BNL-113595-2017-JA

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Submitted to Applied Physics Letters

October 2016

Condensed Matter Physics and Materials Science Department

Brookhaven National Laboratory

**U.S. Department of Energy
USDOE Office of Science (SC),
Basic Energy Sciences (BES) (SC-22)**

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Orbital configuration in CaTiO₃ films on NdGaO₃

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(Dated: September 7, 2016)

Despite its use as a constituent layer for realization of a polar metal and interfacial conductivity, the microscopic study of electronic structure of CaTiO₃ is still very limited. Here, we epitaxially stabilized CaTiO₃ films on NdGaO₃ (110) substrates in a layer-by-layer way by pulsed laser deposition. The structural and electronic properties of the films were characterized by reflection-high-energy-electron-diffraction, X-ray diffraction, and element-specific resonant X-ray absorption spectroscopy. To reveal the orbital polarization and the crystal field splitting of the titanium 3d state, X-ray linear dichroism was carried out on CaTiO₃ films, demonstrating the orbital configuration of $d_{xz}/d_{yz} < d_{xy} < d_{3z^2-r^2} < d_{x^2-y^2}$. To further explore the origin of this configuration, we performed the first-principles density function theory calculations, which linked the orbital occupation to the on-site energy of Ti 3d orbitals. These findings can be important for understanding and designing exotic quantum states in heterostructures based on CaTiO₃.

Alkali titanates ATiO_3 ($A = \text{Ba, Sr, Ca}$) with a prototypical perovskite structure recently have attracted tremendous interest due to the emergence of a vast amount of interesting phenomena in the bulk, thin films and heterostructures^{1–10}. For example, bulk BaTiO_3 (BTO) is a well known B-site ferroelectric material and presents an unexpected polar metal behavior upon electron doping,^{1,11,12} whereas BTO-based films and heterostructures can show significantly enhanced ferroelectricity^{9,10} and interface-induced room temperature multiferroicity.¹³ On the other hand, while bulk SrTiO_3 (STO) is a quantum paraelectric material below 40 K,¹⁴ strained STO films exhibits room temperature ferroelectricity;^{9,15,16} moreover, SrTiO_3 -based heterostructures show the emergence of interfacial high-temperature superconductivity (50~100 K),^{17,18} two-dimensional electron gases,^{2–7} and the coexistence of superconductivity and interfacial ferromagnetism.^{19–21} Besides these extensively studied phenomena, both BTO and STO single crystals are also widely used as substrates for epitaxial thin film synthesis. It is interesting to note that in spite of close similarity in composition and coordination between CaTiO_3 (CTO) and BTO or STO, its investigation is very limited due to the lack of quality single crystals.^{22–24} To further explore possible exotic quantum states, including for example A-site polar metal,¹ the knowledge of electronic structure and related physical properties in high-quality CTO single crystals is thus necessary.

Bulk CTO has a distorted GdFeO_3 -type orthorhombic (*or*) structure ($Pbnm$ space group) below 1486 K [see Fig. 1(a)] with lattice parameters $a = 5.3789 \text{ \AA}$, $b = 5.4361 \text{ \AA}$, and $c = 7.6388 \text{ \AA}$ (in orthorhombic setting) at room temperature.²⁵ In sharp contrast to bulk STO and BTO which show complex phase transitions,^{9,11,12,14} bulk CTO does not undergo any transitions below room temperature.²⁵ In addition, very recently metallic behavior was reported in CTO-based interfaces.²⁶ Importantly, unlike the bulk STO where TiO_6 octahedral tilts are absent, orthorhombic CTO with large octahedral units tilts and rotations can induce further splitting of Ti e_g and t_{2g} subbands. This structural effect can be one of the key factors to induce an anomalous orbital reconstruction in CTO-based interfaces resulting in the formation of quasi *one-dimensional* electronic bands,²⁷ as opposed to the conventional orbital configuration in STO-based perovskite heterojunctions. Based on this view, the exploration of orbital structure of d -electrons in CTO is fundamentally important and yet lack thus far.

In this Letter, we synthesized high quality CaTiO_3 films in a layer-by-layer way by pulsed laser deposition (PLD). The structural and electronic properties of films were investigated by reflection-high-energy-electron-diffraction (RHEED), X-ray diffraction (XRD), and resonant soft X-ray absorption spectroscopy (XAS). To reveal the orbital configuration of Ti $3d$ state, synchrotron based X-ray linear dichroism (XLD) was utilized, revealing d_{xz}/d_{yz} as the lowest state of Ti $3d$ band. To further understand this result, we performed the first-principles density-function-theory (DFT) calculations with the generalized gradient approximation (GGA) which attributed the differences to on-site energy for Ti $3d$ orbitals. These findings can be important for understanding and designing exotic quantum states in heterostructures based on CaTiO_3 .²⁶

As shown in Fig. 1(b), high-quality (001)-oriented (pseudo-cubic notation) CTO films (20 unit cells, $\sim 7.7 \text{ nm}$) were grown in a layer-by-layer fashion on NdGaO_3 (001)-oriented [pseudo-cubic notation, corresponding to (110)-orientation in orthorhombic notation] single crystal substrates by PLD using a KrF excimer laser operating at $\lambda = 248 \text{ nm}$ and 2 Hz pulse rate.²⁶ During the growth low oxygen pressure ($\sim 10^{-6} \text{ Torr}$) was supplied while keeping substrate temperature at 750°C . The layer-by-layer growth was monitored by *in-situ* RHEED. After growth, all samples were cooled down to room temperature at about $15^\circ\text{C}/\text{min}$ rate. Due to larger lattice parameters of NdGaO_3 (NGO) substrates, $a = 5.43 \text{ \AA}$, $b = 5.50 \text{ \AA}$, $c = 7.71 \text{ \AA}$, the epitaxial CTO films on NGO are under tensile strain ($\sim 1\%$). In this work, NGO substrates were carefully selected for the reason that the TiO_6 octahedral rotation angle of CTO films (on NGO substrates) is very close to the bulk CTO and thus the CTO films can be coherently strained.²² As seen in Fig. 1(c), the sharp RHEED patterns of CTO films indicate the development of a desired two-dimensional growth mode, which allows to determine the thickness of CTO films by the number of RHEED intensity oscillations. To further investigate the structural details of CTO films, XRD rocking curve and reciprocal space mapping were measured using $\text{Cu K}\alpha_1$ radiation. As shown in Fig. 2(a), the CTO films on NGO substrates are under expected tensile strain, which is also consistent with previous reports.²² Moreover, the reciprocal space mapping around NGO (-103) reflection [pseudo-cubic notation, see Fig. 2 (b)] further confirms the coherently strained nature of the CTO films.

Next, we investigated the electronic structure of the CTO films by carrying out XAS measurements in a total electron yield detection mode at the beamline 4.0.2 of the Advanced Light Source (ALS, Lawrence Berkeley National Laboratory). Figure 3 shows the linearly polarized XAS spectra at Ti $L_{3,2}$ -edge [see Fig. 3 (a) for the experimental setup]. As seen in Fig. 3(b), four characteristic peaks are observed in Ti L-edge XAS spectra on CTO films, which arise from the excitations from Ti $2p$ core level ($2p_{3/2}$ and $2p_{1/2}$)²⁸ in to Ti $3d$ band (t_{2g} and e_g states).^{29–35} The lineshape and peak energy positions of Ti L-edge XAS

spectra on CTO films are in a good agreement with expected Ti^{4+} oxidation state obtained on the reference bulk STO sample, thus confirming the proper 4+ charge state of Ti ions in our CTO films.

By analyzing the *linearly* polarized XAS spectra, we observed the unusual orbital configuration in CTO films. Generally, in a perovskite structure with cubic symmetry t_{2g} states form degenerate d_{xy} , d_{xz} and d_{yz} subbands, whereas e_g states form degenerate $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ subbands. However, with lower crystal symmetry (e.g. tetragonal or orthorhombic)³⁶, the degeneracy of t_{2g} and e_g states can be broken, leading to two possible orbital configurations, $d_{xy} < d_{xz}/d_{yz} < d_{x^2-y^2} < d_{3z^2-r^2}$ or $d_{xz}/d_{yz} < d_{xy} < d_{3z^2-r^2} < d_{x^2-y^2}$. In principle, these orbital configurations can be probed and distinguished by measuring linearly polarized XAS. This orbital shape selectivity is based on the strong dependence of absorption on the direction of photon polarization vector (E) with respect to crystal axis [see Fig. 3(a)] and thus electronic transitions from Ti core levels in to the unoccupied 3d states contain important information of orbital symmetry. For example, when photon polarization is aligned along the direction of Ti 3d orbital lobes, the contribution of this orbital to the absorption signal is largest^{37,38}. Based on this picture, one can expect that the contribution of linearly polarized XAS signal at Ti $L_{2,3}$ -edge for $E \parallel ab$ and $E \parallel c$ arises mainly from the unoccupied in-plane Ti $d_{xy}/d_{x^2-y^2}$ [I_V] and out-of-plane $d_{xz}/d_{yz}/d_{3z^2-r^2}$ [I_H] states, respectively. Consequently, the orbital state of Ti 3d band can be determined from the sign of XLD $\sim [I_H - I_V]$.²⁹⁻³⁵ As shown in Fig. 3(b), the observed XLD (blue curve) shows that the sign of the first main feature at ~ 457.9 eV is positive, implying that d_{xz}/d_{yz} subbands are the lowest state of Ti 3d band and thus selecting the specific orbital configuration, $d_{xz}/d_{yz} < d_{xy} < d_{3z^2-r^2} < d_{x^2-y^2}$ (see Fig. 4(a)).

To further investigate the orbital structure of Ti 3d states, we acquired O K -edge spectra on CTO films. Generally, in the simple ionic model, due to the fully occupied 2p shell of O ions with $1s^2 2s^2 2p^6$ configuration, the absorption on O K -edge with the transition from 1s to 2p states is blocked in the X-ray absorption process. However, due to the strong hybridization, the *covalent bonding* between the transition metal ion (Ti^{4+}) and oxygen can induce a sizable spectral weight on oxygen 2p character in the total unoccupied density of states³⁹⁻⁴¹. As seen in Fig. 4(b), due to the hybridization between Ti and O, the near-edge two main peaks (~ 530.8 eV and 533.3 eV) derived from Ti t_{2g} and Ti e_g bands, respectively, are indeed present.^{39,42} With this result, the orbital structure of Ti 3d states can be further checked by XLD at O K -edge. As seen in Fig. 4(b) (orange curve), the sign of the first main feature at ~ 530.25 eV is also positive, further corroborating the $d_{xz}/d_{yz} < d_{xy} < d_{3z^2-r^2} < d_{x^2-y^2}$ orbital configuration in our CTO films, which in turn agrees very well with the XLD data at Ti $L_{2,3}$ -edge.

To elucidate the origin of this orbital configuration, we performed DFT calculations with the GGA utilizing the Vienna *ab-initio* simulation package^{43,44}. We applied the Perdew-Becke-Erzenhof parametrization⁴⁵ for the exchange-correlation functional and used the projector augmented wave method⁴⁶. The calculations are done with an energy cutoff of 500 eV and k -point sampling on a $6 \times 6 \times 4$ grid with a $\sqrt{2} \times \sqrt{2} \times 2$ unit cell chosen to accommodate the $a^-a^-c^+$ octahedral rotations and tilts. The atomic positions and c -lattice constants are fully relaxed with 0.01 eV/Å force threshold, whereas a and b lattice parameters are fixed to experimental in-plane lattice constants of NGO. The calculated c -lattice constant of the strained bulk calculation is 7.69 Å showing a good agreement. As shown by the atom-projected density of states (PDOS) on Ca, Ti, and O atoms in Fig. 5(a), both Ca-O and Ti-O have detectable hybridizations but most contributions of the top edge of valence band and the bottom edge of conduction band are from O [red curves in Fig. 5(a)] and Ti [blue curves] bands, respectively. To investigate the crystal field splitting of Ti 3d state, the PDOS of Ti- d states are presented in Fig. 5(b). The crystal field splitting estimated by the distance between band bottom of t_{2g} and e_g bands is about 2.6 eV consistent with experimental value ~ 2.3 eV. To further investigating the shifts within t_{2g} and e_g bands, the Ti-O distances of two distinct Ti-sites are presented in Table I. There are small Jahn-Teller distortions as Ti-O distance in the local octahedral x - and y - axes (z direction parallel to the c axis) are shorten and elongated with the average in-plane Ti-O distance larger than out-of-plane direction. The Table II shows the on-site energy of Ti- d states investigated by Wannier function analysis using the wannier90 package⁴⁷ with the energy window including O 2p- and Ti 3d-derived bands. The on-site energy of d_{xz}/d_{yz} orbitals shows a small modulation due to the Jahn-Teller distortion and the average on-site energy of d_{xz}/d_{yz} orbitals is about 30 meV lower than that of d_{xy} orbital, which is consistent with the experimental observations. However, the calculated on-site energy of $d_{3z^2-r^2}$ orbital is about 60 meV higher than $d_{x^2-y^2}$ orbital, opposite to the experimental data, which needs further investigation. The inconsistency may be due to the missing electron core-hole interaction⁴⁸ that may have stronger effects on the e_g states. It is noted that the origin of crystal field splitting in LaTiO_3 has been investigated for a long time and is still under debate when involving the contribution of La displacements driven crystal field.⁴⁹

In summary, we developed layer-by-layer growth of high-quality orthorhombic CaTiO_3 films and investigated their elec-

tronic and orbital structures of Ti and O ions. A combination of RHEED, XRD and XAS confirmed the high structural and chemical quality of the films. In sharp contrast to cubic SrTiO₃ with the absence of orbital polarization, orbital polarization uncovered in orthorhombic CaTiO₃ has the orbital configuration of $d_{xz}/d_{yz} < d_{xy} < d_{3z^2-y^2} < d_{x^2-y^2}$. These findings can be important to advance functional materials by design to reach exotic orbital states in electron-doped CaTiO₃ single crystals¹ and heterostructures.²⁶

We thank Sang-Wook Cheong for providing us with a sintered CaTiO₃ target. J. C. and Y. C. acknowledge the support by the Gordon and Betty Moore Foundation EPiQS Initiative through Grant No. GBMF4534. X. L. was supported by the Department of Energy Grant No. DE-SC0012375 for his synchrotron work. S. M., and M. K. were supported by the DOD-ARO under Grant No. 0402-17291. The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. The first-principles calculations were performed on the Rutgers University Parallel Computer (RUPC) cluster and supported by the Office of Naval Research Grant N00014-14-1-0613.

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- ¹ N. A. Benedek and T. Biro, *J. Mater. Chem. C* **4**, 4000 (2016).
- ² H. Y. Hwang, Y. Iwasa, M. Kawasaki, B. Keimer, N. Nagaosa, and Y. Tokura, *Nat. Mater.* **11**, 103 (2012).
- ³ F. Granozio, G. Koster, and G. Rijnders, *MRS Bull.* **38**, 1017 (2013).
- ⁴ S. Stemmer and S. J. Allen, *Annu. Rev. Mater. Res.* **44**, 151 (2014).
- ⁵ J. Mannhart, D. H. A. Blank, H. Y. Hwang, A. J. Millis, and J.-M. Triscone, *MRS Bull.* **33**, 1027 (2008).
- ⁶ P. Zubko, S. Gariglio, M. Gabay, P. Ghosez, and J.-M. Triscone, *Annu. Rev. Condens. Matter Phys.* **2**, 141 (2011).
- ⁷ L. Bjaalie, B. Himmetoglu, L. Weston, A. Janotti, and C. G. Van de Walle, *New J. Phys.* **16**, 025005 (2014).
- ⁸ J. Chakhalian, A. J. Millis, and J. Rondinelli, *Nat. Mater.* **11**, 92 (2012).
- ⁹ D. G. Schlom, L.-Q. Chen, C.-B. Eom, K. M. Rabe, S. K. Streiffer, and J.-M. Triscone, *Annu. Rev. Mater. Res.* **37**, 589 (2007).
- ¹⁰ K. J. Choi, M. Biegalski, Y. L. Li, A. Sharan, J. Schubert, R. Uecker, P. Reiche, Y. B. Chen, X. Q. Pan, V. Gopalan, L.-Q. Chen, D. G. Schlom, C. B. Eom, *Science* **306**, 1005 (2004).
- ¹¹ T. Kolodiazny, M. Tachibana, H. Kawaji, J. Hwang, and E. Takayama-Muromachi, *Phys. Rev. Lett.* **104**, 147602 (2010).
- ¹² T. Ishidate, S. Abe, H. Takahashi, and N. Móri, *Phys. Rev. Lett.* **78**, 2397 (1997).
- ¹³ S. Valencia, A. Crassous, L. Bocher, V. Garcia, X. Moya, R. O. Cherifi, C. Deranlot, K. Bouzehouane, S. Fusil, A. Zobelli, A. Gloter, N. D. Mathur, A. Gaupp, R. Abrudan, F. Radu, A. Barthélémy, and M. Bibes, *Nat. Mater.* **10**, 753 (2011).
- ¹⁴ W. Zhong and D. Vanderbilt, *Phys. Rev. B* **53**, 5047 (1996).
- ¹⁵ D. Lee, H. Lu, Y. Gu, S.-Y. Choi, S.-D. Li, S. Ryu, T. R. Paudel, K. Song, E. Mikheev, S. Lee, S. Stemmer, D. A. Tenne, S. H. Oh, E. Y. Tsybal, X. Wu, L.-Q. Chen, A. Gruverman, C. B. Eom, *Science* **349**, 1314 (2015).
- ¹⁶ J. H. Haeni, P. Irvin, W. Chang, R. Uecker, P. Reiche, Y. L. Li, S. Choudhury, W. Tian, M. E. Hawley, B. Craigo, A. K. Tagantsev, X. Q. Pan, S. K. Streiffer, L. Q. Chen, S. W. Kirchoefer, J. Levy, and D. G. Schlom, *Nature* **430**, 758 (2004).
- ¹⁷ J. Ge, Z. Liu, C. Liu, C. Gao, D. Qian, Q. Xue, Y. Liu, and J. Jia, *Nat. Mater.* **14**, 285 (2015).
- ¹⁸ Q. Wang, Z. Li, W. Zhang, Z. Zhang, J. Zhang, W. Li, H. Ding, Y. Ou, P. Deng, K. Chang, J. Wen, C. Song, K. He, J. Jia, S. Ji, Y. Wang, L. Wang, X. Chen, X. Ma, Q. Xue, *Chin. Phys. Lett.* **29**, 037402 (2012).
- ¹⁹ K. Michaeli, A. C. Potter, and P. A. Lee, *Phys. Rev. Lett.* **108**, 117003 (2012).
- ²⁰ J. A. Bert, B. Kalisky, C. Bell, M. Kim, Y. Hikita, H. Y. Hwang, and K. A. Moler, *Nat. Phys.* **7**, 767 (2011).
- ²¹ L. Li, C. Richter, J. Mannhart, and R. C. Ashoori, *Nat. Phys.* **7**, 762 (2011).
- ²² M. D. Biegalski, L. Qiao, Y. Gu, A. Mehta, Q. He, Y. Takamura, A. Borisevich, and L.-Q. Chen, *Appl. Phys. Lett.* **106**, 162904 (2015).
- ²³ T. Fujii, A. Fujishima, T. Hirano, and T. Kobayashi, *Appl. Phys. Lett.* **62**, 3204 (1993).
- ²⁴ S. M. Yang, S. J. Moon, T. H. Kim, and Y. S. Kim, *Curr. Appl. Phys.* **14**, 757 (2014).
- ²⁵ R. Ali and M. Yashima, *J. Solid State Chem.* **178**, 7395 (2005).
- ²⁶ X. Liu, D. Choudhury, Y. Cao, M. Kareev, S. Middey, and J. Chakhalian, *Appl. Phys. Lett.* **107**, 191602 (2015).
- ²⁷ J. Coey, Ariando, and W. Pickett, *MRS Bull.* **38**, 1040 (2013).
- ²⁸ M. Kareev, Yanwei Cao, Xiaoran Liu, S. Middey, D. Meyers, and J. Chakhalian, *Appl. Phys. Lett.* **103**, 231605 (2013).
- ²⁹ J.-S. Lee, Y. W. Xie, H. K. Sato, C. Bell, Y. Hikita, H. Y. Hwang, and C.-C. Kao, *Nat. Mater.* **12**, 703 (2013).
- ³⁰ M. Salluzzo, J. C. Cezar, N. B. Brookes, V. Bisogni, G. M. De Luca, C. Richter, S. Thiel, J. Mannhart, M. Huijben, A. Brinkman, G.

- Rijnders, and G. Ghiringhelli, *Phys. Rev. Lett.* **102**, 166804 (2009).
- ³¹ M. Salluzzo, S. Gariglio, D. Stornaiuolo, V. Sessi, S. Rusponi, C. Piamonteze, G. M. De Luca, M. Minola, D. Marré, A. Gadaleta, H. Brune, F. Nolting, N. B. Brookes, and G. Ghiringhelli, *Phys. Rev. Lett.* **111**, 087204 (2013).
- ³² M. Salluzzo, S. Gariglio, X. Torrelles, Z. Ristic, R. Di Capua, J. Drnec, M. Moretti Sala, G. Ghiringhelli, R. Felici, and N. B. Brookes, *Adv. Mater.* **25**, 2333 (2013).
- ³³ D. Pesquera, M. Scigaj, P. Gargiani, A. Barla, J. Herrero-Martín, E. Pellegrin, S. M. Valvidares, J. Gázquez, M. Varela, N. Dix, J. Fontcuberta, F. Sánchez, and G. Herranz, *Phys. Rev. Lett.* **113**, 156802 (2014).
- ³⁴ Y. Cao, Z. Yang, M. Kareev, X. Liu, D. Meyers, S. Middey, D. Choudhury, P. Shafer, J. Guo, J. W. Freeland, E. Arenholz, L. Gu, and J. Chakhalian, *Phys. Rev. Lett.* **116**, 076802 (2016).
- ³⁵ Y. Cao, X. Liu, P. Shafer, S. Middey, D. Meyers, M. Kareev, Z. Zhong, J.-W. Kim, P. Ryan, E. Arenholz, and J. Chakhalian, *npj Quantum Mater.* **1**, 16009 (2016).
- ³⁶ A. F. Santander-Syro, O. Copie, T. Kondo, F. Fortuna, S. Pailhès, R. Weht, X. G. Qiu, F. Bertran, A. Nicolaou, A. Taleb-Ibrahimi, P. Le Fèvre, G. Herranz, M. Bibes, N. Reyren, Y. Apertet, P. Lecoeur, A. Barthélémy, M. J. Rozenberg, *Nature* **469**, 189 (2011).
- ³⁷ J. Chakhalian, J. W. Freeland, A. J. Millis, C. Panagopoulos, and J. M. Rondinelli, *Rev. Mod. Phys.* **86**, 1189 (2014).
- ³⁸ J. Chakhalian, J. W. Freeland, H.-U. Habermeier, G. Cristiani, G. Khaliullin, M. van Veenendaal, and B. Keimer, *Science* **318**, 1114 (2007).
- ³⁹ F. M. F. de Groot, M. Grioni, J. C. Fuggle, J. Ghijsen, G. A. Sawatzky, and H. Petersen, *Phys. Rev. B* **40**, 5715 (1989).
- ⁴⁰ Y. Cao, X. Liu, M. Kareev, D. Choudhury, S. Middey, D. Meyers, J.-W. Kim, P. J. Ryan, J. W. Freeland, and J. Chakhalian, *Nat. Commun.* **7**, 10418 (2016).
- ⁴¹ Z. Y. Wu, G. Ouvrard, P. Gressier, and C. R. Natoli, *Phys. Rev. B* **55**, 10382 (1997).
- ⁴² M. Arita, H. Sato, M. Higashi, K. Yoshikawa, K. Shimada, M. Sawada, Y. Ueda, H. Namatame, M. Taniguchi, S. Fujiomori, Y. Saitoh, M. Tsubota, F. Iga, and T. Takabatake, *J. Phys. Soc. Jpn.* **76**, 074720 (2007).
- ⁴³ G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996).
- ⁴⁴ G. Kresse and D. Joubert, *Phys. Rev. B* **59**, 1758 (1999).
- ⁴⁵ J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- ⁴⁶ P. E. Blöchl, *Phys. Rev. B* **50**, 17954 (1994).
- ⁴⁷ A. A. Mostofi, J. R. Yates, G. Pizzi, Y.-S. Lee, I. Souza, D. Vanderbilt, and N. Marzari, *Comp. Phys. Commun.* **185**, 2309 (2014).
- ⁴⁸ A. E. Bocquet, T. Mizokawa, K. Morikawa, A. Fujimori, S. R. Barman, K. Maiti, D. D. Sarma, Y. Tokura, and M. Onoda, *Phys. Rev. B* **53**, 1161 (1996).
- ⁴⁹ M. Mochizuki and M. Imada, *New J. Phys.* **6**, 154 (2004).

TABLE I. Ti-O distance for CTO films on NGO (in Å). The direction is defined as the local octahedral axis with z -axis parallel to the growth direction.

	x	y	z
Ti 1	1.984	1.979	1.970
Ti 2	1.979	1.984	1.970
Average	1.982	1.982	1.970

TABLE II. On-site energy of Ti $3d$ orbitals for CTO films on NGO (in eV) estimated from the highest occupied state.

	d_{xz}	d_{yz}	d_{xy}	$d_{3z^2-r^2}$	$d_{x^2-y^2}$
Ti 1	2.78	2.89	2.87	4.25	4.19
Ti 2	2.89	2.78	2.87	4.25	4.19
Average	2.84	2.84	2.87	4.25	4.19

FIG. 1. (a) Schematic views of bulk CaTiO_3 unit cell (orthorhombic notation). (b) Sketch of CTO film on NdGaO_3 (110) substrate. (c) RHEED patterns of CTO film during growth. Yellow curve shows the intensity of RHEED pattern along the cut line, whereas white arrows indicate the half-order-peaks.

FIG. 2. (a) XRD data of CTO films on NGO substrates at room temperature. Inset, zoom in of XRD rocking curve near (002). The main substrate peak (002) corresponds to $3.86 \text{ \AA}$ (pseudo-cubic notation). The black triangle suggests the peak of CTO film. (b) Reciprocal space mapping of CTO films near NGO (-103) reflection (pseudo-cubic notation).

FIG. 3. (a) Schematic of experimental setup. Out-of-plane ($I_H, E \parallel c$) and in-plane ($I_V, E \parallel ab$) linearly polarized X-ray were used to determine the orbital occupancy of out-of-plane states ($d_{xz}/d_{yz}, d_{3z^2-r^2}$) and in-plane states ($d_{xy}, d_{x^2-y^2}$), respectively [E is the linear polarization vector of the photon]. The incident angle θ of X-ray was kept at 20° . (b) XAS/XLD data of CTO films at Ti $L_{2,3}$ -edge at room temperature. Standard XAS for Ti^{4+} spectra was collected on a SrTiO_3 substrate.

FIG. 4. (a) Crystal field splitting and schematic orbital configuration of Ti $3d$ band in CTO films. (b) XAS/XLD data of CTO films at O K-edge at room temperature.

FIG. 5. (a) Atom-projected density of states for Ca, Ti, and O atoms of CTO films on NGO. (b) PDOS for Ti t_{2g} ($d_{xz}, d_{yz},$ and d_{xy}) and e_g ($d_{x^2-y^2}$ and $d_{3z^2-r^2}$) states of CTO films on NGO.