



CHORUS

This is the accepted manuscript made available via CHORUS. The article has been published as:

Fragility of ferromagnetic double exchange interactions and pressure tuning of magnetism in 3d-5d double perovskite  $\text{Sr}_2\text{FeOsO}_6$

L. S. I. Veiga, G. Fabbris, M. van Veenendaal, N. M. Souza-Neto, H. L. Feng, K. Yamaura, and D. Haskel

Phys. Rev. B **91**, 235135 — Published 19 June 2015

DOI: [10.1103/PhysRevB.91.235135](https://doi.org/10.1103/PhysRevB.91.235135)

# Fragility of ferromagnetic double exchange interactions and pressure tuning of magnetism in 3d-5d double perovskite $\text{Sr}_2\text{FeOsO}_6$

L. S. I. Veiga,<sup>1,2,3,\*</sup> G. Fabbris,<sup>1,4</sup> M. van Veenendaal,<sup>1,5</sup> N. M. Souza-Neto,<sup>2</sup> H. L. Feng,<sup>6,7</sup> K. Yamaura,<sup>6,7</sup> and D. Haskel<sup>1,†</sup>

<sup>1</sup>*Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439, USA*

<sup>2</sup>*Laboratório Nacional de Luz Síncrotron - P.O. Box 6192, 13084-971, Campinas, São Paulo, Brazil*

<sup>3</sup>*Instituto de Física “Gleb Wataghin”, Universidade Estadual de Campinas, Campinas, São Paulo 13083-859, Brazil*

<sup>4</sup>*Department of Physics, Washington University, St. Louis, Missouri 63130, USA*

<sup>5</sup>*Department of Physics, Northern Illinois University, De Kalb, Illinois 60115, USA*

<sup>6</sup>*Superconducting Properties Unit, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki, 305-0044, Japan*

<sup>7</sup>*Graduate School of Chemical Science and Engineering, Hokkaido University, Sapporo, Hokkaido, 060-0810, Japan*

The ability to tune exchange (magnetic) interactions between 3d transition metals in perovskite structures has proven to be a powerful route to discovery of novel properties. Here we demonstrate that the introduction of 3d-5d exchange pathways in double perovskites enables additional tunability, a result of the large spatial extent of 5d wave functions. Using x-ray probes of magnetism and structure at high pressure, we show that compression of  $\text{Sr}_2\text{FeOsO}_6$  drives an unexpected continuous change in the sign of Fe-Os exchange interactions and a transition from antiferromagnetic to ferrimagnetic order. We analyze the relevant electron-electron interactions, shedding light into fundamental differences with the more thoroughly studied 3d-3d systems.

## I. INTRODUCTION

First-row (3d) transition metal oxides with perovskite crystal structure ( $\text{ABO}_3$  with A an alkali, alkaline earth or rare earth ion and B a transition metal ion) continue to provide a rich playground for the realization of novel quantum states, a result of a strong interplay between spin, orbital, charge and lattice degrees of freedom. Manipulation of electron correlations at interfaces of heterostructures or under application of electric and magnetic fields in multiferroic structures has unraveled a plethora of new phenomena in these strongly correlated 3d systems<sup>1-5</sup>. In the search for materials with additional tunability, double perovskites with  $\text{A}_2\text{BB}'\text{O}_6$  formula unit (B and B' are distinct TM ions arranged periodically, doubling the unit cell) have emerged as a new fertile ground for exploration of novel quantum states<sup>6,7</sup>. This is because d-orbital occupancy and symmetry, which together with lattice distortions control B-B' electron hopping integrals and therefore transport and exchange (magnetic) interactions, can be independently tuned at B and B' sites. Additionally, the ability to combine the rather localized 3d electron wave functions at B sites with the more delocalized 5d electron wavefunctions of third-row transition metal ions at B' sites, provides a path to further tunability and potential for new functionalities.

While the mechanisms regulating 3d-3d exchange interactions in these oxide structures are rather well understood in terms of Goodenough-Kanamori (G-K) rules<sup>8-11</sup>, the understanding of 3d-5d interactions is much less developed. For example, on-site Coulomb interactions are significantly reduced at 5d sites relative to 3d sites, affecting the strength of Hund's coupling and related strength of double-exchange interactions (i.e., delocalized superexchange involving  $e_g$  electrons)<sup>12-14</sup>. Fur-

thermore, the disparate crystal electric fields (CEF) at 3d and 5d sites, together with sizable spin-orbit interactions in 5d ions with strong nuclear potential alters the energy landscape and modifies electron hopping. As a result, the validity of G-K rules in 3d-5d systems ought to be addressed. The extended 5d orbitals may also require accounting for longer-range exchange pathways beyond first neighbor exchange in order to understand magnetic phenomena. A number of double perovskites of this type have shown remarkable properties including half-metallicity above room temperature in  $\text{A}_2\text{CrWO}_6$ <sup>15</sup>, colossal magnetoresistance in  $\text{Sr}_2\text{FeReO}_6$ <sup>16</sup>, and moderate to large magneto-optical properties in  $\text{Sr}_2\text{CrReO}_6$  and  $\text{Sr}_2\text{CrOsO}_6$ <sup>17</sup>, a testament to the exciting opportunities inherent in the exploration of these versatile structures.

In this work, we explore the use of external pressure (compressive stress) as a tool to modify lattice structure and 3d-5d exchange interactions, allowing us to develop a fundamental understanding of the underlying physics in a model system,  $\text{Sr}_2\text{FeOsO}_6$ . Using x-ray spectroscopic and structural probes in a diamond anvil cell, we find a pressure-induced reversal in the sign of Fe-Os exchange interactions along the crystallographic c-axis of this tetragonal structure, driving a change from an antiferromagnetic (AFM) to a ferrimagnetic (FiM) ground state. The transition is a result of an increase in the difference between cubic crystal fields at Fe and Os sites with pressure, which gradually impairs the ability of  $e_g$  electrons to mediate ferromagnetic (FM) double exchange (DE) interactions along the c-axis. As a result, AFM super exchange (SE) involving  $t_{2g}$  electrons becomes the dominant interaction in both in-plane and out-of-plane directions at high pressure. This mechanism is different than that behind the AFM-FiM transition induced by chemical pressure (Ca substitution for Sr)

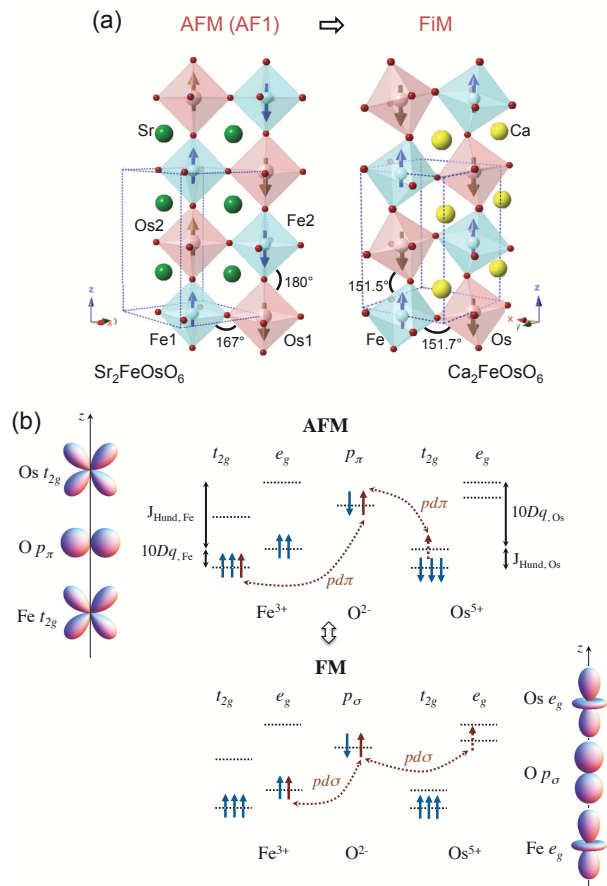


Figure 1. (Color online) (a) Crystal and magnetic structure of  $\text{Sr}_2\text{FeOsO}_6$  and  $\text{Ca}_2\text{FeOsO}_6$  double perovskites. (b) Schematic of double exchange (FM) and superexchange (AFM) interactions between  $\text{Fe}^{3+}$  and  $\text{Os}^{5+}$  ions along  $c$ -axis.

where the weakening of DE-FM interactions is driven by an increased Fe-O-Os bond buckling along  $c$ -axis. That both mechanisms lead to a common ground state is striking evidence for a weakened FM interaction as a result of the delocalized nature of 5d wavefunctions, namely, a small on-site Coulomb interaction and large crystal field at Os sites. The novel pressure-induced transition, unique to the 3d-5d makeup of this double perovskite structure, transforms a material with no remanent magnetization or coercivity into one with robust coercivity ( $\sim 0.5$  T) typical of permanent magnets, aided by the presence of spin-orbit interaction at Os sites. The fragility of FM interactions in this 3d-5d system indicates that modest changes in tensile or compressive strain in engineered epitaxial films could have significant impact on magnetic response providing a path to functional devices.

## II. EXPERIMENTAL AND THEORETICAL METHODS

### A. X-ray absorption spectroscopy

Polycrystalline  $\text{Ca}_2\text{FeOsO}_6$  and  $\text{Sr}_2\text{FeOsO}_6$  samples were prepared by solid-state reaction using high-pressure and high-temperature method as described in Ref.<sup>18,19</sup>. XMCD measurements at Fe  $L_{2,3}$  absorption edges were carried out at ambient pressure and low temperature ( $T=15$  K) at undulator beam line 4-ID-C of the Advanced Photon Source. Experiments were performed in polarization switching mode and any artifact in the XMCD data were removed by consecutive measurements in opposite applied fields ( $H=4$  T). The data were collected using total electron yield (TEY) detection mode.

The ambient and high-pressure XMCD measurements at Os  $L_{2,3}$ -edges were performed at undulator beam line 4-ID-D of the Advanced Photon Source. Higher x-ray harmonics were rejected with two Pd mirrors at 3 mrad incidence angle (critical energy  $\sim 22$  keV) and by detuning the second crystal of a Si(111) monochromator to about 80% of the fundamental's intensity. The measurements were done on powder samples in transmission geometry using a helicity modulation technique (13.3 Hz). An external magnetic field of  $H=4$  T was used; measurements were repeated for opposite field directions to remove any artifacts. For XANES and XMCD experiments at high pressure the x-ray beam was focused to  $18 \times 22 \mu\text{m}^2$  with Kirkpatrick-Baez mirrors. The DAC was prepared with a partially perforated anvil (150 microns wall thickness) opposite a mini-anvil (0.8 mm in height) on top of a fully perforated anvil to minimize x-ray absorption in the diamond anvils. Culet size was 300 microns. The DAC mounts on a variable-temperature insert of a superconducting magnet for low-temperature measurements down to 1.6 K in applied magnetic fields up to 6.5 T. Powders of  $\text{Sr}_2\text{FeOsO}_6$  were loaded into a  $120 \mu\text{m}$  hole in a rhenium gasket pre-indented to  $30 \mu\text{m}$ , together with ruby spheres for in-situ pressure calibration and Neon gas as pressure-transmitting medium.

### B. X-ray diffraction

High-pressure XRD experiments were performed at HPCAT beam line 16-BM-D of the Advanced Photon Source using a symmetric DAC with conical seats and diamond culet size of  $300 \mu\text{m}$ . A  $120\text{-}\mu\text{m}$  hole in a rhenium gasket pre-indented to  $30\mu\text{m}$  was filled with  $\text{Sr}_2\text{FeOsO}_6$  powders together with Au and ruby spheres for *in situ* pressure calibration and He gas as pressure-transmitting medium. Pressure was applied manually using a gearbox control system. The measurements were carried out at  $T = 15$  K with the x-ray energy tuned to 30 keV. The two-dimensional (2D) XRD patterns were recorded with a MAR345 image plate and converted into 1D plots using the FIT2D software<sup>20</sup>. All the XRD analyses were

performed using the LeBail method as implemented in the GSAS/EXPGUI program<sup>21,22</sup>.

### C. FeO<sub>6</sub> and OsO<sub>6</sub> cluster calculations

The theoretical calculations were done for OsO<sub>6</sub> and FeO<sub>6</sub> clusters with octahedral symmetry. The Hamiltonian includes crystal field, spin-orbit interaction, the full multiplet Coulomb interaction and the coupling to the nearest-neighbor oxygens. The parameters are calculated within the Hartree-Fock approximation<sup>23</sup> and rescaled to account for band and screening effects. The rescaling for the non monopole parts of the Coulomb interaction is 0.45 and 0.8, for Os and Fe, respectively. The on-site Coulomb repulsion between the 5d/3d electrons is 3 and 6 eV for Os/Fe. The monopole part of the *pd* Coulomb interaction is taken 5 and 6 eV for Os and Fe, respectively. The charge-transfer energies are 3 and 0.4 eV, for Os and Fe, respectively. For Os, the spin-orbit interaction strength at ambient pressure is 0.45 eV. At higher pressure, the effective spin-orbit interaction strength is reduced to 0.3 eV to account for the increased osmium bandwidth. The cubic crystal field is 3.7 eV. A small exchange field has been applied. Parameters differ slightly between different compounds to fine tune the agreement with the experimental spectra. The calculations for Fe are typical for high-spin 3d<sup>5</sup> compounds. The strong covalency has a relatively weak effect on the spectral line shape. The cubic crystal field is 0.7 eV and the spin-orbit strength at ambient pressure is 59 meV.

## III. RESULTS

### A. Chemical pressure

We start by comparing the structural and electronic properties of Sr<sub>2</sub>FeOsO<sub>6</sub><sup>19,24</sup> to its chemically compressed analog, Ca<sub>2</sub>FeOsO<sub>6</sub><sup>18</sup>. The smaller Ca<sup>2+</sup> ions drive a transition from a tetragonal (*I4/m*) to a distorted monoclinic (*P2<sub>1</sub>/n*) crystal structure (Fig. 1a). In the tetragonal structure, the B/B'O<sub>6</sub> octahedra are rotated by ~ 13 degrees around the *c*-axis, leading to buckled (~ 167 degrees) Fe-O-Os bonds within the *ab* plane but retaining Fe-O-Os collinearity along the *c*-axis. This collinear bonding displays FM coupling of Fe and Os ions, as expected from G-K rules for the coupling between Fe<sup>3+</sup> (3d<sup>5</sup>) and Os<sup>5+</sup> (5d<sup>3</sup>) ions<sup>25</sup>. Surprisingly, the in-plane Fe-Os coupling is AFM despite the relatively small buckling angle, in apparent contradiction with G-K rules which predict AFM coupling at much larger angles<sup>25</sup>. As discussed below, this is a result of weak 3d-5d FM interactions relative to their 3d-3d counterparts, driven by the delocalized nature of the 5d wavefunction. The compressed Ca structure adds a second B/B'O<sub>6</sub> octahedra rotation around [110] (*a*<sup>-</sup>*a*<sup>-</sup>*b*<sup>+</sup> in Glazer notation), leading to deviations from collinearity in both in-plane

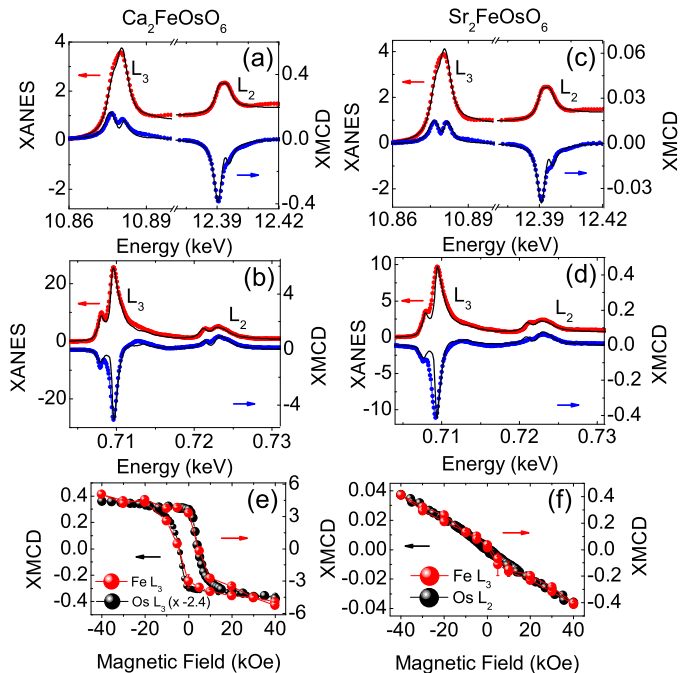


Figure 2. (Color online) Normalized Os and Fe XANES and XMCD L<sub>2,3</sub> edge spectra for (a)-(b) Ca<sub>2</sub>FeOsO<sub>6</sub> and (c)-(d) Sr<sub>2</sub>FeOsO<sub>6</sub> double perovskites measured at ambient pressure. Black lines are results from cluster calculations. (e)-(f) Field-dependence of Fe L<sub>3</sub> ( $E_{L_3}=0.709$  keV) and Os L<sub>2,3</sub> ( $E_{L_2}=12.391$  keV and  $E_{L_3}=10.877$  keV) XMCD peak intensities for Ca<sub>2</sub>FeOsO<sub>6</sub> and Sr<sub>2</sub>FeOsO<sub>6</sub>.

and out-of-plane directions and emergence of FiM order (Fig. 1a). Note that the FM interaction between Fe and Os is mediated by the overlap of *e<sub>g</sub>* orbitals with oxygen *p<sub>σ</sub>* orbitals, highly sensitive to the degree of Fe-O-Os collinearity (Fig. 1b, bottom panel). On the other hand, the AFM interaction is mediated by the overlap of *t<sub>2g</sub>* and oxygen *p<sub>π</sub>* orbitals, which is only weakly modified by buckling (see Eq. 1).

X-ray magnetic circular dichroism (XMCD) measurements at Fe L<sub>2,3</sub> and Os L<sub>2,3</sub> edges confirm the presence of FiM order in the Ca structure and absence thereof in the Sr structure (Fig. 2). The Fe and Os magnetic moments point in opposite directions as evident by the opposite signs of XMCD signals (Fe along applied field). A strong exchange coupling between magnetic sublattices is evident from their correlated magnetization reversal. The Sr structure shows typical AFM response to applied fields, namely, linear dependence of magnetization due to field-induced canting of Fe and Os moments. The low saturation magnetization in the Sr structure at 4 Tesla, ten times smaller than in the Ca structure (Fig. 2 e-f), is indicative of strong exchange interactions favoring a nearly collinear AFM arrangement of magnetic moments with small canting.

Since spin-orbit interactions can affect electronic structure at 5d sites, we performed a theoretical analysis of the x-ray absorption data using OsO<sub>6</sub> and FeO<sub>6</sub> cluster cal-



culations including single and double ligand-hole states. A good agreement between the experimental and theoretical spectra is obtained (see Fig. 2 a-d). Calculated orbital and spin moments for Os are  $m_l = -\langle L_z \rangle = 0.27 \mu_B/\text{Os}$ ,  $m_s = -2\langle S_z \rangle = -2.72 \mu_B/\text{Os}$  ( $m_{\text{Os}} = m_l + m_s = -2.45 \mu_B/\text{Os}$ ). The spin sum rule requires knowledge of  $\langle T_z \rangle$ , where  $T_z$  is the magnetic dipole operator. We used  $\langle T_z \rangle = -0.09$ . Although small, neglecting this quantity could lead to an underestimation of the spin by more than 20%. The orbital magnetization at Os sites is opposite to the spin magnetization, as expected for a less than half-filled 5d orbital occupancy (calculated number of 5d holes is  $n_h = 6.38$ ). The corresponding quantities for Fe sites are  $m_l = 0.044 \mu_B/\text{Fe}$ ,  $m_s = 4.34 \mu_B/\text{Fe}$  ( $m_{\text{Fe}} = 4.38 \mu_B/\text{Fe}$ ; number of 3d holes  $n_h = 4.35$ ). The XMCD-derived orbital and spin moments as well as net saturated magnetization ( $m_{\text{Fe}} + m_{\text{Os}} = 1.93 \mu_B$ ) are in good agreement with DFT calculations<sup>26</sup> and SQUID measurements<sup>19</sup>. The results confirm a high-spin ground state for Fe, with covalency (and S-O interactions at Os sites) responsible for the reduction in moment values from the expected  $5(3)\mu_B$  of  $\text{Fe}^{3+}$  ( $\text{Os}^{5+}$ ) ions in octahedral CEF (neutron diffraction experiments have so far failed to converge on a consistent description of the magnitude of local moments in either structure<sup>27,28</sup>). The orbital-to-spin moment ratio is ten times larger at Os sites due to the stronger S-O interaction.

The ground-state expectation value of the angular part of the spin-orbit coupling,  $\langle \mathbf{L} \cdot \mathbf{S} \rangle$ , can be obtained from the branching ratio (BR) of the isotropic Os absorption spectra  $BR = I_{L_3}/I_{L_2}$ , with  $I_{L_{2,3}}$  the integrated white line intensities at  $L_{2,3}$  edges, through  $BR = (2+r)/(1-r)$  with  $r = \langle \mathbf{L} \cdot \mathbf{S} \rangle / n_h$  and  $n_h$  the number of holes in the 5d states<sup>29</sup>. We obtain a BR value of 2.6(1) for both compounds, corresponding to  $\langle \mathbf{L} \cdot \mathbf{S} \rangle = 0.99\hbar^2$  for the unoccupied 5d electron states. Even though the spin-orbit interaction strength,  $\zeta$ , used in the calculations is comparable to that in the iridates, the spin-orbit coupling in osmates is significantly reduced with respect to these compounds<sup>30-32</sup>. While the S-O interaction is still significant, Os cannot be described in the strong spin-orbit coupling limit where 3 electrons would occupy  $j_{\text{eff}} = 3/2$  states<sup>30-32</sup> as this would yield  $\langle \mathbf{L} \cdot \mathbf{S} \rangle = 9\zeta/10Dq + 3/2 = 2.66\hbar^2$  using the values from the cluster calculation. A description of Os 5d states in terms of pure crystal field ( $t_{2g}$ ) states is not correct either, as this corresponds to quenched orbital magnetization and a statistical BR=2. This places the osmates in an intermediate regime where S-O interactions compete with Hund's exchange in the presence of a dominant CEF interaction in agreement with calculations<sup>26</sup>. S-O and CEF interactions acting on Os 5d electrons are expected to be a source of magnetic anisotropy and explain the sizable coercivity of FiM  $\text{Ca}_2\text{FeOsO}_6$ .

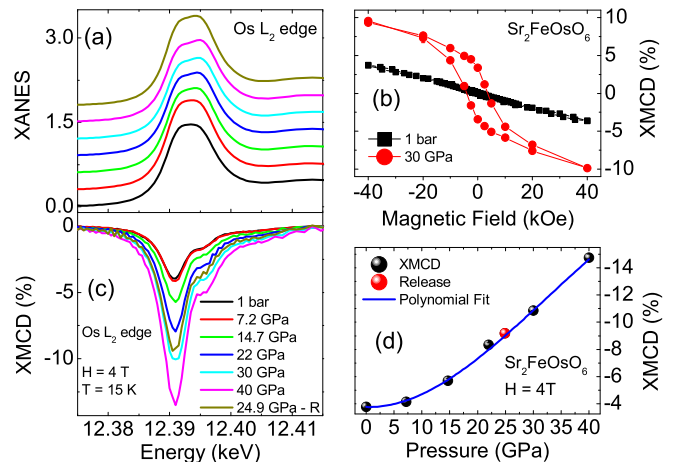


Figure 3. (Color online) (a) Pressure dependence of Os  $L_2$ -edge XANES for  $\text{Sr}_2\text{FeOsO}_6$ . (b) Field-dependence of Os  $L_2$ -edge XMCD intensity at ambient pressure and at 30 GPa showing emergence of FM response in the Os sub lattice. (c)-(d) Os  $L_2$ -edge XMCD as a function of applied pressure. Data collected after partial pressure release (24.9 GPa) are also shown.

## B. Compression experiments

We now turn to the effect of hydrostatic pressure on the structural and electronic ground state of  $\text{Sr}_2\text{FeOsO}_6$ . As seen in Fig. 3 c-d, a continuous increase in XMCD signal is observed under pressure reaching four times its ambient pressure value at 40 GPa (although not matching the saturation value of the Ca structure). The emergence of a FM response in the Os sublattice is clearly seen in the field-dependent XMCD data, where large coercivity (0.5 Tesla) comparable to that of the Ca structure (0.85 Tesla) is observed (Fig. 3b). Remanent magnetization ( $\sim 0.23 \mu_B/\text{Os}$ ) also emerges. This presents a dramatic change from the negligible coercivity and remanence measured at ambient pressure (Fig. 3b). We note that the XMCD signal fully reverts in size upon pressure reduction from 40 GPa to 24.9 GPa with no measurable hysteresis. It appears that the exchange coupling of Os and Fe moments along the c-axis continuously transforms from FM towards AFM under lattice compression leading to a FiM response, mimicking the behavior of the chemically compressed Ca structure (Fig. 1a).

One may be tempted to conclude that the driving force for the magnetic transition is a pressure-induced monoclinic distortion with related deviation in Fe-O-Os c-axis bonding from collinearity. However, our low temperature (15 K) x-ray powder diffraction measurements show that the Sr structure remains tetragonal to 56 GPa. The XRD patterns were fitted using LeBail method (EXPGUI-GSAS) within the  $I4/m$  tetragonal space group. LeBail refinement yields lattice parameters but does not provide fractional atomic coordinates. Figure 4a shows the XRD patterns for  $\text{Sr}_2\text{FeOsO}_6$  at

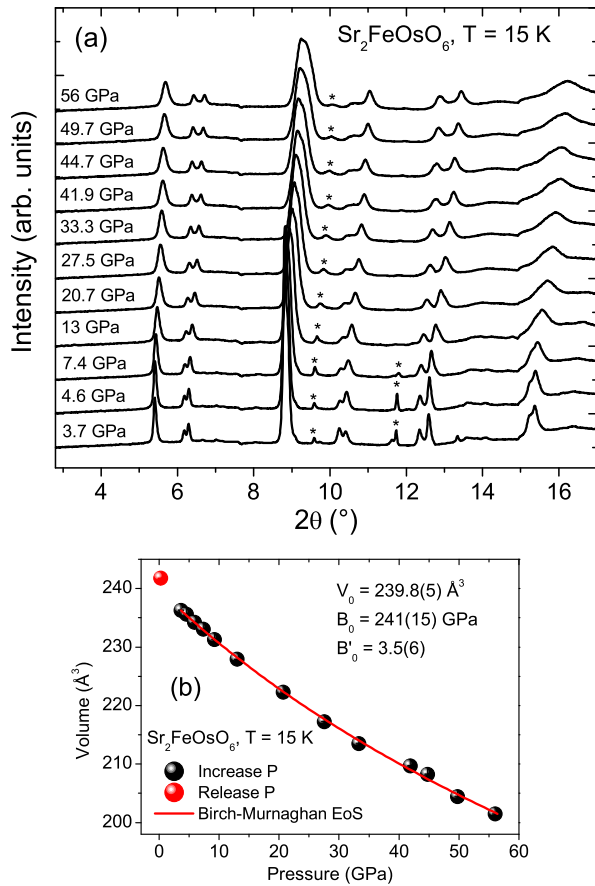


Figure 4. (Color online) (a) Angular dispersive x-ray powder diffraction of  $\text{Sr}_2\text{FeOsO}_6$  as a function of pressure at  $T = 15$  K. The Bragg peaks marked as \* are from Ruby spheres and Au powder. (b) Pressure-volume relationship and its fit to a third-order Birch-Murnaghan equation of state (EoS).

different pressure points. No discontinuities in lattice parameters or signatures of a structural phase transition were found in the entire pressure range measured. The measured pressure-volume relationship was fitted to a third-order Birch-Murnaghan equation of state, yielding the bulk modulus and its derivative,  $B_0 = 241(15)$  GPa,  $B'_0 = 3.5(6)$  and an ambient pressure volume of  $V_0 = 239.8(5) \text{ \AA}^3$  (Fig. 4b).

Ca doping drives a continuous *reduction* in  $c/a$  ratio, a result of larger buckling in  $c$ -axis Fe-O-Os bonding compressing the  $c$ -axis lattice parameter faster than the  $a$ -axis lattice parameter (Fig. 5b). This contrasts with the *increase* in  $c/a$  ratio with pressure (Fig. 5a), which indicates that such  $c$ -axis buckling does not take place in the Sr structure. Indeed, an inspection of the tetragonal lattice parameters as a function of pressure indicates that the  $a$ -axis contraction rate is almost 2-fold that of the  $c$ -axis  $(\Delta a/a_0)/\Delta P = -0.1138(3) \text{ \%/GPa}$ ;  $(\Delta c/c_0)/\Delta P = -0.0679(4) \text{ \%/GPa}$ , with the  $c/a$  ratio minimally enhanced up to the highest pressure measured ( $\sim 3\%$ ). An enhanced  $c/a$  ratio is also observed upon cooling the Sr structure at ambient pressure (inset of

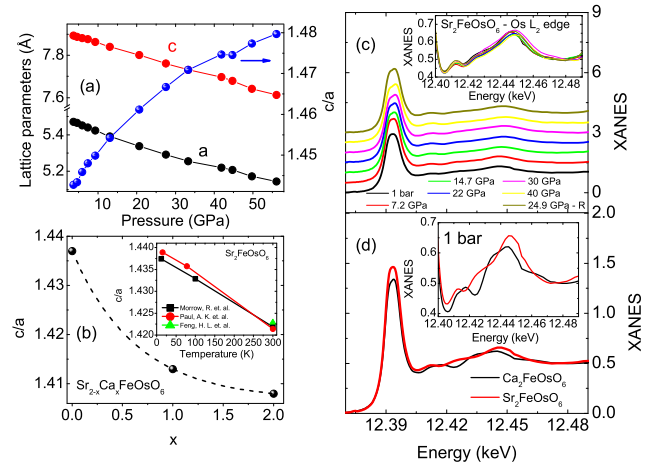


Figure 5. (Color online) (a) Tetragonal lattice parameters and  $c/a$  ratio refined within  $I4/m$  tetragonal space group. (b)  $c/a$  ratio as a function of Ca doping in  $\text{Sr}_{2-x}\text{Ca}_x\text{FeOsO}_6$ , and as a function of temperature (ambient pressure) in  $\text{Sr}_2\text{FeOsO}_6$ , reproduced from Ref. 19,24,28. (c) Pressure dependence of Os  $L_2$ -edge XAFS for  $\text{Sr}_2\text{FeOsO}_6$ . (d) Comparison of Os  $L_2$ -edge XAFS signal in  $\text{Ca}_2\text{FeOsO}_6$  and  $\text{Sr}_2\text{FeOsO}_6$  at ambient pressure.

Fig. 5b), which is known to retain tetragonal symmetry with increased in-plane Fe-O-Os buckling. Forcing a model to our diffraction data where the  $c$ -axis contracts more than the  $a$ -axis results in an unphysical  $c/a$  ratio of 1.36. Such large reduction in  $c/a$  ratio would correspond to a significant change in local structure and manifest sizable changes in the X-ray absorption fine structure (XAFS) data (Fig. 5d). However, our XAFS data at the Os  $L_2$  edge shows no significant change to 40 GPa (Fig. 5c). Since XAFS is highly sensitive to deviations in Os-O-Fe bonding from collinearity we conclude that this bonding remains collinear along the  $c$ -axis and therefore the transition to a FiM state under pressure has a different origin than that induced by chemical pressure.

#### IV. DISCUSSION

Experimental and theoretical reports on the nature of exchange interactions in  $\text{Sr}_2\text{FeOsO}_6$  have addressed the origin of AFM order in this structure at ambient pressure<sup>27,28,33</sup>. In fact, two different AFM configurations (AF1 and AF2, Fig. 6c) are observed by neutron diffraction to coexist at low temperature, the AF2 phase appearing on cooling below 67 K and becoming dominant below 55 K (85% at 2 K)<sup>27,28</sup>. The AF1 phase consists of FM Fe-Os chains along the  $c$ -axis, while half of Fe-Os bonds become AFM coupled in the AF2 phase. The change in magnetic structure on cooling may be associated with a lattice distortion in which short (AFM) and long (FM) Fe-Os distances are created<sup>27</sup>.

Our powder XRD experiment at high pressure is not sensitive enough to probe for a possible modulation in Fe-

Os distances in the c-axis direction in the AF2 phase as reported in Ref.<sup>27</sup>. High pressure single crystal diffraction experiments will be needed to detect whether this modulation, if present, persists under pressure. In any event, both AF1 and AF2 phases carry no net magnetization and are indistinguishable to the XMCD probe. Assuming that the AF2 phase is the ground state at ambient pressure, the application of pressure is seen to drive a second order, reversible transformation into a ferrimagnetic phase. We next discuss the possible origins for this transition.

Comparing the excitations from  $\text{Fe}^{3+}$  ions ( $3d^5$ ,  $t_{2g}^3 e_g^2$  high-spin configuration) and  $\text{Os}^{5+}$  ions ( $5d^3$ ,  $t_{2g}^3 e_g^0$  configuration) along the z-direction (c-axis), the energy gain due to super exchange mediated by the  $t_{2g}$  electrons can be approximated by:

$$\Delta E_{SE} \approx -2 \frac{\alpha^2 (pd\pi)^4}{\Delta^2 U} \quad (1)$$

where  $\Delta$  is the charge-transfer energy for osmium and oxygen,  $U$  is the charge transfer from the Fe site to the Os site,  $(pd\pi)$  is the Slater-Koster overlap integral between  $t_{2g}$  orbitals and the  $p\pi$ -bonding oxygen orbitals.  $\alpha$  is the ratio of the overlap integrals between Os and Fe, where  $(pd\pi)$  is significantly larger between Os-O than Fe-O. The factor 2 comes from the fact we are dealing with two  $t_{2g}$  orbitals ( $yz$  and  $zx$ ) that delocalize in the  $z$  direction. The delocalization of the  $e_g$  orbital ( $d_{3z^2-r^2}$  orbitals) gives rise to an effective double exchange between Fe and Os given to lowest order by:

$$\Delta E_{DE} \approx - \frac{\alpha^2 ((pd\sigma)(\cos^4 \frac{180^\circ - \theta}{2}))^4}{\Delta^2} \times \frac{6J_{Hund,Os}}{(U + 10Dq_{Os} - 10Dq_{Fe})^2} \quad (2)$$

where  $\theta$  is the buckling angle along  $z$  direction. The antiferromagnetic charge transfer energy is larger for  $e_g$  electrons mainly due to the difference in crystal fields ( $10Dq_{Os} - 10Dq_{Fe}$ ) since the  $e_g$  double exchange requires an excitation into the empty Os  $e_g$  orbitals, which are high in energy. The energy gain for the double exchange comes from the ferromagnetic alignment of the magnetic moments of Fe and Os which facilitate the delocalization of the  $3z^2 - r^2$  electrons. The energy gain is given by  $6J_{Hund,Os}$  if we assume a simple Hund's exchange interaction between the spins on Os. Since the 5d orbitals have a relatively large spatial extent, the Coulomb exchange on Os is significantly smaller than that on Fe. However, the double exchange benefits strongly from the larger hopping matrix elements of the  $e_g$  orbitals compared to the  $t_{2g}$  orbitals. In the presence of a buckling of the octahedra, the double exchange is more strongly reduced due to the fact that the oxygen  $\sigma$ -bonding orbitals lie along the c-axis, whereas the  $\pi$ -bonding orbitals are perpendicular to it. The buckling is included by the  $\cos^4(180^\circ - \theta)/2$ , where  $\theta=180^\circ$  is the angle in the absence of buckling. Buckling therefore reduces the double exchange along the c-axis.

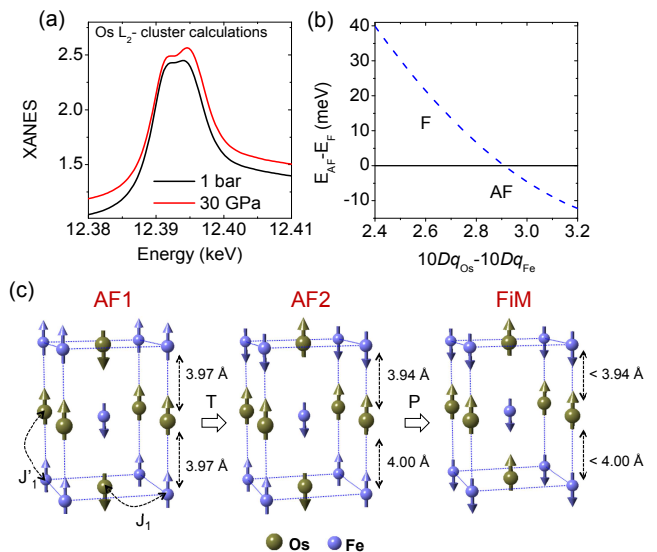


Figure 6. (a) XANES spectra obtained from cluster calculations using octahedral crystal field values of  $10Dq = 3.7$  eV and  $4.2$  eV for ambient pressure and  $30$  GPa, respectively. (b) Energy difference between FM and AFM Fe-Os coupling along the c-axis as a function of the difference in crystal electric field at Os and Fe sites. (c) Evolution of magnetic structure with cooling (T) and applied pressure (P).  $J_1$  ( $J_1'$ ) denotes nearest-neighbor exchange between Fe and Os moments. The Fe-Os distances in AF1 and AF2 structures are taken from Ref.<sup>27</sup>. Note that the magnetic unit cell of the AF2 phase is doubled along the c-axis.

Based on the energetics involved in the DE and SE interactions, there are two direct consequences of the reduction in the Fe-O-Os bond lengths. First, there is an increase in the hopping integrals between the TM ions and the oxygens. These are given by the tight-binding parameters  $pd\sigma_{TM-O}$  and  $pd\pi_{TM-O}$  for the  $\sigma$ -bonding  $e_g$  orbitals and  $\pi$ -bonding  $t_{2g}$  orbitals, respectively. Both hopping matrix elements have a  $r_{TM-O}^{-3.5}$  dependence on the TM-O distance. Additionally, both the SE and DE interactions have, to leading order, a similar dependence on the hopping integrals. Therefore, changes in the relative strengths of the DE and SE interactions are a higher-order effect. This is confirmed by numerical calculations using Fe-O-Os clusters with parameters consistent with those used to calculate the x-ray absorption spectra, which showed a minimal dependence of the relative strengths of the exchange interactions with the hopping integrals. The second quantity affected by the reduction of the TM-O distance is the CEF. Here, the magnetic exchange interactions are affected differently. The DE involves the exchange of an  $e_g$  electron between the Fe and the Os ion. To leading order the gain in energy due to the DE is given by the Eq. 2. We see that the DE is directly proportional to the (weak) Hund's rule coupling  $J_{Hund,Os}$  on the osmium ion. A decrease in lattice parameters causes an increase in the difference between the Os and Fe crystal-field parameters  $10Dq_{Os} - 10Dq_{Fe}$ , lead-

ing to a further reduction of the double exchange interaction. This has been confirmed by cluster calculations where a transition from a FM to AFM Fe-Os coupling is obtained. The on-site parameters are those used in the calculations of x-ray absorption spectra (Fig. 2). Since the effect of the spin-orbit interaction on the ground state is relatively small, the interaction strength was set to zero to obtain a clear spin transition. The hopping parameter  $pd\sigma$  between Os and oxygen is 1.4 eV. The value of  $pd\pi$  is  $0.45pd\sigma$ . The hopping parameters for Fe are two times smaller. Figure 6b shows the difference between the antiferromagnetic and ferromagnetic states as a function of the difference between the osmium and iron crystal fields. The increase in crystal fields stabilizes the antiferromagnetic state, by reducing the double exchange interaction, as expected from Eq. 2. The difference in energy between the two spin states changes by several tens of meV for a change in crystal field by a few hundreds of meV. Evidence for pressure-induced changes in CEF parameter at Os sites is seen in the evolution of the  $L_2$ -edge white line (Fig. 3a), the enhanced spectral weight in the high-energy side reproduced in cluster calculations with a 0.5 eV increase in crystal field strength (Fig. 6a).

An understanding of the pressure induced magnetic transition naturally follows. Upon lattice compression the reduction in all Fe-Os distances and related increase in (cubic) CEF energy causes a weakening of an already fragile Fe-Os DE-FM interaction relative to the SE-AFM interaction along the c-axis. The in-plane Fe-Os coupling remains AFM at all temperatures and pressures due to the persistent in-plane Fe-O-Os buckling. The transition to AFM coupling in Fe-Os bonds along the c-axis leads to emergence of FiM order in the compressed structure. Although full, collinear FiM order is not achieved at 40 GPa (based on field dependent data and comparison to Ca analog), the transition appears to be second order as no detectable hysteresis was observed on pressure release.

The high degree of tunability of exchange interactions under pressure is unique to the 3d-5d makeup of this double-perovskite structure, namely, the delocalized 5d state reduces the onsite Coulomb interaction and increases CEF resulting in weaker DE-FM Fe-Os interac-

tions compared to those found in 3d-3d analogs. For example, the FM state of  $\text{La}_2\text{MnNiO}_6$  remains unchanged to at least 38 GPa, a result of strong on-site (Hund's) coupling on Mn sites<sup>34</sup>. The ability to not only dramatically alter the magnetic state with external stimuli but to do so in a continuous fashion is appealing for applications where tunability of coercivity and saturation magnetization is desired. While undoped  $\text{Sr}_2\text{FeOsO}_6$  requires sizable pressures ( $> 10$  GPa) to induce significant changes in coercivity and net magnetization, one can envision doping Ca into the Sr structure to attain proximity to a FiM state<sup>28</sup> hence enabling much smaller pressures (or strain in films) to drive the AFM-FiM transition in a reversible way; e.g., with dynamical compression/decompression. Furthermore, the ability to achieve sizable coercive fields (0.5 Tesla) by manipulating indirect (3d-5d) exchange interactions with pressure coupled with S-O interactions at 5d sites presents an interesting opportunity in the search for rare-earth free permanent magnets<sup>35,36</sup>.

## ACKNOWLEDGMENTS

Work at Argonne is supported by the US Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC-02-06CH11357. L. S. I. Veiga is supported by FAPESP (SP-Brazil) under Contract No. 2013/14338-3. M. v. V was supported by DOE-BES under Award No. DEFG02-03ER46097. This research was supported in part by the World Premier International Research Center of the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan, the Japan Society for the Promotion of Science (JSPS) through a Grant-in-Aid for Scientific Research (25289233). We would like to thank Changyong Park and Curtis Kenny-Benson for their assistance at 16-BM-D beamline, Sergey N. Tkachev for assistance with gas loading, and Richard Rosenberg for help with soft x-ray measurements. We also thank GSECARS for use of the gas loading and laser drilling facilities.

\* Present address: Deutsches Elektronen-Synchrotron DESY, Notkestrasse 85, D-22607 Hamburg, Germany

† [haskel@aps.anl.gov](mailto:haskel@aps.anl.gov)

<sup>1</sup> M. Huijben, G. Rijnders, D. H. A. Blank, S. Bals, S. V. Aert, J. Verbeeck, G. V. Tendeloo, A. Brinkman, and H. Hilgenkamp, *Nat Mater* **5**, 556 (2006).

<sup>2</sup> A. Ohtomo, D. A. Muller, J. L. Grazul, and H. Y. Hwang, *Nature* **419**, 378 (2002).

<sup>3</sup> S.-W. Cheong and M. Mostovoy, *Nat Mater* **6**, 13 (2007).

<sup>4</sup> Y. Tokunaga, N. Furukawa, H. Sakai, Y. Taguchi, T.-h. Arima, and Y. Tokura, *Nat Mater* **8**, 558 (2009).

<sup>5</sup> R. Ramesh and N. A. Spaldin, *Nat Mater* **6**, 21 (2007).

<sup>6</sup> T. Saha-Dasgupta, *J. Supercond. Nov. Magn.* **26**, 1991 (2013).

<sup>7</sup> V. Pardo and W. E. Pickett, *Phys. Rev. B* **80**, 054415 (2009).

<sup>8</sup> P. W. Anderson, *Phys. Rev.* **79**, 350 (1950).

<sup>9</sup> J. B. Goodenough, *Phys. Rev.* **100**, 564 (1955).

<sup>10</sup> J. B. Goodenough, *J. Phys. Chem. Solids* **6**, 287 (1958).

<sup>11</sup> J. Kanamori, *J. Phys. Chem. Solids* **10**, 87 (1959).

<sup>12</sup> C. Zener, *Phys. Rev.* **82**, 403 (1951).

<sup>13</sup> J. Kanamori and K. Terakura, *J. Phys. Soc. Jpn.* **70**, 1433 (2001).

<sup>14</sup> P. Anderson and H. Hasegawa, *Phys. Rev.* **100**, 675 (1955).

<sup>15</sup> J. B. Philipp, P. Majewski, L. Alff, A. Erb, R. Gross, T. Graf, M. S. Brandt, J. Simon, T. Walther, W. Mader, et al., *Phys. Rev. B* **68**, 144431 (2003).



- <sup>16</sup> K.-I. Kobayashi, T. Kimura, Y. Tomioka, H. Sawada, K. Terakura, and Y. Tokura, *Phys. Rev. B* **59**, 11159 (1999).
- <sup>17</sup> H. Das, M. De Raychaudhury, and T. Saha-Dasgupta, *Applied Physics Letters* **92**, (2008).
- <sup>18</sup> H. L. Feng, M. Arai, Y. Matsushita, Y. Tsujimoto, Y. Guo, C. I. Sathish, X. Wang, Y.-H. Yuan, M. Tanaka, and K. Yamaura, *J. Am. Chem. Soc.* **136**, 3326 (2014).
- <sup>19</sup> H. L. Feng, Y. Tsujimoto, Y. Guo, Y. Sun, C. I. Sathish, and K. Yamaura, *High Pressure Res.* **33**, 221 (2013).
- <sup>20</sup> A. P. Hammersley, S. O. Svensson, M. Hanfland, A. N. Fitch, and D. Hausermann, *High Pressure Res.* **14**, 235 (1996).
- <sup>21</sup> A. C. Larson and R. B. Von Dreele, *General structure analysis system (GSAS)*, Los Alamos National Laboratory (2000).
- <sup>22</sup> B. H. Toby, *J. Appl. Crystallogr.* **34**, 210 (2001).
- <sup>23</sup> B. T. Thole, G. van der Laan, J. C. Fuggle, G. A. Sawatzky, R. C. Karnatak, and J.-M. Esteve, *Phys. Rev. B* **32**, 5107 (1985).
- <sup>24</sup> A. K. Paul, M. Jansen, B. Yan, C. Felser, M. Reehuis, and P. M. Abdala, *Inorganic Chemistry* **52**, 6713 (2013).
- <sup>25</sup> J. B. Goodenough, *Magnetism and the Chemical Bond* (Interscience, New York, 1963).
- <sup>26</sup> H. Wang, S. Zhu, X. Ou, and H. Wu, *Phys. Rev. B* **90**, 054406 (2014).
- <sup>27</sup> A. K. Paul, M. Reehuis, V. Ksenofontov, B. Yan, A. Hoser, D. M. Többens, P. M. Abdala, P. Adler, M. Jansen, and C. Felser, *Phys. Rev. Lett.* **111**, 167205 (2013).
- <sup>28</sup> R. Morrow, J. F. Freeland, and P. Woodward, *Inorg. Chem.* **53**, 7983 (2014).
- <sup>29</sup> G. van der Laan and B. T. Thole, *Phys. Rev. Lett.* **60**, 1977 (1988).
- <sup>30</sup> B. J. Kim, H. Ohsumi, T. Komesu, S. Sakai, T. Morita, H. Takagi, and T. Arima, *Science* **323**, 1329 (2008).
- <sup>31</sup> D. Haskel, G. Fabbris, M. Zhernenkov, P. P. Kong, C. Q. Jin, G. Cao, and M. van Veenendaal, *Phys. Rev. Lett.* **109**, 027204 (2012).
- <sup>32</sup> M. A. Laguna-Marco, D. Haskel, N. Souza-Neto, J. C. Lang, V. V. Krishnamurthy, S. Chikara, G. Cao, and M. van Veenendaal, *Phys. Rev. Lett.* **105**, 216407 (2010).
- <sup>33</sup> S. Kanungo, B. Yan, M. Jansen, and C. Felser, *Phys. Rev. B* **89**, 214414 (2014).
- <sup>34</sup> D. Haskel, G. Fabbris, N. M. Souza-Neto, M. van Veenendaal, G. Shen, A. E. Smith, and M. A. Subramanian, *Phys. Rev. B* **84**, 100403 (2011).
- <sup>35</sup> H. Zeng, J. Li, J. P. Liu, W. Z. L., and S. Sun, *Nature (London)* **420**, 395 (2002).
- <sup>36</sup> B. Balamurugan, B. Das, W. Y. Zhang, R. Skomski, and S. D. J., *J. Phys. Condens. Matter* **26**, 064204 (2014).