Soft x-ray absorption spectroscopy and magnetic circular dichroism as *operando* probes of complex oxide electrolyte gate transistors

Cite as: Appl. Phys. Lett. **116**, 201905 (2020); https://doi.org/10.1063/1.5138645 Submitted: 14 November 2019 • Accepted: 09 May 2020 • Published Online: 21 May 2020

Biqiong Yu, Guichuan Yu, Jeff Walter, et al.



ARTICLES YOU MAY BE INTERESTED IN

Scattering mechanisms and mobility enhancement in epitaxial BaSnO₃ thin films probed via electrolyte gating APL Materials **8**, 071113 (2020); https://doi.org/10.1063/5.0017227

Electronic structure of epitaxial perovskite films in the two-dimensional limit: Role of the surface termination Applied Physics Letters **116**, 201601 (2020); https://doi.org/10.1063/5.0002985

Oxygen vacancies: The (in)visible friend of oxide electronics Applied Physics Letters **116**, 120505 (2020); https://doi.org/10.1063/1.5143309





Appl. Phys. Lett. **116**, 201905 (2020); https://doi.org/10.1063/1.5138645 © 2020 Author(s).

Soft x-ray absorption spectroscopy and magnetic circular dichroism as operando probes of complex oxide electrolyte gate transistors

Cite as: Appl. Phys. Lett. **116**, 201905 (2020); doi: 10.1063/1.5138645 Submitted: 14 November 2019 · Accepted: 9 May 2020 · Published Online: 21 May 2020



Biqiong Yu,¹ Guichuan Yu,¹ Jeff Walter,^{2,3} Vipul Chaturvedi,² Joseph Gotchnik,² Sajna Hameed,¹ John W. Freeland,⁴ Chris Leighton,^{2,a)} (b) and Martin Greven^{1,a)} (b)

AFFILIATIONS

School of Physics and Astronomy, University of Minnesota, Minneapolis, Minnesota 55455, USA

²Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455, USA

³Department of Physics, Augsburg University, Minneapolis, Minnesota 55454, USA

⁴Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439, USA

^{a)}Authors to whom correspondence should be addressed: leighton@umn.edu and greven@umn.edu

ABSTRACT

Electrolyte-based transistors utilizing ionic liquids/gels have been highly successful in the study of charge-density-controlled phenomena, particularly in oxides. Experimental probes beyond transport have played a significant role, despite challenges in their application in electric double-layer transistors. Here, we demonstrate the application of synchrotron soft x-ray absorption spectroscopy (XAS) and x-ray magnetic circular dichroism (XMCD) as *operando* probes of the charge state and magnetism in ion-gel-gated ferromagnetic perovskite films. Electrochemical response via oxygen vacancies at positive gate bias in LaAlO₃(001)/La_{0.5}Sr_{0.5}CoO_{3- δ} is used as a test case. XAS/XMCD measurements of 4–25 unit-cell-thick films first probe the evolution of hole doping (from the O *K*-edge pre-peak) and ferromagnetism (at the Co *L*-edges), to establish a baseline. *Operando* soft XAS/XMCD of electrolyte-gated films is then demonstrated, using optimized spin-coated gels with a thickness of ~1 μ m and a specific composition. The application of gate voltages up to +4 V is shown to dramatically suppress the O *K*-edge XAS pre-peak intensity and Co *L*-edge XMCD, thus enabling the Co valence and ferromagnetism to be tracked upon gate-induced reduction. Soft XAS and XMCD, with appropriate electrolyte design, are thus established to be viable for the *operando* characterization of electrolyte-gated oxides.

Published under license by AIP Publishing. https://doi.org/10.1063/1.5138645

Electric double-layer transistors (EDLTs) employing ionic liquids/gels have proven to be successful in the study of charge-density-dependent effects in many materials.^{1–4} This approach allows the density of doped carriers to be varied in a single device to extremely high charge densities (>10¹⁴ cm⁻²),^{1–14} at least an order of magnitude above conventional (e.g., SiO₂-based) field-effect devices. EDLTs are, thus, widely used to study electronic and magnetic phase transitions^{1–18} and map phase diagrams.^{11,16} For instance, electrically induced superconductivity was observed in electrolyte-gated KTaO₃⁸ and SrTiO₃¹⁴ and high-temperature superconductors.^{2,10,16–18} Control of the insulator–metal transition was achieved in VO₂^{12,19–21} and nickelates,^{7,13} and modulation of magnetism was found to be possible in Ti_{1-x}Co_xO₂,⁹ La_{1-x}Sr_xMnO₃,^{6,22} and La_{1-x}Sr_xCoO_{3-δ}.²³⁻²⁵

It is increasingly recognized that EDLT operating mechanisms are typically not purely electrostatic and that there exists a range of

alternative responses.^{4,19,21,23–28} In oxides, for example, the gate response can be electrochemical, where the electric double-layer (EDL) electric field induces redox chemistry, often via oxygen vacancy (Vo) formation/annihilation. Evidence for this originally came from transport measurements in a controlled atmosphere, with tracking of irreversibility.^{21,23,29–33} Recently, however, synchrotron-based hard x-ray diffraction^{24,34–36} and hard x-ray absorption spectroscopy (XAS),^{34,37} as well as neutron reflectometry,^{24,25} have been developed as *operando* probes of EDLTs, complementing transport. By *operando*, here we refer to measurements made *in situ*, during operation of an EDLT, i.e., under biasing. Our recent *operando* x-ray diffraction on ion-gel-gated La_{0.5}Sr_{0.5}CoO_{3– δ} (LSCO) highlighted the importance of gate-bias polarity: a large lattice expansion was found at positive gate bias (V_g) due to V_O formation, whereas only minor structural changes occurred at negative V_g.²⁴ Importantly, the V_g-induced V_O penetrated

the entire film thickness, confirmed by depth-sensitive neutron reflectometry; this is enabled by the high diffusivity of V_O in LSCO, which focuses much attention on redox control of these compounds.^{23–25,36,38,39} In particular, at the x = 1 composition, positive bias can eventually induce a transformation to the V_O-ordered SrCoO_{2.5} brownmillerite phase, which can then be reversibly transformed back to the perovskite phase, drawing a substantial amount of interest.^{36,38}

Although the application of EDLTs is growing, an elementsensitive *operando* probe such as XAS, which enables element-specific determination of valence, is not fully developed. Some absorption spectroscopy studies in the hard x-ray regime^{34,37} provided insight into EDLT gating mechanisms, but *soft* XAS at the O K and transition-metal L edges, which directly probes the transition-metal electronic/magnetic structure, has not yet been performed in an *operando* manner. By *operando* XAS on oxide EDLTs, we mean here that such measurements are made during biasing, on the beamline. The main challenges in such *operando* measurements (in contrast to *ex situ* studies of non-volatile gate effects) include penetrating thick electrolyte layers with soft x-rays and extracting absorption signals.

Here, we establish soft XAS and x-ray magnetic circular dichroism (XMCD), its magnetic variant, as operando probes of charge state and magnetism in electrolyte-gated (specifically ion-gel-gated) epitaxial LSCO films. Baseline information is first gathered from 4 to 25 unit-cell-thick bare films by determining the evolution in hole doping from O K edge XAS and in ferromagnetism from Co L edge XMCD. The ion gel (i.e., ionic liquid in a polymer network) used for operando measurements was optimized in terms of thickness (to $\sim 1 \,\mu$ m) and composition. We show that, upon applying $V_g = +4$ V, the O K edge XAS pre-peak intensity is strongly suppressed, indicating a substantial decrease in effective hole density. Concomitantly, the Co magnetic moment is substantially reduced, as revealed in energy- and magneticfield-dependent XMCD. These results, which complement previous x-ray diffraction and neutron reflectometry,^{23,24} not only yield insight into gating mechanisms in oxide EDLTs but also demonstrate a powerful element-sensitive approach to operando studies of gated oxides.

As described previously,²³ epitaxial LSCO films were grown using high-pressure-oxygen reactive sputtering at 1.4 Torr of O2 from ceramic LSCO targets onto $10 \times 10 \text{ mm}^2$ LaAlO₃(001) (LAO) substrates at 600 °C. Extensive structural, chemical, magnetic, and transport characterization studies have been published.⁴⁰⁻⁴³ To prepare EDLTs, 28-unit-cell-thick films were patterned into $3 \times 3 \text{ mm}^2$ channels between two Pt side-gate electrodes.^{23,24} Ion gels based on the ionic liquids 1-ethyl-3-methylimidazolium bis(trifluoro-methylsulfonyl) imide (EMI:TFSI) or 1-ethyl-3-methylimidazolium dicyanamide (EMI:DCA) in poly(vinylidene fluoride-co-hexafluoropropylene) (P(VDF-HFP)) were spin-coated across the channel and gate electrodes to complete devices. EMI:TFSI was chosen for consistency with previous work, whereas EMI:DCA was chosen as it is oxygen-free and, thus, may avoid contamination of the O K edge. Devices were then wired up and immediately loaded into the beamline vacuum chamber (kept at $< 10^{-8}$ Torr).

Soft synchrotron x-ray measurements were performed at beamline 4-ID-C of the Advanced Photon Source. Three different detectors/ measurement modes are available: total-electron-yield (TEY) mode, total-fluorescence-yield (TFY) mode, and reflectivity (REF) mode. TEY mode is dominated by the photoelectric effect, and its probing depth is, thus, limited to the top unit cells. TFY mode measures emitted fluorescence photons and, thus, has a larger probing depth due to the longer photon mean-free-path. REF mode deals with the reflection of the x-ray beam by the sample/device at a specific angle, with intensity dependent on the real and imaginary parts of the refractive index. Based on this, bare films were measured in TEY and TFY modes, in grazing-incidence geometry. For operando gating, on the other hand, in order to utilize both TFY and REF modes, the films were rotated by 30° facing the x-ray beam, with the fluorescence and reflectivity detectors at 90° and 60°, respectively [Fig. 3(a)]. TEY mode was not used in gating experiments, as the overlying ion gel inhibits release of photoelectrons. The incident polarization was switched between left-circular and right-circular during the measurements. The sum $(I^+ + I^-)$ of these signals probes the electronic environment (XAS), whereas the difference $(I^+ - I^-)$ contains magnetic information (XMCD). In our analysis, the XMCD intensities were obtained as follows: (i) in order to minimize systematic errors, spectra were collected with the magnetic field both along and opposite to the beam direction. The resultant XMCD spectra are the difference of the two (see Fig. S1 for separate I^+ and Γ intensities); (ii) the XAS ($I^+ + \Gamma$) spectra were normalized to the main peak for different gate biases/film thickness; (iii) the normalization factors from step (ii) were then used to correct the XMCD intensity. The EDLTs were operated at $<10^{-8}$ Torr, with V_g applied at 310 K for 30 min, with in situ monitoring of electronic transport. Operando XAS and XMCD were performed at 75 K (well below the Curie temperature, $T_{\rm C} \approx 220$ K, of the investigated 28 u.c. films), with a magnetic field H = 4000 Oe along the x-ray beam; 75 K was chosen so that a large magnetic moment could be reached while keeping the saturation field safely below the maximum available (4600 Oe).

We first gathered baseline information for LAO(001)/LSCO films by probing the evolution of hole doping and magnetism in bare films. Figure 1 shows the O K- and Co L-edge XAS and XMCD spectra (TFY) of films of 4, 8, and 25 unit cells (u.c.). The data are normalized to 1 at the main peaks (540 eV for the O K edge; 780 eV for the Co L edge). The O K edge pre-peak near 527 eV is seen in all films [Fig. 1(a)], and its intensity noticeably decreases with the decreasing thickness. This pre-peak has been well characterized in bulk LSCO and linked to the O 2p hole density.44 The clear pre-peak decrease with the decreasing thickness, thus, indicates an obvious decrease in effective hole doping in thinner films. Earlier work linked this to an increase in O deficiency δ near the substrate, leading to a decrease in effective hole doping, i.e., $x_{\rm eff} = x - 2\delta$, in the simplest model.⁴¹ This O deficiency was, in turn, linked to Vo ordering, which was shown to be the lattice mismatch accommodation mechanism in this system.⁴² This effect is also seen in the Co L-edge XAS [Fig. 1(b)], from the \sim 0.6 eV shift to lower energy; this is also known to indicate a decrease in Co valence. $^{\!\!\!\!\!^{45}}$ Consequently, the Co magnetic moment is reduced on going from thicknesses of 25 to 8 u.c.. In particular, as seen from the Co L-edge TFY XMCD in Fig. 1(d), we find no evidence for ferromagnetism in the 4 u.c. film, whereas 8 and 25 u.c. films are clearly ferromagnetic. Using the XMCD sum rule,46 we estimate a Co spin magnetic moment of 0.63(4) $\mu_{\rm B}/{\rm Co}$ for the bare 25 u.c. film. This is consistent with the value of \sim 0.7 $\mu_{\rm B}$ /Co reported in previous work at this in-plane field and the same temperature.⁴⁷ In bulk LSCO, it is known that O holes also form magnetic states at the Fermi level and that the O moment increases with doping.⁴⁴ We indeed observe an



FIG. 1. (a) O *K*-edge and (b) Co *L*-edge XAS spectra of LaAIO₃(001)/ La_{0.5}Sr_{0.5}CoO_{3.5} films with thicknesses of (*t*) 4, 8, and 25 unit cells (u.c.). (c) O *K*edge and (d) Co *L*-edge XMCD spectra of the same films. All data were taken with grazing incidence x-rays in TFY mode, at a temperature of T = 30 K, with a field of H = 4600 Oe along the incident beam (i.e., the full field was in the film plane). In (b), a shift from 25 to 8 u.c. is observed (about 0.6 eV at the L_3 edge, as indicated). Inset in (c): TEY XMCD spectra near the pre-peak.

evolution of magnetism at O hole sites in TEY mode [Fig. 1(c), inset; see Fig. S2 for corresponding XAS spectra] although the low signal-tonoise ratio in TFY mode [Fig. 1(c)] results in an inability to resolve this signal. XMCD spectra at the O K edge were not measured further since, as noted, the TEY mode was not possible in gating experiments.

A pivotal challenge in operando soft XAS and XMCD measurements is to optimize the thickness of the ion gel overlying the gated films: while a thin gel is desirable because of the low x-ray penetration depth ($\sim 1 \,\mu m$ at the Co L edge) and to minimize the effect of Fluorine (the gel contains F; see Figs. S3-S7 for the F K-edge effect), the gel must be thick enough to function electrically and achieve uniform gating. Optimization of ion gels for operando soft XAS/XMCD was achieved via a series of spin-coating experiments on Si/SiO_x substrates. Solutions with various polymer:ionic liquid:acetone (solvent) ratios (by mass) were prepared, heated to \sim 35 °C, and spun at 1500 rpm for 30 s. Tilt-view (45° with respect to the substrate plane) secondary electron scanning electron microscopy (SEM) images were then collected using a JEOL JSM-6010 PLUS/LA microscope, at an accelerating voltage of 5 kV. Images collected near an intentional scratch, so that the ion gel thickness (d) could be extracted, are shown in Fig. 2. Panels (a)-(d) and (e)-(h), for EMI:TFSI and EMI:DCA gels, respectively, show that ion gels become thinner with increasing ratios of ionic liquid and/or solvent. Excessively high ionic liquid/solvent ratios result in an "island and hole" morphology [Figs. 2(d) and 2(h)], unsuitable for gating. We, thus, established the optimized solutions to be in the range of 1:150:50 for EMI:TFSI [Fig. 2(c)] and 1:350:50 for EMI:DCA [Fig. 2(g)], resulting in $d \approx 1.5-2.5 \,\mu\text{m}$. Upon testing optimized EMI:DCA gels, however, (in fact, any EMI:DCA gels), we observed that the LSCO resistance increased by several orders of magnitude in a matter of minutes following spin coating, whereas minimal changes $(<0.1\%/\text{min}, \text{ consistent with previous work}^{23})$ were observed for



FIG. 2. Tilt-view (45°) secondary electron scanning electron microscopy images of ion gels spin-coated on Si/SiO_x substrates at different ratios (by mass) of PVDF-HFP:ionic liquid:acetone, as shown. The ionic liquid was (a)–(d) EMI:TFSI and (e)–(h) EMI:DCA. Each coated film was scratched with a blade to enable thickness determination, with the resulting value (d) shown in each panel.

EMI:TFSI. The rest of the work presented here will, thus, utilize the 1:150:50 EMI:TFSI gel.

With ion gels optimized, we performed operando XAS/XMCD measurements of an electrolyte-gated LSCO film (28 u.c. thickness). Figure 3(a) shows a schematic of the experimental setup. Throughout this study, only positive biases were applied, as a model test case. As noted, this $V_{\rm g}$ polarity results in $V_{\rm O}$ formation through the entire volume of LSCO films in this thickness regime, resulting in the large resistivity²³ and lattice parameter increase²⁴ and a concomitant decrease in magnetization and Curie temperature. Figures 3(b) and 3(d) show the O K edge electronic structure changes measured at 75 K, after warming up and applying $V_{\rm g} = +4$ V at 310 K. Most noticeably, the 527 eV O 2p pre-peak is seen to be essentially extinguished at $V_g = +4$ V, in both TFY [Fig. 3(b)] and REF [Fig. 3(d), inset] modes. This suppression is consistent with the formation of a high density of V_O at positive biases, decreasing the effective hole concentration ($x_{\rm eff} \!=\! x - 2\delta$) by compensation of doped holes. Consistently, the Co L3 edge XAS peak shifts $\sim 1.2 \text{ eV}$ to lower energy at $V_g = +4 \text{ V}$ [Fig. 3(c); see Fig. S5 for XAS taken in REF mode], indicating decreasing Co formal valence. The responses of the O K edge and Co L edge spectra to operando gating are, thus, qualitatively consistent. We note that, in addition to the LSCO films, both the LAO substrate and the ion gel include oxygen.



FIG. 3. (a) Schematic of the device and experimental setup for operando XAS/ XMCD measurements of ion-gel-gated $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ (LSCO) films. The orange area is the LSCO film (28 unit-cell-thick), and the gray pads are Pt electrodes for bias voltage application and operando transport measurements. The sample is rotated by $\theta = 30^{\circ}$ such that both reflectivity and fluorescent channels can be probed. For XMCD (Fig. 4), a field of H = 4000 Oe was applied along the x-ray beam, resulting in a field of about 3500 Oe in the film plane. The x-ray beam was defocused to cover the entire sample and minimize beam damage. Gate bias (V_g)-dependent XAS taken in (b) REF mode at the O K edge, (c) TFY mode at the Co L_3 edge, and (d) TFY mode at the O K edge. "*" denotes the pre-peak around 527 eV, as highlighted in the inset in (d). All data were taken at T = 75 K. Note that the apparent negative intensity around 785 eV in (c) likely arises from a re-absorbance of the scattered fluorescent photons, due to which the actual background is lower than the estimated background around this energy.

The slight spectral changes at the O K edge above 530 eV might, thus, involve not only LSCO but also the ion gel, e.g., through beam damage.

Subsequent gate-induced magnetism changes were probed via Co L_3 -edge XMCD. Figures 4(a) and 4(b) show the energy dependence of the TFY and REF XMCD, respectively; these data were obtained at 75 K with an effective magnetic field in the film plane of \sim 3500 Oe. At $V_{\sigma} = 0$, a peak appears around 780.5 eV in TFY mode, whereas two peaks are seen in REF mode due to interference effects, indicative of a substantial Co moment, as expected. Upon application of $V_g = +4 \text{ V}$, these peaks essentially vanish, meaning that the Co moment is strongly suppressed by the hole doping decrease due to Vo formation, as evidenced by XAS. Figure 4(c) shows the corresponding hysteresis loops measured at the peak energy (~780.5 eV). The loops show pronounced magnetization and hysteresis (1740 Oe coercivity) at $V_{\rm g} = 0$. At $V_g = +4 V$, however, the saturation magnetization decreases substantially (by a factor of \sim 7), in agreement with previous neutron reflectometry measurements.²⁴ In the latter, a decrease in peak magnetization by a factor of ~ 8 was observed at 30 K for $V_g = +3$ V; our operando XMCD results are, thus, in quantitative agreement with previous neutron reflectometry.

In summary, we have demonstrated *operando* soft XAS/XMCD measurements on electrolyte-gated oxides, using ion-gel-gated LSCO films as a test case. Baseline information of hole doping and ferromagnetism was first established by measuring O *K*- and Co *L*-edge XAS/XMCD on bare LAO/LSCO films with thicknesses of 4, 8, and 25 u.c.



FIG. 4. Gate voltage (*V*_g) dependence of the ferromagnetic properties of 28-unitcell-thick La_{0.5}Sr_{0.5}CoO_{3- δ} probed by XMCD at the Co *L*₃ edge in (a) TFY and (b) REF modes. Data were taken at *T* = 75 K with *H* = 4000 Oe along the x-ray beam. (c) Change of XMCD hysteresis loops with *V*_g, as measured in REF XMCD mode at 75 K with a phonon energy of 780.5 eV. Forward (F) and reverse (R) sweeps are contrasted for clarity. The error bars due to the scale factor estimation for the XMCD data are less than the symbol size for both 0 V and +4 V. Errors are 1 std and comparable to the symbol size in (a) and (b). Lines are given as guides to the eye.

To overcome the penetration depth problem, the ion gel was optimized with regard to the composition and thickness, with the latter reaching $\sim 1 \,\mu$ m. Data for gated films were then obtained in TFY and REF modes. The application of $V_{\rm g} = +4$ V resulted in dramatic suppression of the O K edge XAS pre-peak, indicating a significant decrease in hole doping due to V_O formation at positive $V_{\rm g}$. Concomitantly, a significantly reduced Co moment was observed in energy- and field-dependent XMCD spectra. Our investigation of LSCO-based ion-gel EDLTs via *operando* soft XAS/XMCD, therefore, provides direct evidence for electrochemical changes in hole doping and magnetism. This lays the foundation for *operando* soft XAS/XMCD studies of other electrolyte-gated oxides, also relevant to *operando* studies of battery, ionic conductor, and supercapacitor materials.

See the supplementary material for (i) separate I^+ and I^- Co *L*-edge intensities in TFY mode for the ungated 25 u.c. film, (ii) O *K*-edge XAS data in TEY mode for all ungated films, and (iii) details on a F *K*-edge effect.

This work was primarily supported by the National Science Foundation through the UMN MRSEC under No. DMR-1420013. Parts of this work were carried out in the Characterization Facility, UMN, which receives partial support from NSF through the MRSEC program. Portions of this work were also conducted in the Minnesota Nano Center, which was supported by the National Science Foundation through the National Nano Coordinated Infrastructure Network, Award No. NNCI-1542202. This research used resources of the Advanced Photon Source, a DOE Office of Science User Facility operated by the Argonne National Laboratory under Contract No. DE-AC02-06CH11357.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

REFERENCES

- ¹C. H. Ahn, A. Bhattacharya, M. D. Ventra, J. N. Eckstein, C. D. Frisbie, M. E. Gershenson, A. M. Goldman, I. H. Inoue, J. Mannhart, A. J. Millis, A. F. Morpurgo, D. Natelson, and J. M. Triscone, Rev. Mod. Phys. **78**, 1185 (2006).
 ²A. M. Goldman, Annu. Rev. Mater. Res. **44**, 45 (2014).
- ³S. Z. Bisri, S. Shimizu, M. Nakano, and Y. Iwasa, Adv. Mater. **29**, 1607054 (2017).
- ⁴C. Leighton, Nat. Mater. 18, 13 (2019).
- ⁵H. Yuan, H. Shimotani, A. Tsukazaki, A. Ohtomo, M. Kawasaki, and Y. Iwasa, Adv. Funct. Mater. **19**, 1046 (2009).
- ⁶A. S. Dhoot, C. Israel, X. Moya, N. D. Mathur, and R. H. Friend, Phys. Rev. Lett. **102**, 136402 (2009).
- ⁷R. Scherwitzl, P. Zubko, I. G. Lezama, S. Ono, A. F. Morpurgo, G. Catalan, and J. M. Triscone, Adv. Mater. 22, 5517 (2010).
- ⁸K. Ueno, S. Nakamura, H. Shimotani, H. T. Yuan, N. Kimura, T. Nojima, H. Aoki, Y. Iwasa, and M. Kawasaki, Nat. Nanotechnol. 6, 408 (2011).
- ⁹Y. Yamada, K. Ueno, T. Fukumura, H. T. Yuan, H. Shimotani, Y. Iwasa, L. Gu, S. Tsukimoto, Y. Ikuhara, and M. Kawasaki, Science **332**, 1065 (2011).
- ¹⁰ A. T. Bollinger, G. Dubuis, J. Misewich, A. T. Bollinger, I. Božović, D. Pavuna, and J. Yoon, Nature 472, 458 (2011).
- ¹¹J. T. Ye, Y. J. Zhang, R. Akashi, M. S. Bahramy, R. Arita, and Y. Iwasa, Science 338, 1193 (2012).
- ¹²M. Nakano, K. Shibuya, D. Okuyama, T. Hatano, S. Ono, M. Kawasaki, Y. Iwasa, and Y. Tokura, Nature **487**, 459 (2012).
- ¹³S. Asanuma, P.-H. Xiang, H. Yamada, H. Sato, I. H. Inoue, H. Akoh, A. Sawa, K. Ueno, H. Shimotani, H. Yuan, M. Kawasaki, and Y. Iwasa, Appl. Phys. Lett. 97, 142110 (2010).
- ¹⁴K. Ueno, S. Nakamura, N. Kimura, A. Ohtomo, M. Kawasaki, H. Shimotani, Y. Iwasa, H. Aoki, T. Nojima, and K. Ueno, Nat. Mater. 7, 855 (2008).
- ¹⁵W. Xie, X. Zhang, C. Leighton, and C. D. Frisbie, Adv. Electron. Mater. 3, 1600369 (2017).
- ¹⁶X. Leng, J. Garcia-Barriocanal, S. Bose, Y. Lee, and A. M. Goldman, Phys. Rev. Lett. **107**, 027001 (2011).
- ¹⁷H. Sato, K. Hanzawa, H. Hiramatsu, H. Hosono, and T. Kamiya, Proc. Natl. Acad. Sci. 113, 3986 (2016).
- ¹⁸T. Miyakawa, J. Shiogai, S. Shimizu, M. Matsumoto, Y. Ito, T. Harada, K. Fujiwara, T. Nojima, Y. Itoh, T. Aida, Y. Iwasa, and A. Tsukazaki, Phys. Rev. Mater. 2, 031801(R) (2018).
- ¹⁹H. Ji, J. Wei, and D. Natelson, Nano Lett. **12**, 2988 (2012).
- ²⁰Z. Yang, Y. Zhou, and S. Ramanathan, J. Appl. Phys. 111, 014506 (2012).

- ²¹J. Jeong, N. Aetukuri, T. Graf, T. D. Schladt, M. G. Samant, and S. S. P. Parkin, Science **339**, 1402 (2013).
- ²²L. M. Zheng, X. Renshaw Wang, W. M. Lü, C. J. Li, T. R. Paudel, Z. Q. Liu, Z. Huang, S. W. Zeng, K. Han, Z. H. Chen, X. P. Qiu, M. S. Li, S. Yang, B. Yang, M. F. Chisholm, L. W. Martin, S. J. Pennycook, E. Y. Tsymbal, J. M. D. Coey, and W. W. Cao, Nat. Commun. 9, 1897 (2018).
- ²³J. Walter, H. Wang, B. Luo, C. D. Frisbie, and C. Leighton, ACS Nano 10, 7799 (2016).
- ²⁴J. Walter, G. Yu, B. Yu, A. Grutter, B. Kirby, J. Borchers, Z. Zhang, H. Zhou, T. Birol, M. Greven, and C. Leighton, Phys. Rev. Mater. 1, 071403(R) (2017).
- ²⁵J. Walter, T. Charlton, H. Ambaye, M. R. Fitzsimmons, P. P. Orth, R. M. Fernandes, and C. Leighton, Phys. Rev. Mater. 2, 111406(R) (2018).
- ²⁶S. H. Kim, K. Hong, W. Xie, K. H. Lee, S. Zhang, T. P. Lodge, and C. D. Frisbie, Adv. Mater. **25**, 1822 (2013).
- 27 T. Fujimoto and K. Awaga, Phys. Chem. Chem. Phys. 15, 8983 (2013).
- ²⁸H. Du, X. Lin, Z. Xu, and D. Chu, J. Mater. Sci. 50, 5641 (2015).
- ²⁹H. Yuan, H. Shimotani, J. Ye, S. Yoon, H. Aliah, A. Tsukazaki, M. Kawasaki, and Y. Iwasa, J. Am. Chem. Soc. **132**, 18402 (2010).
- ³⁰M. Li, W. Han, J. Jeong, M. G. Samant, and S. S. P. Parkin, Nano Lett. **13**, 4675 (2013).
- ³¹H. T. Yi, B. Gao, W. Xie, S. W. Cheong, and V. Podzorov, Sci. Rep. 4, 6604 (2014).
- ³²S. Bubel, A. J. Hauser, A. M. Glaudell, T. E. Mates, S. Stemmer, and M. L. Chabinyc, Appl. Phys. Lett. **106**, 122102 (2015).
- ³³T. D. Schladt, T. Graf, N. B. Aetukuri, M. Li, A. Fantini, X. Jiang, M. G. Samant, and S. S. P. Parkin, ACS Nano 7, 8074 (2013).
- ³⁴Y. Dong, H. Zhou, D. D. Fong, W. Wu, Z. Luo, C. Gao, and H. Xu, APL Mater. 5, 051101 (2017).
- ³⁵X. Leng, J. Pereiro, J. Strle, G. Dubuis, A. T. Bollinger, A. Gozar, J. Wu, N. Litombe, C. Panagopoulos, D. Pavuna, and I. Božović, npj Quantum Mater. 2, 35 (2017).
- ³⁶N. Lu, P. Zhang, Q. Zhang, R. Qiao, Q. He, H. B. Li, Y. Wang, J. Guo, D. Zhang, Z. Duan, Z. Li, M. Wang, S. Yang, M. Yan, E. Arenholz, S. Zhou, W. Yang, L. Gu, C. W. Nan, J. Wu, Y. Tokura, and P. Yu, Nature **546**, 124 (2017).
- ³⁷A. M. Perez-Muñoza, P. Schioa, R. Polonid, A. Fernandez-Martineze, A. Rivera-Calzadaa, J. C. Cezarc, E. Salas-Coleraf, G. R. Castrof, J. Kinneyh, C. Leona, J. Santamariaa, J. Garcia, and A. M. Goldman, Proc. Natl. Acad. Sci. 114, 215 (2017).
- ³⁸Q. Lu and B. Yildiz, Nano Lett. 16, 1186 (2016).
- ³⁹D. A. Gilbert, A. J. Grutter, P. D. Murray, R. V. Chopdekar, A. M. Kane, A. L. Ionin, M. S. Lee, S. R. Spurgeon, B. J. Kirby, B. B. Maranville, A. T. N'Diaye, A. Mehta, E. Arenholz, K. Liu, Y. Takamura, and J. A. Borchers, *Phys. Rev. Mater.* 2, 104402 (2018).
- ⁴⁰M. A. Torija, M. Sharma, M. R. Fitzsimmons, M. Varela, and C. Leighton, J. Appl. Phys. **104**, 023901 (2008).
- ⁴¹M. A. Torija, M. Sharma, J. Gazquez, M. Varela, C. He, J. Schmitt, J. A. Borchers, M. Laver, S. El-Khatib, and C. Leighton, Adv. Mater. 23, 2711 (2011).
- ⁴²J. Gazquez, S. Bose, M. Sharma, M. A. Torija, S. J. Pennycook, C. Leighton, and M. Varela, APL Mater. 1, 012105 (2013).
- ⁴³S. Kelly, F. Galli, J. Aarts, S. Bose, M. Sharma, and C. Leighton, Appl. Phys. Lett. **105**, 112909 (2014).
- ⁴⁴S. Medling, Y. Lee, H. Zheng, J. F. Mitchell, J. W. Freeland, B. N. Harmon, and F. Bridges, Phys. Rev. Lett. **109**, 157204 (2012).
- ⁴⁵J. W. Freeland, J. X. Ma, and J. Shi, Appl. Phys. Lett. **93**, 212501 (2008).
- ⁴⁶C. T. Chen, Y. U. Idzerda, H. J. Lin, N. V. Smith, G. Meigs, E. Chaban, G. H. Ho, E. Pellegrin, and F. Sette, Phys. Rev. Lett. **75**, 152 (1995).
- ⁴⁷J. Walter, S. Bose, M. Cabero, G. Yu, M. Greven, M. Varela, and C. Leighton, Phys. Rev. Mater. 2, 111404(R) (2018).