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Citation: Appl. Phys. Lett. **113**, 261603 (2018); doi: 10.1063/1.5063540 View online: https://doi.org/10.1063/1.5063540 View Table of Contents: http://aip.scitation.org/toc/apl/113/26 Published by the American Institute of Physics



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Metallic conduction and ferromagnetism in $MAI_2O_4/SrTiO_3$ spinel/perovskite heterostructures (M = Fe, Co, Ni)

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(Received 28 September 2018; accepted 7 December 2018; published online 28 December 2018)

Recently, a high mobility quasi-two-dimensional electron gas has been reported for the heterointerface between two insulating and nonmagnetic oxides of spinel γ -Al₂O₃ and perovskite SrTiO₃ (STO). Herein, we fabricated the epitaxial heterostructure with Al-based magnetic spinel oxide *M*Al₂O₄ (*M* = Fe, Co, Ni) on perovskite STO. Remarkably, all the *M*Al₂O₄ (*M* = Fe, Co, Ni) films exhibit ferromagnetic behavior up to room temperature. Although FeAl₂O₄/STO is insulating, the NiAl₂O₄/STO and CoAl₂O₄/STO heterointerfaces are found to be highly metallic and exhibit the anomalous Hall effect (AHE) at temperatures below 30 K. Their Hall mobility is as high as 3×10^4 cm² V⁻¹ s⁻¹, comparable to that of the γ -Al₂O₃/STO interface. There has been evidence of oxygen-vacancy-related magnetism in γ -Al₂O₃/STO at temperatures below 5 K, while the enhanced AHE in NiAl₂O₄/STO and CoAl₂O₄/STO likely comes from the magnetic proximity effect induced by the top ferromagnetic *M*Al₂O₄ spinel films. *Published by AIP Publishing*. https://doi.org/10.1063/1.5063540

The metallic interface between two insulating oxides, where a quasi-two-dimensional electron gas (q-2DEG) resides, provides a promising platform for the exploration of emergent phenomena.^{1,2} Its attractive physical properties, such as superconductivity,³ ferromagnetism,⁴ high electron mobility,⁵ strong gating field,^{6,7} quantum Hall effect,⁸ and photoexcitation effect,^{9,10} have drawn extensive interest. So far, the isostructural perovskite-type interface, particularly LaAlO₃/SrTiO₃ (LAO/STO),¹ has been investigated intensively. However, the high mobility q-2DEG discovered at the non-isostructural interface between spinel γ -Al₂O₃ and perovskite STO remains underinvestigated.^{2,11–14} In addition to the remarkably high electron mobility (1.4×10^5 cm² V⁻¹ s⁻¹ at 2 K), the spinel structure of γ -Al₂O₃ also provides the opportunity to introduce intrinsic ferromagnetism into the heterostructure, which remains unexplored.

Herein, we epitaxially grew three new heterostructures, consisting of MAl_2O_4 (M = Fe, Co, Ni) top films and (001)-oriented TiO₂-terminated STO substrates and investigated their interfacial conduction and ferromagnetism. Remarkably, all the MAl_2O_4 (M = Fe, Co, Ni) films exhibit ferromagnetic behavior up to room temperature. We further found that the NiAl₂O₄/STO and CoAl₂O₄/STO interfaces are metallic and ferromagnetic at low temperatures, as indicated by the appearance of the anomalous Hall effect (AHE). The AHE of the MAl_2O_4/STO interfaces (M = Ni, Co) remains sizable up to 30 K, in contrast to γ -Al₂O₃/STO which shows AHE below 5 K. Moreover, the anomalous Hall resistance (R_{AHE}) undergoes a negative to positive sign change when the top film of the heterostructure changes from γ -Al₂O₃ to MAl_2O_4 . We proposed that the AHE

in γ -Al₂O₃/STO is due to the oxygen vacancy induced ferromagnetism in proximity to the STO surface, while the AHE in NiAl₂O₄/STO and CoAl₂O₄/STO probably comes from the magnetic proximity effect induced by the ferromagnetic *M*Al₂O₄ spinel films. Different from NiAl₂O₄/STO and CoAl₂O₄/STO interfaces, FeAl₂O₄/STO is insulating.

Films were grown on TiO₂-terminated STO single crystal substrates $(5 \text{ mm} \times 5 \text{ mm} \times 0.5 \text{ mm} \text{ in dimensions})$ by pulsed laser deposition using a KrF laser with a wavelength of 248 nm. During deposition, the substrate temperature was maintained at 650 °C and the oxygen pressure was kept at 1×10^{-5} mbar. The laser fluence was 2 J cm⁻², and the repetition rate was 1 Hz. The target-substrate distance was fixed at 5 cm. After deposition, the samples were cooled to room temperature without changing oxygen pressure. For the γ -Al₂O₃ deposition, a commercial Al₂O₃ single crystal target was used. MAl_2O_4 (M = Fe, Co, Ni) ceramic targets were adopted for other films. These targets were prepared by sintering the mixture of appropriate amounts of Al₂O₃ with Fe₂O₃, Co₃O₄, and NiO powders first at 1200 °C for 10 h and then after pressing at 1350 °C for 36 h. The film growth rate is approximately 0.08 Å/s. The epitaxial growth of the crystalline films was confirmed by both reflection high-energy electron diffraction (RHEED) and high-resolution X-ray diffraction (XRD) measurements. Heterostructures with 4 nm thickness top films are employed for transport and magnetic measurements, while heterostructures with 40 nm top films are used for XRD measurements. Ultrasonic Al wire bonding was used to get electric connection, and the van der Pauw geometry was adopted.

Figure 1(a) is a schematic illustration of the spinel/ perovskite (MAl_2O_4/STO) oxide heterostructure. The epitaxial growth of spinel MAl_2O_4 (M = Fe, Co, Ni) films on the

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FIG. 1. (a) A schematic sketch of the spinel/perovskite (MAl2O4/STO) oxide heterostructure (M = Fe, Co, Ni). Lattice structures of the spinel and perovskite are shown below. The box represents one unit cell, and the lattice parameter of MAl₂O₄ is about twice that of STO. (b) X-ray diffraction (XRD) θ -2 θ scan of the γ -Al₂O₃, NiAl₂O₄, CoAl₂O₄, and FeAl₂O₄ films grown on TiO2-terminated STO substrates. The inset shows the XRD θ -2 θ scan around the STO (002) reflection. (c) Omega Rocking curves of the epitaxial films in spinel/perovskite heterostructures.

perovskite STO substrate is due to their compatible oxygen sub-lattice, as the lattice parameter of MAl_2O_4 is about twice that of STO.² Although γ -Al₂O₃ and STO show a good lattice match (1%), NiAl₂O₄, CoAl₂O₄, and FeAl₂O₄ exhibit larger lattice mismatch with the STO substrate (>3%) as summarized in Table I. Consequently, the γ -Al₂O₃ film can be epitaxially grown on the STO (001) substrate with a persistent layer-by-layer two-dimensional growth mode as confirmed by RHEED and high-resolution transmission electron microscopy,^{13,15} while the NiAl₂O₄, CoAl₂O₄, and FeAl₂O₄ films show the 3D island growth mode. Despite this, the epitaxial growth of NiAl₂O₄, CoAl₂O₄, and FeAl₂O₄ films with the thickness of 40 nm on STO is confirmed by the XRD measurements. As shown in Fig. 1(b), for the θ -2 θ scan in the region of 10°-80°, (004) spinel Bragg peaks are observed on the left side of the corresponding STO peaks of (002). The out-of-plane lattice parameters of y-Al₂O₃, NiAl₂O₄, CoAl₂O₄, and FeAl₂O₄ films determined by XRD are 8.02, 8.03, 8.08, and 8.16 Å, respectively. This indicates that all the MAl₂O₄ films are well strainrelaxed. In addition, for the films of NiAl₂O₄ and FeAl₂O₄, the impurity phase of $MAIO_2$ (M = Ni, Fe) at 16.6° is detected. For the NiAl₂O₄ film, an extra impurity phase of Ni (200) crystal phase at 51.7° is also observed. These impurity phases could stem from the reduction environment of low oxygen pressure $(1 \times 10^{-5} \text{ mbar})$ and high temperature

TABLE I. Lattice parameters of γ -Al₂O₃ and MAl₂O₄ (M = Fe, Co, Ni) in bulk from reports and in films shown in text deduced by XRD data, their mismatches with the STO substrate, the full widths at half maximum (FWHM) of rocking curves for the films, their bandgaps, and conductivities of the STO-based heterointerfaces at room temperature.

	γ-Al ₂ O ₃	NiAl ₂ O ₄	CoAl ₂ O ₄	FeAl ₂ O ₄
Bulk lattice parameter	7.911 ³⁵	8.05 ^{36,37}	8.10 ^{28,38}	8.16 ^{28,38}
Mismatch with the STO substrate (%)	1.3	3.1	3.7	4.5
FWHM of the film (deg)	0.214	0.089	0.086	0.087
Film lattice parameter	8.02	8.03	8.08	8.16
Bandgap (eV)	8.7 ^{17,39}	3.4 ⁴⁰	3.68 ⁴¹	1.78 ²⁴
Room temperature $R_{\rm s}$ (Ω / \Box)	278	57.8	138	$>10^{8}$

(650 °C) adopted during the film deposition.¹⁶ However, the low diffraction intensity indicates that the amount of these impurities is rather low. Notably, these impurity phases survive after the annealing at 300 °C in 1 bar oxygen for 3 h; meanwhile, the interface becomes insulating. Therefore, such impurity phases contribute negligibly to the interface conduction as discussed later. This is also consistent with the fact that MAl_2O_4 (M = Fe, Co, Ni) films grown on (LaAlO₃)_{0.3}(Sr₂TaAlO₆)_{0.7} (LSAT) substrates are insulating in nature (see in supplementary material S1). Figure 1(c) shows the Rocking curves of the (004) spinel films grown on STO substrates. The full widths at half maximum (FWHM) of the curves determined by Gaussian fitting are shown in Table I. All MAl_2O_4 (M = Fe, Co, Ni) films display good crystallinity. In addition, compared to MAl_2O_4 spinel films, the relatively large FWHM (0.21°) of the γ -Al₂O₃ film might be due to its less ordered crystallographic structure which contains cation vacancies.¹⁷

Transport measurements show that FeAl₂O₄/STO is highly insulating. However, the metallic conduction is obtained in γ -Al₂O₃/STO and MAl₂O₄/STO (M = Ni, Co) heterostructures, as shown in Fig. 2(a). Compared to γ -Al₂O₃/STO whose sheet resistance (R_s) is 278 Ω / \Box at room temperature, NiAl₂O₄/STO and CoAl₂O₄/STO have smaller $R_{\rm s}$ which are 57.8 Ω/\Box and 138 Ω/\Box , respectively. Figures 2(b)–2(d) display the Hall resistance (R_{xy}) of γ -Al₂O₃/STO, NiAl₂O₄/STO, and CoAl₂O₄/STO as a function of magnetic field (B) in the temperature range from 295 to 2 K. When temperature is high (T > 100 K), R_{xy} varies linearly with the applied field for all samples. This is the typical behavior of the normal Hall effect (NHE). Cooling the samples to 100 K, R_{xy} shows a nonlinear dependence on the magnetic field. In the meanwhile, the magnetic field-dependent magnetoresistance $[MR = (R_{xx}(B)/R_{xx} (B=0) - 1]$ traces follow a belllike shape, where MR-B displays a U-shape at a low field, and shift to a bell-shape at a high field. These features suggest that the conductivity comes from two or more carriers as previously reported by Joshua et al.¹⁸ and Kim et al.¹⁹ and can be fitted by a two-band model (see supplementary material S2). However, R_{xy} exhibits a stronger curvature in the



FIG. 2. (a) Temperature-dependent sheet resistances (R_s) of q-2DEGs in γ -Al₂O₃/STO, NiAl₂O₄/STO, and $CoAl_2O_4/STO$ heterostructures. (b)-(d) Magnetic dependence of Hall resistances (R_{xy}) in the three heterostructures at different temperatures, respectively. (e) Example for the determination of the normal Hall effect (NHE) and the anomalous Hall effect (AHE) from the total Hall effect for NiAl2O4/STO at 2K. Measured and calculated results are presented as thick green and thin black lines, respectively. Temperature dependence of (f) sheet carrier densities, n_s , and (g) Hall mobilities, μ , in these heterostructures.

low-field range when further cooled below a critical temperature of approximately 30 K, which is beyond the capture of the two-band model. To describe the R_{xy} –B relation at T < 30 K, we adopted an extended two-band model that combines the two-band conduction-dominated NHE with an AHE as reported before^{20,21} (see supplementary material S2)

$$R_{xy} = R_{NHE} + R_{AHE} = R_{NHE} + \alpha L\left(\frac{mB}{k_BT}\right), \qquad (1)$$

where R_{NHE} and R_{AHE} represent the Hall resistance from two-band conduction and AHE, respectively. The Langevin function *L* is introduced to simulate the step-shaped AHE curve in form, α is a scale factor, and *m* is magnetic moment.

Figure 2(e) displays the determination of the anomalous Hall resistance, R_{AHE} , from R_{xy} . The results of Eq. (1) (thin black line) well reproduce the measured R_{xy} (thick green line). Basically, the normal Hall resistance (R_{NHE}) varies smoothly with B in the whole field range, with slightly but identifiable curve bending. In contrast, R_{AHE} is constant in the high-field range and undergoes a drastic change as Bsweeps through zero field. It also becomes clear that AHE appears below 5K for y-Al₂O₃/STO and 30K for both NiAl₂O₄/STO and CoAl₂O₄/STO. Based on R_{NHE} in Eq. (1), the temperature-dependent density (n_s) and Hall mobility (μ) of the carriers confined in heterostructures can be deduced [Figs. 2(f) and 2(g)]. The n_s of q-2DEGs is nearly constant from 295 K to 2 K. At 2 K, the γ -Al₂O₃/STO possesses the lowest n_s with a value of 3×10^{15} cm⁻². The NiAl₂O₄/STO heterointerface has the highest n_s (2.2 × 10¹⁶ cm⁻²) which is higher than that of γ -Al₂O₃/STO by a factor of 7. The n_s of $CoAl_2O_4/STO$ is 9.8×10^{15} cm⁻². These extremely high carrier densities indicate that 3D STO bulk conduction contributes to the measured conductivity. With regard to μ , these three heterostructures have comparable values in the range of $2.7-3.4 \times 10^4$ cm² V⁻¹ s⁻¹ at 2 K, also consistent with the mobility for bulk STO.^{1,13} It is noteworthy that FeAl₂O₄/ STO grown under the same condition as NiAl₂O₄/STO and CoAl₂O₄/STO is highly insulating. This means that the Albased spinel/perovskite interface is extremely sensitive to the introduction of the magnetic ions.

The metallic conduction in STO-based heterostructures comes from electrons located on the STO side. The high n_s

in γ -Al₂O₃/STO and *M*Al₂O₄/STO (*M* = Ni, Co) could result from the formation of oxygen vacancies in STO due to interfacial redox reactions.^{2,13,15,22} However, the insulating FeAl₂O₄/STO heterointerface might stem from two reasons. On the one hand, the Fe-based oxide has poor ability to reduce the STO substrate during the film deposition.²³ On the other hand, the bandgap of FeAl₂O₄ (1.78 eV²⁴) is much lower than that of STO (3.2 eV), and any reconstructed electrons tend to accumulate in the spinel films rather than transferring to the heterointerface.²⁵

Figures 3(a)-3(c) show the R_{AHE} variation with respect to B at different temperatures for γ-Al₂O₃/STO and MAl₂O₄/STO (M = Ni, Co). The R_{AHE} of γ -Al₂O₃/STO has the same sign as B, while that of MAl_2O_4/STO (M = Ni, Co) is opposite to B. Similar crossover in the sign of R_{AHE} has also been observed between SrRuO₃ and La_{1-x}Sr_xCoO₃ (x = 0.17) crystals.²⁶ But the explanation for such a phenomenon remains open, which could result from the intrinsic different origins of the magnetism. Moreover, in the magnetic saturation state, such as under B = -10 T at 2 K, R_{AHE} is as large as 0.013 Ω for γ -Al₂O₃/ STO, while it is 0.008 Ω for NiAl₂O₄/STO and 0.012 Ω for CoAl₂O₄/STO. Figure 3(d) summarizes R_{AHE} for these three heterointerfaces as a function of temperature. Clearly, the AHE appears at $T \leq 30 \,\mathrm{K}$ for $M \,\mathrm{Al}_2 \,\mathrm{O}_4 / \mathrm{STO}$ ($M = \mathrm{Ni}$, Co), whereas only below 5 K for γ -Al₂O₃/STO as discussed before. Shortly, the AHE of the MAl_2O_4/STO (M = Ni, Co) is dramatically different from that of γ -Al₂O₃/STO.

In order to uncover the origin of AHE in γ -Al₂O₃/STO and MAl_2O_4/STO (M = Ni, Co) heterointerfaces, magnetic measurements were performed using a superconducting quantum interference device (SQUID) magnetometer [as shown in Fig. 3(e)]. Remarkably, these three MAl_2O_4/STO (M = Fe, Co, Ni) heterostructures exhibit unexpected ferromagnetic properties up to room temperature. Notably, the $CoAl_2O_4$ and FeAl₂O₄ show spin-glass-like ground states in bulk below the Curie-Weiss temperatures (5K for CoAl2O4 and 12K for $FeAl_2O_4$,^{27,28} and the NiAl₂O₄ is paramagnetic.²⁹ In the meantime, the ferromagnetism of γ -Al₂O₃/STO is very weak (see supplementary material S3). At room temperature [inset of Fig. 3(e)], the magnetizations of FeAl₂O₄, CoAl₂O₄, and NiAl₂O₄ are 135.3, 76.4, and 69.4 emu/cm³ when B = 6 T, respectively, which are much lower than the magnetization of Fe_3O_4 (about 480 emu/cm³ at room temperature).³⁰ When the



FIG. 3. (a)–(c) Anomalous Hall resistances, R_{AHE} , in γ -Al₂O₃/STO, NiAl₂O₄/STO, and CoAl₂O₄/STO heterostructures as a function of magnetic field at different temperatures. (d) Anomalous Hall resistances (at B = -10 T) as a function of temperatures for these three samples. (e) Magnetization curves as a function of magnetic field (M-H) for γ -Al₂O₃ and MAl₂O₄ (M = Fe, Co, Ni) films with a thickness of 4 nm measured at 10 K. The inset is the M-H measured at 300 K.

temperature is 10 K, FeAl₂O₄ has the strongest magnetization, which is as large as 291.3 emu/cm³ at B = 6 T, while CoAl₂O₄ and NiAl₂O₄ have comparable magnetization, which are 196.2 and 177.9 emu/cm³, respectively. As for the interface between γ -Al₂O₃ and STO, the conduction comes from the oxygen vacancies, which could result in ferromagnetism and thus the AHE as the origin of the ferromagnetism in LAO/STO.31-33 These oxygen vacancies not only induce a complex multi-orbital reconstruction and thus the mobile q-2DEG but also result in the spin splitting of the electronic states, giving rise to localized Ti 3d electrons and thus magnetism. Salluzzo et al.³³ experimentally proved that the oxygen vacancies play a decisive role in the interfacial magnetism in LAO/STO, whereas the much higher upper limit temperature (30 K) of AHE observed in our MAl_2O_4/STO (M = Ni, Co) heterostructures than that of γ -Al₂O₃/STO (5 K) indicates that the oxygen-vacancy-related AHE in MAl₂O₄/STO is relatively weak.

It has also been suggested that interdiffusion of magnetic cations into STO could result in a similar transport behavior in manganite-buffered LAO/STO heterostructures.²⁰ Since the interdiffusion of cations is also a common phenomenon in the spinel/perovskite heterostructure, such as γ -Al₂O₃/STO,² we cannot rule out the possibility of the interdiffusion of magnetic ions into STO as a possible origin of AHE at MAl₂O₄/STO heterointerfaces. However, such interdiffusion of magnetic ions into STO could result in the Kondo effect, which is absent here. Finally, since the top films are found to be ferromagnetic, we therefore assume that the AHE in MAl₂O₄/STO (*M* = Ni, Co) comes from the magnetism induced by a magnetic proximity effect as reported for the EuTiO₃-buffered LAO/STO heterostructure.³⁴

In summary, we epitaxially grew MAl_2O_4/STO (M = Fe, Co, Ni) heterostructures in comparison to the γ -Al₂O₃/STO heterostructure. Remarkably, all the MAl_2O_4 (M = Fe, Co, Ni) films exhibit ferromagnetic behavior up to room temperature. The heterointerface of FeAl₂O₄/STO is highly insulating. In contrast, NiAl₂O₄/STO and CoAl₂O₄/STO are metallic conducting. AHE is observed in most of the metallic interfaces of γ -Al₂O₃/STO, NiAl₂O₄/STO, and CoAl₂O₄/STO. While the AHE in γ -Al₂O₃/STO is likely due to the magnetism induced by oxygen vacancies, the AHE in NiAl₂O₄/STO and CoAl₂O₄/STO most likely comes from the magnetic proximity effect induced by the top ferromagnetic spinel films.

See supplementary material for XRD data of $NiAl_2O_4$ films prepared under different oxygen pressures, on different substrates (STO, LSAT), and after the oxygen annealing; two-band model fitting of interface conduction; and magnetization of spinel/perovskite heterostructures.

We acknowledge the support of the National Basic Research of China (No. 2016YFA0300701), the National Natural Science Foundation of China (Nos. 11520101002 and 51590880), and the Key Program of the Chinese Academy of Sciences.

- ²Y. Z. Chen, N. Bovet, F. Trier, D. V. Christensen, F. M. Qu, N. H. Andersen, T. Kasama, W. Zhang, R. Giraud, J. Dufouleur, T. S. Jespersen, J. R. Sun, A. Smith, J. Nygård, L. Lu, B. Büchner, B. G. Shen, S. Linderoth, and N. Pryds, Nat. Commun. 4, 1371 (2013).
- ³N. Reyren, S. Thiel, A. D. Caviglia, L. Fitting Kourkoutis, G. Hammerl, C. Richter, C. W. Schneider, T. Kopp, A.-S. Rüetschi, D. Jaccard, M. Gabay, D. A. Muller, J.-M. Triscone, and J. Mannhart, Science **317**, 1196 (2007).
- ⁴A. Brinkman, M. Huijben, M. Van Zalk, J. Huijben, U. Zeitler, J. C. Maan, W. G. Van Der Wiel, G. Rijnders, D. H. A. Blank, and H. Hilgenkamp, Nat. Mater. 6, 493 (2007).
- ⁵Y. Z. Chen, F. Trier, T. Wijnands, R. J. Green, N. Gauquelin, R. Egoavil, D. V. Christensen, G. Koster, M. Huijben, N. Bovet, S. Macke, F. He, R. Sutarto, N. H. Andersen, J. A. Sulpizio, M. Honig, G. E. D. K. Prawiroatmodjo, T. S. Jespersen, S. Linderoth, S. Ilani, J. Verbeeck, G. Van Tendeloo, G. Rijnders, G. A. Sawatzky, and N. Pryds, Nat. Mater. 14, 801 (2015).

¹A. Ohtomo and H. Y. Hwang, Nature **427**, 423 (2004).

- ⁶W. Niu, Y. Zhang, Y. Gan, D. V. Christensen, M. V. Soosten, E. J. Garcia-Suarez, A. Riisager, X. Wang, Y. Xu, R. Zhang, N. Pryds, and Y. Chen, Nano Lett. **17**, 6878 (2017).
- ⁷W. N. Lin, J. F. Ding, S. X. Wu, Y. F. Li, J. Lourembam, S. Shannigrahi, S. J. Wang, and T. Wu, Adv. Mater. Interfaces 1, 1300001 (2014).
- ⁸F. Trier, G. E. D. K. Prawiroatmodjo, Z. Zhong, D. V. Christensen, M. Von Soosten, A. Bhowmik, J. M. G. Lastra, Y. Chen, T. S. Jespersen, and N. Pryds, Phys. Rev. Lett. **117**, 096804 (2016).
- ⁹Y. Lei, Y. Li, Y. Z. Chen, Y. W. Xie, Y. S. Chen, S. H. Wang, J. Wang, B. G. Shen, N. Pryds, H. Y. Hwang, and J. R. Sun, Nat. Commun. **5**, 5554 (2014).
- ¹⁰H. Yan, Z. Zhang, S. Wang, H. Zhang, C. Chen, and K. Jin, ACS Appl. Mater. Interfaces 9, 39011 (2017).
- ¹¹D. V. Christensen, M. von Soosten, F. Trier, T. S. Jespersen, A. Smith, Y. Chen, and N. Pryds, Adv. Electron. Mater. **3**, 1700026 (2017).
- ¹²P. Schütz, F. Pfaff, P. Scheiderer, Y. Z. Chen, N. Pryds, M. Gorgoi, M. Sing, and R. Claessen, Phys. Rev. B 91, 165118 (2015).
- ¹³Y. Z. Chen, N. Bovet, T. Kasama, W. W. Gao, S. Yazdi, C. Ma, N. Pryds, and S. Linderoth, Adv. Mater. 26, 1462 (2014).
- ¹⁴S. W. Lee, Y. Liu, J. Heo, and R. G. Gordon, Nano Lett. **12**, 4775 (2012).
- ¹⁵T. Q. Ngo, N. J. Goble, A. Posadas, K. J. Kormondy, S. Lu, M. D. McDaniel, J. Jordan-Sweet, D. J. Smith, X. P. A. Gao, A. A. Demkov, and J. G. Ekerdt, J. Appl. Phys. **118**, 115303 (2015).
- ¹⁶Y. S. Jung, W. L. Yoon, Y. S. Seo, and Y. W. Rhee, Catal. Commun. 26, 103 (2012).
- ¹⁷B. Ealet, M. H. Elyakhloufi, E. Gillet, and M. Ricci, Thin Solid Films 250, 92 (1994).
- ¹⁸A. Joshua, S. Pecker, J. Ruhman, E. Altman, and S. Ilani, Nat. Commun. 3, 1129 (2012).
- ¹⁹J. S. Kim, S. S. A. Seo, M. F. Chisholm, R. K. Kremer, H. U. Habermeier, B. Keimer, and H. N. Lee, Phys. Rev. B 82, 201407 (2010).
- ²⁰H. R. Zhang, Y. Zhang, H. Zhang, J. Zhang, X. Shen, X. X. Guan, Y. Z. Chen, R. C. Yu, N. Pryds, Y. S. Chen, B. G. Shen, and J. R. Sun, Phys. Rev. B **96**, 195167 (2017).
- ²¹F. Gunkel, C. Bell, H. Inoue, B. Kim, A. G. Swartz, T. A. Merz, Y. Hikita, S. Harashima, H. K. Sato, M. Minohara, S. Hoffmann-Eifert, R. Dittmann, and H. Y. Hwang, Phys. Rev. X 6, 031035 (2016).
- ²²K. J. Kormondy, A. B. Posadas, T. Q. Ngo, S. Lu, N. Goble, J. Jordan-Sweet, X. P. A. Gao, D. J. Smith, M. R. McCartney, J. G. Ekerdt, and A. A. Demkov, J. Appl. Phys. **117**, 095303 (2015).

- Appl. Phys. Lett. 113, 261603 (2018)
- ²³A. B. Posadas, K. J. Kormondy, W. Guo, P. Ponath, J. Geler-Kremer, T. Hadamek, and A. A. Demkov, J. Appl. Phys. **121**, 105302 (2017).
- ²⁴H. Y. Mu, F. T. Li, X. T. An, R. H. Liu, Y. L. Li, X. Qian, and Y. Q. Hu, Phys. Chem. Chem. Phys. **19**, 9392 (2017).
- ²⁵W. Niu, W. Liu, M. Gu, Y. Chen, X. Zhang, M. Zhang, Y. Chen, J. Wang, J. Du, F. Song, X. Pan, N. Pryds, X. Wang, P. Wang, Y. Xu, Y. Chen, and R. Zhang, Adv. Electron. Mater. 4, 1800055 (2018).
- ²⁶T. Miyasato, N. Abe, T. Fujii, A. Asamitsu, S. Onoda, Y. Onose, N. Nagaosa, and Y. Tokura, Phys. Rev. Lett. **99**, 086602 (2007).
- ²⁷G. M. Kalvius, A. Krimmel, O. Hartmann, F. J. Litterst, R. Wäppling, V. Tsurkan, and A. Loidl, Phys. B: Condens. Matter 404, 660 (2009).
- ²⁸N. Tristan, J. Hemberger, A. Krimmel, H. A. Krug Von Nidda, V.
- Tsurkan, and A. Loidl, Phys. Rev. B 72, 174404 (2005).
- ²⁹S. Kamali, J. Magn. Magn. Mater. **433**, 155 (2017).
- ³⁰Y. Z. Chen, J. R. Sun, Y. N. Han, X. Y. Xie, J. Shen, C. B. Rong, S. L. He, and B. G. Shen, J. Appl. Phys. **103**, 07D703 (2008).
- ³¹N. Pavlenko, T. Kopp, E. Y. Tsymbal, G. A. Sawatzky, and J. Mannhart, Phys. Rev. B 85, 020407 (2012).
- ³²N. Pavlenko, T. Kopp, E. Y. Tsymbal, J. Mannhart, and G. A. Sawatzky, Phys. Rev. B 86, 064431 (2012).
- ³³M. 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).
- ³⁴D. Stornaiuolo, C. Cantoni, G. M. De Luca, R. Di Capua, E. Di Gennaro, G. Ghiringhelli, B. Jouault, D. Marrè, D. Massarotti, F. M. Granozio, I. Pallecchi, C. Piamonteze, S. Rusponi, F. Tafuri, and M. Salluzzo, Nat. Mater. **15**, 278 (2016).
- ³⁵R. S. Zhou and R. L. Snyder, Acta Crystallogr., Sect. B 47, 617 (1991).
- ³⁶Y. S. Han, J. B. Li, X. S. Ning, and B. Chi, J. Am. Ceram. Soc. 87, 1347 (2004).
- ³⁷M. G. Brik, A. Suchocki, and A. Kamińska, Inorg. Chem. **53**, 5088 (2014).
- ³⁸A. Walsh, S. H. Wei, Y. Yan, M. M. Al-Jassim, J. A. Turner, M. Woodhouse, and B. A. Parkinson, Phys. Rev. B 76, 165119 (2007).
- ³⁹M. Yazdanmehr, S. J. Asadabadi, A. Nourmohammadi, M. Ghasemzadeh, and M. Rezvanian, Nanoscale Res. Lett. 7, 448 (2012).
- ⁴⁰S. Jayasree, A. Manikandan, S. Arul Antony, A. M. Uduman Mohideen, and C. Barathiraja, J. Supercond. Nov. Magn. 29, 253 (2016).
- ⁴¹P. Bhavani, A. Manikandan, S. K. Jaganathan, S. Shankar, and S. A. Antony, J. Nanosci. Nanotechno. **18**, 1388 (2018).