

Supplementary information

Orbital-overlap-driven hybridization in 3d-transition metal perovskite oxides LaMO_3 ($M = \text{Ti-Ni}$) and La_2CuO_4

Chun-Yu Liu,^{1,2,*} Lorenzo Celiberti,³ Régis Decker,¹ Kari Ruotsalainen,¹ Katarzyna Siewierska,¹ Maximilian Kusch,¹ Ru-Pan Wang,⁴ Dong Jik Kim,⁵ Israel Ibukun Olaniyan,^{5,6} Daniele Di Castro,^{7,8} Keisuke Tomiyasu,^{9, 10} Emma van der Minne,¹¹ Yorick A. Birkhölzer,¹¹ Ellen M. Kiens,¹¹ Iris C. G. van den Bosch,¹¹ Komal N. Patil,¹² Christoph Baeumer,¹¹ Gertjan Koster,¹¹ Masoud Lazemi,¹² Frank M. F. de Groot,¹² Catherine Dubourdieu,^{5,6} Cesare Franchini,^{3,13} and Alexander Föhlisch^{1, 2, †}

¹Institute for Methods and Instrumentation for Synchrotron Radiation Research, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, 12489 Berlin, Germany

²Institut für Physik und Astronomie, Universität Potsdam, 14476 Potsdam, Germany

³University of Vienna, Faculty of Physics and Center for Computational Materials Science, Vienna, Austria

⁴Institute for Nanostructure and Solid State Physics, Hamburg University, 22761 Hamburg, Germany

⁵Institute Functional Oxides for Energy-Efficient IT, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, 14109 Berlin, Germany

⁶Freie Universität Berlin, Physical Chemistry, 14195 Berlin, Germany

⁷Dipartimento di Ingegneria Civile e Ingegneria Informatica, Università di Roma Tor Vergata, Via del Politecnico 1, I-00133 Roma, Italy

⁸CNR-SPIN, Università di Roma Tor Vergata, Via del Politecnico 1, I-00133 Roma, Italy

⁹Department of Physics, Tohoku University, Sendai 980-8578, Japan

¹⁰Nissan ARC Limited, Natsushima-cho 1, Yokosuka 237-0061, Japan

¹¹MESA+ Institute for Nanotechnology, University of Twente, Faculty of Science and Technology, 26 P.O. Box 217, 7500 AE Enschede, The Netherlands

¹²Materials Chemistry and Catalysis, Debye Institute for Nanomaterials Science, Utrecht University, Universiteitsweg 99, 3584 CG, Utrecht, The Netherlands

¹³Department of Physics and Astronomy 'Augusto Righi', Alma Mater Studiorum - Università di Bologna, Bologna, 40127 Italy

* chun-yu.liu@helmholtz-berlin.de

† alexander.foehlisch@helmholtz-berlin.de

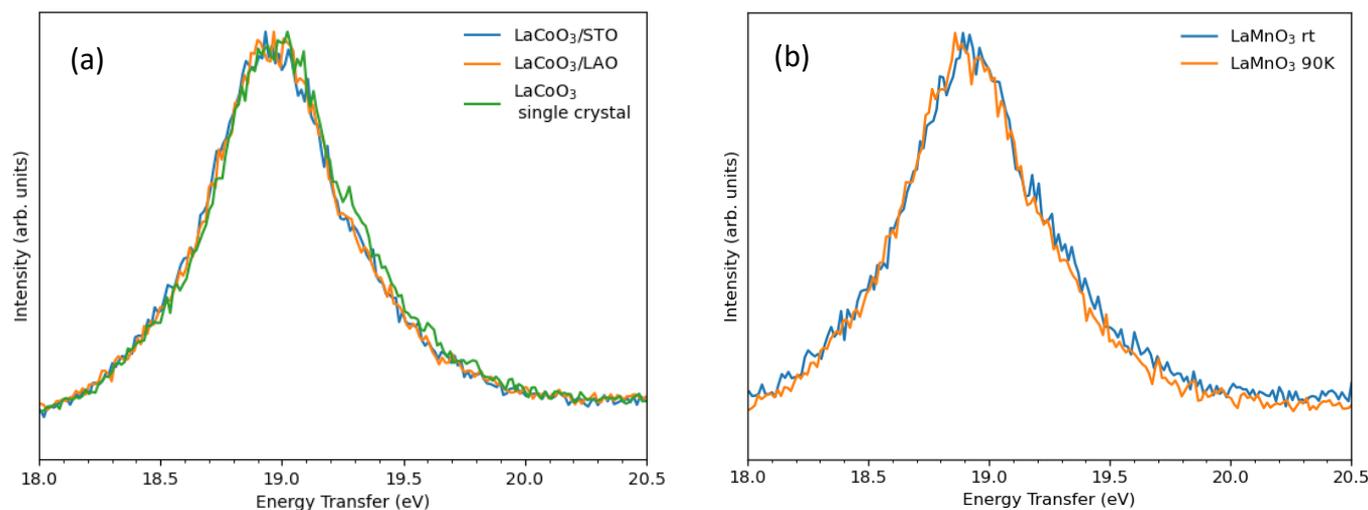


Fig. S1. **Strain and temperature effects on the La ${}^3\text{D}_1$ state observed with resonant inelastic X-ray scattering (RIXS).** (a) RIXS spectra of LaCoO_3 single crystal and thin films on different substrates. STO = SrTiO_3 substrate (tensile strain), LAO = LaAlO_3 substrate (compressive strain). (b) RIXS spectra of LaMnO_3 at two temperatures. rt = room temperature.

Table S1. **Fitted result of all compounds.** The model fit is composed of two Voigt profiles representing RIXS 3D_1 and 3D_2 atomic terms. The gamma (γ , Lorentzian parameter) is fixed to the values from LaAlO_3 ($\gamma_{D1} = 0.103$ eV, $\gamma_{D2} = 0.169$ eV). The Gaussian parameters σ_{D1} and σ_{D2} , representing combined chemical broadening factors, are coupled. The energy separation of the two peaks is fixed to 0.212 eV. The two-Voigt peaks' intensity ratio is fixed to 1. The rest parameters are set free. The standard errors are evaluated based on best model fit with least-squares method.

| Sample | 3D_1 center (eV) | σ_{D1} (eV) | 3D_2 center (eV) | σ_{D2} (eV) |
|---------------------------|---------------------|--------------------|---------------------|--------------------|
| LaTiO_3 | 18.798±0.003 | 0.268±0.004 | 19.010±0.003 | 0.268±0.004 |
| LaVO_3 | 18.818±0.002 | 0.195±0.004 | 19.030±0.002 | 0.195±0.004 |
| LaCrO_3 | 18.820±0.003 | 0.175±0.004 | 19.032±0.003 | 0.175±0.004 |
| LaMnO_3 | 18.835±0.003 | 0.208±0.004 | 19.047±0.003 | 0.208±0.004 |
| LaFeO_3 | 18.855±0.002 | 0.215±0.004 | 19.067±0.002 | 0.215±0.004 |
| LaCoO_3 | 18.876±0.002 | 0.199±0.003 | 19.088±0.002 | 0.199±0.003 |
| LaNiO_3 | 18.813±0.003 | 0.239±0.004 | 19.025±0.003 | 0.239±0.004 |
| La_2CuO_4 | 18.716±0.002 | 0.239±0.003 | 18.928±0.002 | 0.239±0.003 |
| LaAlO_3 | 18.956±0.001 | 0.027±0.003 | 19.168±0.001 | 0.027±0.003 |