fig. 3 shows the density of states corresponding to un-

strained film, and the films under compressive and tensile strains. The top most panels show the total density of states, while the three following panels show the d density of states projected to Co ions in the layers 3, 2 and 1 (see Fig. 2).

Focusing on the left panels in Fig. 3, shown for the unstrained film, we find that the d_{xy} , d_{yz} , d_{xz} states corresponding to the octahedral crystal field split t_{2g} manifold of Co d states are filled up in both spin channels, while the $d_{3z^2-r^2}$ and $d_{x^2-y^2}$ states corresponding to the octahedral crystal field split e_g manifold of Co d states are empty in both spin channels. This clearly suggests the LS state of the Co ions in all three layers of the film, also supported by the calculated zero magnetic moment at the Co sites. The presence of extra BiO layer in the film provides uncompensated charge, which is expected to give rise to metallic character of the film following the polar discontinuity model.¹⁹ We find this uncompensated charge to be spin-polarized, with a magnetic moment of 0.43 μ_B in each Bi, which align antiferromagnetically in the BiO layer, with two of the spins pointing up and two pointing down out of the four Bi ions in the layer. This gives rise to a net zero moment

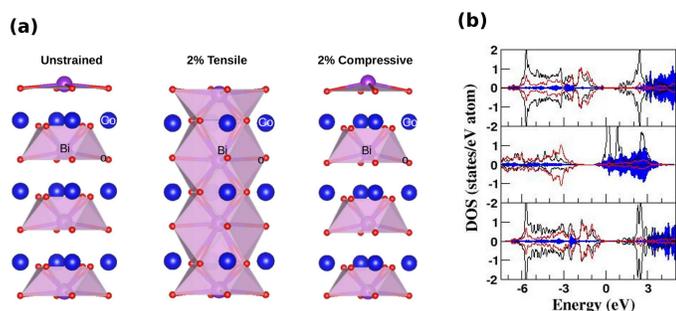


Fig. 4 (Color online) Left panel: The Bi-O environment, shown as shaded polyhedra in case of unstrained and strained films. Note the significant change in Bi-O environment under tensile strain. Right panel: Density of states projected onto Co *d* (black solid lines) and O *p* (red solid lines) states corresponding to middle CoO₂ layer and the contribution of Bi states neighboring the middle CoO₂ layer (blue shaded area) for the unstrained film (top), film under tensile strain (middle) and film under compressive strain (bottom).

in the film, and a near insulating nature of the film.

Application of 2% compressive strain keeps the electronic structure of the film more or less unchanged, as anticipated from the trend in structural changes, discussed in the previous section. As shown in middle panels of Fig. 3, the Co ions in all three different layers are found to maintain the LS state with completely filled d_{xy} , d_{yz} , d_{xz} states and completely empty $d_{3z^2-r^2}$ and $d_{x^2-y^2}$ states. The magnetic moment of Bi in the extra BiO layer is found to be nearly same as in unstrained film with a value of $0.39 \mu_B$ at each Bi site, which similar to the case of unstrained film, align antiferromagnetically in the BiO layer.

The application of tensile strain, on the other hand, is found to be much more effective, as shown in the right panels in Fig 3. While application of 2% tensile maintains the LS state of the Co ions in the 3rd and 1st CoO₂ layers, with completely filled d_{xy} , d_{yz} , d_{xz} states and completely empty $d_{3z^2-r^2}$ and $d_{x^2-y^2}$ states, major changes happen to Co ions belonging to the 2nd layer. We find the d_{xy} states to be completely filled, with d_{yz} , d_{xz} , $d_{3z^2-r^2}$ and $d_{x^2-y^2}$ states to be filled (empty) in majority (minority) spin channel, giving rise to HS $t_{2g}^4 e_g^2$ configuration. The calculated magnetic moment of Co ions in the 2nd layer turned out to $3.12 \mu_B$ in each Co site, in good agreement with the experimental estimate of the ordered moment of HS Co³⁺ of $3.24 \mu_B$ at 5K in bulk BiCoO₃ at ambient condition.⁶ We find the ordering of the HS Co spins in the 2nd layer to be antiferromagnetic, which also follows the C-type antiferromagnetic ordering of the HS Co spins in bulk phase.¹

The stabilization of the HS state of Co in the middle CoO₂ layer under tensile strain is curious and needs investigation. First of all, we checked whether the non-stoichiometry of the

studied film has any role to play on this issue. For this, we repeated calculations by removing the extra BiO layer from the top. This created oxygen coordination of Co to be pyramidal, octahedral and octahedral in the top (3rd), middle (2nd) and bottom (1st) layers. Even in this case, the effect of tensile strain is found to cause LS to HS transition in the middle layer. Having confirmed that nonstoichiometry has no role to play in this interesting behavior, the possible suspect is the role of Bi³⁺. Motivated by this, we investigated the O environment around Bi atoms in the unstrained and strained films. We find a remarkable change in the environment of Bi under tensile strain. While for unstrained film as well as for film under compressive strain, the Bi atoms around the middle Co layer have eight Bi-O short bonds and four Bi-O long bonds, under tensile strain the Bi positions shift making twelve Bi-O bondlengths of nearly similar values, causing a significant change in BiO polyhedra, as shown in left panel of Fig. 4. This change in Bi environment gets reflected in the hybridization of Bi states with that of Co, as seen in the partial density of states plot projected to Co-*d* and O-*p* and Bi states in the middle layer, as shown in right panel of Fig 4. There is clear evidence of significantly enhanced covalency between Bi and Co upon tensile strain. We have further carried out calculation considering the case with Bi replaced by La. This resulted in LS configuration of Co in the middle layer, confirming the role of Bi in driving the HS state of Co in the middle layer under tensile strain.

4 Summary

To summarize, we carried out a theoretical investigation of BiCoO₃ compound in ultra-thin film geometry. We studied the structural, electronic and magnetic properties. Our first-principles study shows that the realization of ultra-thin film geometry, causes substantial structural changes, most importantly compression of the lattice constant along the growth direction. This compression which acts like an uniaxial pressure, in turn changes the local oxygen neighborhood around Co ions from polar pyramidal coordination in bulk phase to octahedral coordination in thin film geometry. This drives the HS to LS transition of the Co³⁺ ions, suggesting thin film geometry to be a possible route to drive the LS transition of Co in BiCoO₃. We further studied the effect of strain on the thin film geometry. We considered the compressive as well as tensile strain. For the studied thin-film, we found the tensile strain to be more effective than the compressive strain in terms of switching the Co spin-state. Our study shows that application of tensile strain is able to cause layer selective switching of Co ions. This curious behavior is found to be driven by change in Bi environment. The DFT energetics of spin-state transition is well known to depend on the choice of the exchange-correlation functional.²⁰ However, similar trend

obtained in our results and that of the study involving uniaxial axis,⁸ provide confidence in our conclusion. Note that while our study was carried out within framework of GGA+*U*, the study reported in Ref.⁸ involved calculations with the choice of Hybrid functional.²¹ We hope that our study will generate interest in synthesis of ultra-thin films of BiCoO₃ and investigation of our theoretical proposals.

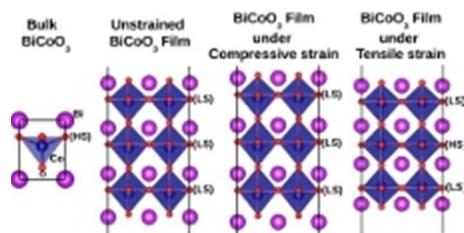
5 Acknowledgment

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BiCoO₃ in bulk and in film geometry. Marked are Co spin states.
80x39mm (72 x 72 DPI)