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Magnetic phase and magneto-resistive effects in vanadium oxide epitaxial nanoclusters

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ABSTRACT

The metal-insulator transition and the original magnetic phase that appear in vanadium oxide nanoclusters epitaxially embedded in an MgO matrix are studied via electron transport, magneto-resistance, and X-ray circular dichroism measurements. The metal-insulator transition temperature is observed to be in the range of 1.5–27 K. We observe, from 0.3 K to at least 125 K, a superparamagnetic behavior, whereas vanadium oxide, in its bulk phase, is reported to be anti-ferromagnetic (AF) at low temperatures. This striking feature is consistent with either ferromagnetic spin pairing or spin canting in the AF spin order along the 1D vanadium ion chains of the Magnéli phase or for the VO₂(A)-like phase. Finally, the observed magneto-resistive effect, which reached up to 8% at low temperatures, indicates ferromagnetic behavior for some of the nanoparticles. This enables their integration in spintronic devices that could be combined with metal-insulator switching and magneto-resistive effects.

Among the materials that exhibit strong electron correlation effects, vanadium oxides have been extensively studied for many years due to their first-order metal-insulator (MI) transition. For example, VO₂ has a transition temperature “ T_{MI} ” close to room temperature at 342 K^{1,2} and V₂O₃ has a T_{MI} value of 168 K.^{3,4} The V_nO_{2n-1} Magnéli oxide structure is regarded as an intermediate between these two oxides. In its bulk, the structure is made of parallel chains of V sites that share edges with the surrounding oxygen octahedrons. These chains are infinite in the limit case of VO₂ ($n = \infty$), shrink to two atoms in the case of V₂O₃ ($n = 2$), and possess n V atoms for V_nO_{2n-1} oxides.³ These 1D ionic chains exhibit an intrinsic magnetic order below the Néel temperature (T_N), and an anti-ferromagnetic (AF) coupling of vanadium spins appears along the chains that are magnetically decoupled.³ Interestingly, both T_N and T_{MI} present strong variations with n in these Magnéli oxides, as summarized in Ref. 3. T_N varies from 0 to 170 K, which allows modulating the magnetic properties of oxides via stoichiometry variations. Above T_N , their relatively weak magnetism is constant with temperature and is attributed to Pauli paramagnetism.⁵ Below T_N , some recent studies have suggested the possibility of the coexistence of a weak Curie–Weiss paramagnetic behavior with the AF order, such as in strained or doped bulk VO₂^{6–8}

or V₂O₃ films and nanoparticles.⁹ A ferromagnetic signature was even assumed in some cases, such as VO_x nanotubes,^{10–12} whose origins remain unexplained.

Here, we study epitaxially grown vanadium oxide clusters embedded in an MgO insulating matrix using an original technique similar to that reported in our previous works that focused on Cr₂O₃ clusters.^{13,14} Islands form spontaneously due to the dewetting of metallic V on MgO during growth and before oxidation and MgO capping. It appears that reducing the vanadium oxide to nanometric epitaxial clusters dramatically alters their magnetic properties. The clusters are proven to carry a non-negligible magnetic moment, as revealed through magneto-resistance (MR) and X-ray magnetic circular dichroism (XMCD) measurements. These results indicate that there are modifications to the spin configuration along the 1D vanadium chains relative to unstrained, bulk, and vanadium oxides. These observations could enable applications that combine the MI transition and spintronic effects into a single device that exploits the magnetization of the clusters through the MR effect.

The samples are grown on an MgO [001] substrate using e-beam guns for molecular beam epitaxy (MBE) in a 10^{−10} mbar base pressure chamber. A 20-nm MgO layer is deposited at 500 °C followed by

vanadium (0.15 nm) at 200 °C to form the 3D epitaxial vanadium clusters¹⁵ with a (001)[100]MgO/(001)[110] epitaxial relationship. A 3-nm MgO layer is then deposited at 200 °C, while the pressure increases to the 10^{-8} mbar range, and the atomic oxygen partial pressures contribute to the V oxidation. The stack is then annealed at 500 °C to promote the complete V oxidation.

Devices devoted to in-plane resistance measurements [see Fig. 1(a)] are fabricated using deposition through a shadow mask of Ti/Au electrodes with lateral sizes on the order of 100 micrometers. Magneto-transport measurements are performed in a 4He static cryostat with a magnetic field H applied in the junction plane. The X-ray absorption (XAS) and XMCD spectra are measured at the SOLEIL synchrotron on the DEIMOS beamline in the Total Electron Yield Mode.^{16,17} The dichroic measurements are performed with a photon beam under an applied magnetic field at a normal incidence to the sample. Magnetization curves are obtained by acquiring the XAS signal at the V L_3 edge while varying the magnetic field. For each H value, we acquire the signal for left and right X-ray polarizations and subtract both signals.

The 3D growth of V on MgO is observed using atomic force microscopy (AFM) [Fig. 1(b)]. The clusters appear as anisotropic in shape and are aligned along the MgO[110] direction. The typical dimensions are a height in the range of 4–6 nm, a length of 200–300 nm, and a width of 80–150 nm, but some scarce larger clusters with a height up to 45 nm are also observed (see [supplementary material Fig. S1](#)). This is consistent with the dewetting of vanadium on

MgO, followed by complete oxidation, as is shown below through XAS measurements.

The typical shape of the epitaxial clusters is also observed through cross-sectional transmission electron microscopy (TEM) images [Fig. 1(c)]. The clusters are flat, 5-nm thick, and more than 30-nm wide, which are consistent with the AFM results. We observe a continuity of vertical planes through the interface between MgO and the vanadium oxide clusters, which proves the epitaxial relationship of these clusters with MgO. The small size and distortion of the clusters prevent the systematic evaluation of their crystalline orientation. However, our observations (see [supplementary material Fig. S2](#) for details) are consistent with a structure close to the (A)-tetragonal phase of VO_2 ,^{18,19} which is reported to have lattice parameters close to $a = b = 8.43 \text{ \AA}$ and $c = 7.68 \text{ \AA}$. Such a crystalline phase is metastable in bulk¹⁸ but could be favored in MgO(001). The cube-on-cube growth for VO_2 (001)//MgO(001) and VO_2 [100]//MgO[100] would lead to a low epitaxial lattice mismatch (-0.3%) with cubic MgO ($a_{\text{MgO}} = 4.20 \text{ \AA}$). We consider this $\text{VO}_2(\text{A})$ -like phase as one of the possible alternatives for the cluster phase.

Electronic transport measurements show that the I-V curves [Fig. 1(d) inset] are systematically nonlinear at different temperatures. In this granular system, electrons tunnel between different clusters through the MgO insulating matrix.^{20,21} Such a mechanism requires the clusters to be in a conducting state. Considering the dispersion in the cluster sizes [Fig. 1(b) and Fig. S1] and the inter-cluster distances, the conduction is likely non-homogenous throughout the film. There may be some percolation paths,²² which could be modified by varying the applied bias voltage. The I-V curves are hysteretic at room temperature (see Fig. S3), as is well known for the case of VO_2 and exploited in memristor devices,²³ but this effect decreases at lower temperatures [Fig. 1(d) inset]. We performed I-T measurements from RT down to 1.5 K, systematically proving a hysteretic resistive transition as a function of temperature. Figure 1(d) shows a slow decrease in the current followed by an abrupt transition at $T_{\text{MI}} = 1.8 \text{ K}$ from a relatively conducting state to a highly resistive state. The inverse transition is observed at higher temperatures ($T_{\text{MI}} = 27 \text{ K}$). No other abrupt transitions are observed, which suggests a homogeneous phase inside the oxide clusters without large spatial fluctuations in the oxygen stoichiometry. We consider two possible alternatives consistent with this observation: The $\text{VO}_2(\text{A})$ -like phase may, in strained clusters, have a different behavior compared to the bulk (in which no MI transitions are reported) and possibly explain our observations. Alternatively, if we assume that the structures are Magnéli phases (see the $T_{\text{MI}}(n)$ curve in Ref. 3), we observe that T_{MI} is in the low range for vanadium oxides. In bulk V_8O_{15} , T_{MI} is equal to 70 K, and there is no MI transition for bulk V_7O_{13} (conductive for all T). Our transport observations are, therefore, also possibly consistent with a Magnéli phase close to V_8O_{15} with a lower T_{MI} than bulk due to the effects of strain.

In Fig. 2(a), the XAS results from the $L_{2,3}$ edges of vanadium do not exactly fit the reference spectra of bulk VO_2 or V_2O_3 oxides, which are quite close.^{24–26} The global shape of the experimental spectra can be reproduced²⁷ by assuming a contribution from V^{3+} ions²⁸ in an octahedral environment. However, we cannot reproduce some of the shoulders or the relative intensities of the L_2 and L_3 peaks with either V^{3+} or V^{4+} valence states. This indicates a strong distortion of the structure relative to the bulk oxide phases, as confirmed below through XMCD observations. Furthermore, the presence of metallic vanadium,

FIG. 1. Vanadium oxide epitaxial clusters deposited on an MgO (001) substrate and capped with MgO. (a) Scheme of the devices, with in-plane injection of the current via two electrodes; (b) AFM image of the clusters on an uncapped surface (the inset shows the height profile across a typical cluster with a 4.5 nm height); (c) high-resolution TEM observation for the cross section of an uncapped cluster that is flat and about 5 nm thick (the vertical atomic planes are continuous through the MgO/cluster interface, and the crystalline axes are indicated in MgO and in the cluster for a $\text{VO}_2(\text{A})$ phase of vanadium oxide); (d) I-T measurement through the cluster assembly with a decreasing (black and blue curve) or increasing (red curve) temperature with an abrupt and hysteretic MI transition (the inset shows the I-V curves at 10, 20, and 30 K and are consistent with a tunneling transport mechanism).

FIG. 2. (a) XAS spectra measured at 0.3 K at the vanadium $L_{2,3}$ edges (black and gray curves for the two polarizations) with a normal incidence of the beam. The calculated reference spectra are given for comparison: V^{3+} ions in a strained octahedral oxygen environment (D_{4h} symmetry) under a crystalline field $Dq = 0.11$ eV, $Ds = 0.05$ eV, and $Dt = 0.05$ eV (blue curve) and in a C_{3v} symmetry (red curve); (b) experimental XMCD spectrum at 0.3 K under a 6.5 T magnetic field and (blue and red curves) simulations following the same hypotheses as in (a) (the inset shows a hypothetical spin configuration along a height vanadium ion chain with spin canting); (c) XMCD signal at the L_3 edge as a function of temperature; (d) XMCD magnetization curve measured at 0.3 K at $E = 516$ eV, with an increasing (black) or decreasing (blue) magnetic field. The curves are fitted with a Langevin function (red curve) assuming a free magnetic dipole $m = 0.37 \mu_B$ in the super-paramagnetic assembly.

which could also be compatible with our XAS spectra,²⁹ is ruled out based on the TEM observations of homogenous clusters (Fig. 1) and the occurrence of MI transitions. We believe that there is a mixture of ions in the V^{3+} and V^{4+} states, which is consistent with fully oxidized vanadium in a highly distorted phase. The temperature-dependent XAS spectra are given in the [supplementary material](#) (see Fig. S4). The results do not show major changes with temperature, which is in contrast to previous reports.^{2,40}

In Fig. 2(b), the XMCD spectra measured at the $V L_{2,3}$ edge show a surprisingly large signal (10%) (i.e., the difference of the spectra normalized to the sum) when measured at $T = 0.3$ K, under a 6.5 T magnetic field. This clearly demonstrates that oxide clusters carry a magnetic moment, which is not expected in the bulk AF phase. This signal is observed from 0.3 to 120 K, where its amplitude falls below the experimental detection limits [Fig. 2(c)]. Due to the overlapping L_2 and L_3 peaks^{29,30} and to the ambiguous oxidation state of vanadium ions, the magnetic moment cannot be estimated using sum rules.^{31–33} Simulations of the dichroic spectra²⁷ on vanadium ions (either V^{3+} or V^{4+}) do not yield such a large dichroic signal if we assume an octahedral configuration (D_{4h} symmetry) for the surrounding oxygen ions for any crystalline field. A C_{3v} (ammonia-like symmetry) oxygen environment around the vanadium³⁴ is required to reproduce this order of magnitude and the approximate shape of the experimental XMCD spectra. This again suggests a strong modification of the crystalline phase in these vanadium oxides compared to bulk.

The M-H magnetization curves measured at the vanadium L_3 edge of the XMCD maximum for magnetic fields between -6.5 T and

$+6.5$ T at 0.3 K showed an S-shaped variation without any noticeable coercive field. The curves show a good fit with the Langevin function $L[m\mu_0 H/(k_B T)]$ [Fig. 2(d)]. This behavior is consistent with a super-paramagnetic assembly of magnetic dipoles; the free magnetic moments m fluctuate due to thermal excitations. The fit provides an estimate of the free magnetic moment m of $0.37 \pm 0.02 \mu_B$ at 0.3 K. There are some similarities between this result and the work of Li *et al.*¹¹ that reported the appearance of super-paramagnetism in VO_2 nanowires due to the generation of oxygen vacancies. They suggested that vanadium ions form dimers in which the spins are ferromagnetically exchange-coupled due to oxygen vacancies, but were decoupled with other ions along the infinite-spin chains. The appearance of magnetization in the nanometric clusters may be due to the ferromagnetic pairing of vanadium spins inside dimers that form along the finite vanadium chains. Another hypothesis as an analogy with another work⁵ could rely on the spin canting of a few degrees relative to the AF order that is expected in bulk [Fig. 2(b) inset]. We moreover cannot exclude within this last scenario that vanadium ions play a different role depending on their positions inside the 1D chain.³ For instance, there could be different spin canting angles for the edges from those at the middle of the chains.

Whatever the real vanadium spin configuration, the origin of its change relative to the bulk state could be explained by one of the following hypotheses. (1) The oxide crystalline structure can be close to the vanadium Magnéli phase described in Ref. 3 but modified with a large biaxial stress due to the epitaxial relationship with the underlying MgO. The dramatic influence of the hydrostatic pressure on the T_M and T_N temperatures has been underlined in different studies on Magnéli V_nO_{2n-1} bulk materials^{3,35,36} and could modify the spin exchange coupling between vanadium ions (the TEM and X-ray diffraction observations, though partial, nevertheless do not indicate such a phase). (2) The epitaxial relationship could stabilize a metastable phase.³⁷ This includes the A-phase, which is close to the rutile structure but with the presence of zig-zag vanadium chains instead of linear chains whose magnetic and transport properties have not been systematically measured.^{18,19} Here, this hypothesis is not fully satisfying since this metastable phase does not reportedly show a MI transition, at least not in bulk. A recent density-functional theory calculation³⁸ on bulk vanadium oxides predicted the appearance of a phase exhibiting a ferromagnetic order under a high pressure strain. This phase could explain the magnetic behavior observed in some vanadium oxide thin films.^{6–8}

Finally, we observe that the magnetization in these oxide clusters leads to MR effects at low temperatures. Applying an in-plane magnetic field from -5 to $+5$ T noticeably modifies the conductance, which follows a bell-shaped curve (Fig. 3). At 10 K, the total amplitude of the MR effect is close to $+8\%$. At 5 K, the signal is much noisier due to a higher resistance state, but it overall follows the same behavior. At higher temperatures, the long acquisition time (half an hour) correlated with the non-negligible memristive effects hinders the observations of a clean MR hysteretic curve.

The origin of the MR effect itself is attributed either to a giant tunneling magneto-resistive effect between oxide clusters or to an anisotropic MR effect,^{20,39} which would be intrinsic to each cluster. Whatever the mechanism, this reflects the behavior of the magnetic moments present in the clusters and the subsequent spin polarization of the charge carriers. The observation of smooth variations of I with

FIG. 3. Magneto-resistance curves measured at 5 and 10 K at a bias voltage of 100 V with an in-plane magnetic field.

H is consistent with the information discerned from the XMCD, i.e., the magnetization is mainly due to super-paramagnetic behavior.¹¹ These results are again consistent with the work of Li *et al.*¹¹ based on chemically grown VO₂ nanotubes that reported a high MR effect, but at RT. Nevertheless, we observe a large coercive field in the I-H curves (Fig. 3), which is in contrast to the XMCD magnetization curves, corresponding to a hysteresis in the maxima of the current when close to ± 0.4 T.

We believe that, as mentioned above, some percolation paths may conduct the electric current in the cluster assembly. This provides much more weight in the MR curves to the clusters that form these paths, which could be much larger than the typical clusters described above (5 nm high) as they have slightly different shapes or epitaxial strains (Fig. S1). If the magnetic properties of the clusters vary widely with their size, shape, or strain, it is expected that the largest clusters will exhibit a larger magnetic anisotropy or spin exchange coupling on larger length scales along the vanadium chains. This would lead to a larger energy barrier for magnetization switching and to a magnetic coercive field, which is absent in other clusters. This implies that besides the super-paramagnetic assembly of small clusters, there is a population of larger clusters in the ferromagnetic state.¹⁰ Within this hypothesis, these clusters would contribute in a negligible way to the total magnetization measured using XMCD because they correspond to a negligible fraction of vanadium ions, but they would noticeably contribute to the MR signal. However, a quantitative evaluation of the fraction of ferromagnetic clusters cannot be deduced from these data.

In conclusion, the physical MBE technique reported here appears to be an original and facile way to form nanoclusters of vanadium oxide and to force their epitaxial relationship with an MgO matrix. That is, we achieved flat islands of vanadium oxide epitaxially grown on MgO. These structures show a clear MI transition in the range of 1.5–27 K and a magnetic signal up to 125 K, which is related to super-paramagnetic behavior. We moreover observe a MR signal and evidence of some ferromagnetic clusters. The precise nature of the vanadium oxide phase cannot be definitely determined due to the very small amount of probed vanadium atoms and to the nanometric size and shape of the clusters. We considered the possibility of a Magnéli phase close to V₈O₁₅, which is not magnetic in bulk, and of a VO₂-like

(A) phase that would be stabilized due to epitaxial strain. The possibility of another ferro-magnetic phase of the oxide, similar to the phase predicted in Ref. 38, should be considered.

From a practical perspective, exploiting the population of magnetic, especially ferromagnetic, vanadium oxide clusters could benefit the fabrication of spintronics devices by adding an additional degree of freedom for the manipulation of these systems. We envision devices that combine the MR effect to read a memory state and a voltage-induced effect through a gate that could switch the conductive state to modify the logical node. These types of applications would require T_{MI} to be increased to room temperature. We envision a modulation to both T_{MI} and the magnetic properties by modifying the strain, oxygen stoichiometry, or size distribution of the clusters, which could play crucial roles in these oxides.

See the [supplementary material](#) for the details of the structural configuration of the vanadium oxide clusters and for the temperature-dependent XAS and XMCD data.

REFERENCES

- ¹F. J. Morin, *Phys. Rev. Lett.* **3**, 34 (1959).
- ²N. B. Aetukuri, A. X. Gray, M. Drouard, M. Cossale, L. Gao, A. H. Reid, R. Kukreja, H. Ohldag, C. A. Jenkins, E. Arenholz, K. P. Roche, H. A. Dürr, M. G. Samant, and S. S. P. Parkin, *Nat. Phys.* **9**, 661 (2013).
- ³U. Schwingenschlögl and V. Eyert, *Ann. Phys.* **13**, 475 (2004).
- ⁴A. S. McLeod, E. van Heumen, J. G. Ramirez, S. Wang, T. Saerbeck, S. Guenon, M. Goldflam, L. Anderregg, P. Kelly, A. Mueller, M. K. Liu, I. K. Schuller, and D. N. Basov, *Nat. Phys.* **13**, 80 (2017).
- ⁵C. Yin, R. Zhang, G. Qian, Q. Fu, C. Li, M. Wang, C. Zhu, L. Wang, S. Yuan, X. Zhao, and H. Tao, *Appl. Phys. Lett.* **110**, 172404 (2017).
- ⁶T.-H. Yang, S. Nori, H. Zhou, and J. Narayan, *Appl. Phys. Lett.* **95**, 102506 (2009).
- ⁷K. L. Holman, T. M. McQueen, A. J. Williams, T. Klimczuk, P. W. Stefens, H. W. Zandbergen, Q. Xu, F. Ronning, and R. J. Cava, *Phys. Rev. B* **79**, 245114 (2009).
- ⁸R. Zhang, Q. S. Fu, C. Y. Yin, C. L. Li, X. H. Chen, G. Y. Qian, C. L. Lu, S. L. Yuan, X. J. Zhao, and H. Z. Tao, *Sci. Rep.* **8**, 17093 (2018).
- ⁹V. A. Blagojevic, J. P. Carlo, L. E. Brus, M. L. Steigerwald, Y. J. Uemura, S. J. L. Billinge, W. Zhou, P. W. Stephens, A. A. Aczel, and G. M. Luke, *Phys. Rev. B* **82**, 094453 (2010).
- ¹⁰L. Krusin-Elbaum, D. M. Newns, H. Zeng, V. Derycke, J. Z. Sun, and R. Sandstrom, *Nature* **431**, 672 (2004).
- ¹¹Z. Li, Y. Guo, Z. Hu, J. Su, J. Zhao, J. Wu, J. Wu, Y. Zhao, C. Wu, and Y. Xie, *Angew. Chem., Int. Ed.* **55**, 8018 (2016).
- ¹²R. Molaei, R. Bayati, S. Nori, D. Kumar, J. T. Prater, and J. Narayan, *Appl. Phys. Lett.* **103**, 252109 (2013).
- ¹³D. Halley, N. Najjari, H. Majjad, L. Joly, P. Ohresser, F. Scheurer, C. Ulhaq-Bouillet, S. Berciaud, B. Doudin, and Y. Henry, *Nat. Com.* **5**, 3167 (2014).
- ¹⁴D. Halley, N. Najjari, F. Godel, M. Hamieh, B. Doudin, and Y. Henry, *Phys. Rev. B* **91**, 214408 (2015).
- ¹⁵E. Román, Y. Huttel, M. F. López, R. Gago, A. Climent-Font, A. Muñoz-Martín, and A. Cebollada, *Surf. Sci.* **600**, 497 (2006).
- ¹⁶P. Ohresser, E. Otero, F. Choueikani, K. Chen, S. Stanesco, F. Deschamps, T. Moreno, F. Polack, B. Lagarde, J. P. Daguette *et al.*, *Rev. Sci. Instrum.* **85**, 013106 (2014).
- ¹⁷J.-P. Kappler, E. Otero, W. Li, L. Joly, G. Schmerber, B. Muller, F. Scheurer, F. Leduc, B. Gobaut, L. Poggini *et al.*, *J. Synchrotron Radiat.* **25**, 1727 (2018).
- ¹⁸Y. Oka, T. Yao, and N. Yamamoto, *J. Mater. Chem.* **1**, 815 (1991).
- ¹⁹S. R. Popuri, A. Artemenko, C. Labrugere, M. Miclau, A. Villesuzanne, and M. Pollet, *J. Solid State Chem.* **213**, 79 (2014).
- ²⁰S. Maekawa, S. Takahashi, and H. Imamura, in *Spin Dependent Transport in Magnetic Nanostructures*, edited by S. Maekawa and T. Shinjo (CRC Press, 2002), Chap. 4.

- ²¹M. Pauly, J.-F. Dayen, D. Golubev, J.-B. Beaufrand, B. P. Pichon, B. Doudin, and S. Bégin-Colin, *Small* **8**, 108 (2012).
- ²²A. Cohen, A. Frydman, and R. Berkovits, *Solid State Commun.* **129**, 291 (2004).
- ²³J. A. J. Rupp, M. Querré, A. Kindsmüller, M. P. Belland, E. Janod, R. Dittmann, R. Waser, and D. J. Wouters, *J. Appl. Phys.* **123**, 044502 (2018).
- ²⁴D. Ruzmetov, S. D. Senanayake, and S. Ramanathan, *Phys. Rev. B* **75**, 195102 (2007).
- ²⁵M. W. Haverkort, Z. Hu, A. Tanaka, W. Reichelt, S. V. Streltsov, M. A. Korotin, V. I. Anisimov, H. H. Hsieh, H.-J. Lin, C. T. Chen *et al.*, *Phys. Rev. Lett.* **95**, 196404 (2005).
- ²⁶T. Schmitt, L.-C. Duda, M. Matsubara, and M. Mattesini, *Phys. Rev. B* **69**, 125103 (2004).
- ²⁷M. Retegan, *crispy v0,7,2* (2019). DOI:10.5281/zenodo.1451209, <https://zenodo.org/badge/latestdoi/53660512>
- ²⁸M. F. Jager, C. Ott, P. M. Kraus, C. J. Kaplan, W. Pouse, R. E. Marvel, R. F. Haglund, D. M. Neumark, and S. R. Leone, *Proc. Nat. Acad. Sci. U. S. A.* **114**, 9958 (2017).
- ²⁹Y. Huttel, G. van der Laan, C. M. Teodorescu, P. Bencok, and S. S. Dhesei, *Phys. Rev. B* **67**, 052408 (2003).
- ³⁰J. Okabayashi, S. Miyasaka, K. Hemmi, K. Tanaka, S. Tajima, H. Wadati, A. Tanaka, Y. Takagi, and T. Yokoyama, *J. Phys. Soc. Jpn.* **84**, 104703 (2015).
- ³¹B. T. Thole, P. Carra, F. Sette, and G. van der Laan, *Phys. Rev. Lett.* **68**, 1943 (1992).
- ³²P. Carra, B. T. Thole, M. Altarelli, and X. Wang, *Phys. Rev. Lett.* **70**, 694 (1993).
- ³³C. T. Chen, Y. U. Idzerda, H. Lin, N. V. Smith, G. Meigs, E. Chaban, G. H. Ho, E. Pellegrin, and F. Sette, *Phys. Rev. Lett.* **75**, 152 (1995).
- ³⁴H. F. Pen, L. H. Tjeng, E. Pellegrin, F. M. F. de Groot, G. A. Sawatzky, M. A. van Veenendaal, and C. T. Chen, *Phys. Rev. B* **55**, 15500 (1997).
- ³⁵S. K. Kim, E. Colombier, N. Ni, S. L. Bud'ko, and P. C. Canfield, *Phys. Rev. B* **87**, 115140 (2013).
- ³⁶H. Ueda, K. Kitazawa, T. Matsumoto, and H. Takagi, *Solid State Commun.* **125**, 83 (2003).
- ³⁷E. Strelcov, A. Tselev, I. Ivanov, J. D. Budai, J. Zhang, J. Z. Tischler, I. Kravchenko, S. V. Kalinin, and A. Kolmakov, *Nano Lett.* **12**, 6198 (2012).
- ³⁸S. Xu, Y. Shen, K. A. Hallman, R. F. Haglund, and S. T. Pandelides, *Phys. Rev. B* **95**, 125105 (2017).
- ³⁹M. Erkhinsky, J. De la Venta, and I. K. Schuller, *J. Appl. Phys.* **114**, 143901 (2013).
- ⁴⁰J.-H. Park, L. H. Tjeng, A. Tanaka, J. W. Allen, C. T. Chen, P. Metcalf, J. M. Honig, F. M. F. de Groot, and G. A. Sawatzky, *Phys. Rev. B* **61**, 11506 (2000).