Spin transition in $SrFeO_2$ under pressure by x-ray spectroscopy

J.-P. Rueff*
Synchrotron SOLEIL, L'Orme des Merisiers, BP 48 St Aubin, 91192 Gif-sur-Yvette, France
and Laboratoire de Chimie Physique-Matière et Rayonnement, Sorbonne Université, CNRS, 75005 Paris, France

V. Balédent
Université Paris-Saclay, CNRS, Laboratoire de Physique des Solides, 91405 Orsay, France

K. Higashi and H. Kageyama
Graduate School of Engineering, Kyoto University, Nishikyo, Kyoto 615-8581, Japan

(Received 20 August 2020; revised 7 December 2020; accepted 10 December 2020; published 17 December 2020)

We have investigated the local Fe electronic changes in the square planar Fe(II) compound $SrFeO_2$ by x-ray emission (XES) and x-ray absorption spectroscopy (XAS) through the pressure-induced spin transition up to 60 GPa. The analysis of Fe $K\beta$ XES confirms the transition under pressure from a high spin to intermediate spin state at $P_c = 43$ GPa while XAS at the Fe K edge reveals the spectral signatures of the lattice compression under pressure. Simulations of the XAS spectra point to significant changes in Fe-p states across P_c and highlight the active role of the Sr-p states at the transition.

DOI: 10.1103/PhysRevB.102.235138

I. INTRODUCTION

Spin transitions are widely observed, important phenomena with potential use for ultrafast switches, data storage devices, and optical displays [1]. Spin transitions are generally found in octahedrally coordinated $3d$ transition metal (TM) compounds such as oxides [2,3], metal-organic complexes [4,5], molecular magnets [6,7], or superconductors [8,9]. In the presence of the crystal electric field in O_h symmetry, the $3d$ orbitals are split into t_{2g} and e_g orbitals, whose energy gap depends on the crystal field strength. The filling of these orbitals by the $3d$ electrons governs the TM spin state and is determined by the competition between the crystal field strength and the intra-atomic exchange interaction. External perturbations such as temperature, pressure, magnetic field, or light pulses can modify the relative strength of these interactions, eventually inducing a spin state transition. The stability of the spin state has profound consequences on the materials behavior because it affects its structural stability, magnetic ordering, and transport properties, which explains its broad interest for researchers in condensed matter physics, molecular chemistry, or mineralogy.

Recently, Kawakami *et al.* [10] have reported a spin state transition in the Fe(II) $SrFeO_2$ compound under pressure. The $SrFeO_2$ structure is similar to that of $SrCuO_2$, the parent compound for a high-Tc superconductor. As shown in Fig. 1, it consists of FeO_2 2D layers separated by Sr atoms [11] with Fe sitting in a square planar site with D_{4h} symmetry. Using Mössbauer spectroscopy, x-ray diffraction, and transport measurements, the authors showed that the Fe spin changes from a high spin (HS, $S = 2$) to intermediate spin state (IS, $S = 1$) state around $P_c = 33$ GPa; the spin transition is accompanied by a transition from an antiferromagnetic (AFM) insulating state to likely a ferromagnetic (FM) half-metallic state; at the same time, an anomalous drop of the lattice parameters is found at P_c. This makes $SrFeO_2$ the first example of a fourfold coordinated TM compound undergoing a spin transition. Several new compounds were recently found with Fe in a square planar environment such as $CaFeO_2$ [12] and the structurally related two-legged spin ladder compound $Sr_3Fe_2O_5$ [13]. Interestingly, $Sr_3Fe_2O_5$ which is akin to $SrFeO_2$ undergoes a pressure-induced spin state transition, an insulator to metal transition, and AFM to FM transition with a magnetic transition at 34 GPa [14].

In this article, we provide a detailed view at the local Fe level of the transition mechanism and change of the electronic structure under pressure in $SrFeO_2$ as observed with x-ray emission spectroscopy (XES) at the Fe $K\beta$ emission line and x-ray absorption spectroscopy (XAS) at the Fe K edge [15]. Due to the resonant excitation, x-ray spectroscopy in the hard x-ray range is an effective element and orbital selective probe of the electronic properties in transition metal compounds, while being compatible with high-pressure environment. The results confirm the spin state transition from HS to IS state at high pressure and demonstrate that significant changes in Fe-p states occur across P_c and highlight the active role of the Sr-p states at the transition, more generally illustrating how spin-state, structure, magnetism, and stereochemistry are tightly related in $3d$ compounds.

II. RESULTS AND DISCUSSION

A. Methodology

A $SrFeO_2$ sample was synthesized at Kyoto University as described in Ref. [10]. The sample was prepared as powder and loaded in a membrane-driven diamond anvil cell (DAC)

---

*jean-pascal.rueff@synchrotron-soleil.fr

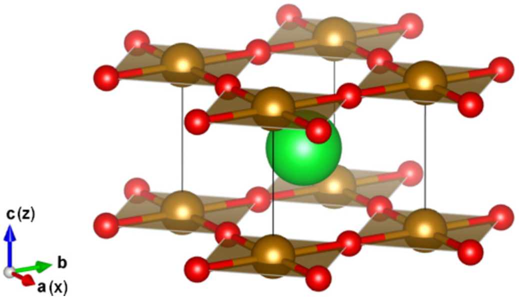

FIG. 1. $SrFeO_2$ structure in the $P4/mmm$ space group highlighting the square planar environment of Fe (yellow balls) surrounding by four O atoms (red balls). The Sr atom (green ball) lies in the interplane region. The local x and z axes are aligned with the a and c directions.

with 300 μm culet size. We used Re as gasket material with a 150 μm hole. The *in situ* pressure was estimated from the photo luminescence of ruby chips that were placed in the sample chamber. We performed two successive loadings of the pressure cell to cover the entire pressure range with two different pressure transmitting media: neon gas for the 6–60 GPa pressure range and a 1:4 methanol-ethanol mixture to complete the data set at 0 GPa and 50 GPa only. The two data sets were eventually combined because no visible difference could be detected between them, in either the XAS and XES spectral shape or behavior under pressure.

The experiment has been carried out using the GALAXIES x-ray spectroscopy beamline at Synchrotron SOLEIL [16]. The incident photons were monochromatized by a cryogenically cooled Si(111) double-crystal monochromator and focused onto the sample by a toroidal mirror in a 30 μm × 80 μm spot. The Fe Kβ spectra were measured on the beamline XES spectrometer in transmission geometry through the DAC at a scattering angle of 15°. The spectrometer was equipped with a Si(531) 1-m spherically bent crystal analyzer operated around the Bragg angle of 73.1° and a silicon drift diode (SDD) as detector. The XES spectra were acquired in a continuous scanning mode by sweeping the emission energy from 7020 to 7080 eV at a fixed incident photon energy of 9000 eV. This energy was found to yield the strongest emission intensity in the DAC. At some selected pressure, we also acquired high-resolution XAS spectra in the partial fluorescence yield (PFY) mode by setting the spectrometer emission energy at the maximum of the Kβ emission line while sweeping the incident photon energy through the Fe K edge. This method—also known as high-energy resolution fluorescence detected (HERFD) XAS—yields the absorption spectrum with improved intrinsic resolution with respect to conventional XAS as the core-hole lifetime broadening has been partly removed owing to the second-order scattering process [17].

B. Results

1. XES

The Fe Kβ XES spectra are shown in Fig. 2 as a function of pressure P. To emphasize the spectral changes in the figure, the spectra were normalized to the maximum intensity and aligned in energy. The spectra are composed of a large intensity peak and a weaker, low-energy satellite respectively referred to as K$\beta_{1,3}$ and Kβ'. As is now well established, the Kβ spectral shape and specially the satellite region are sensitive to the magnitude S of the local spin state of the 3d ion [18,19].

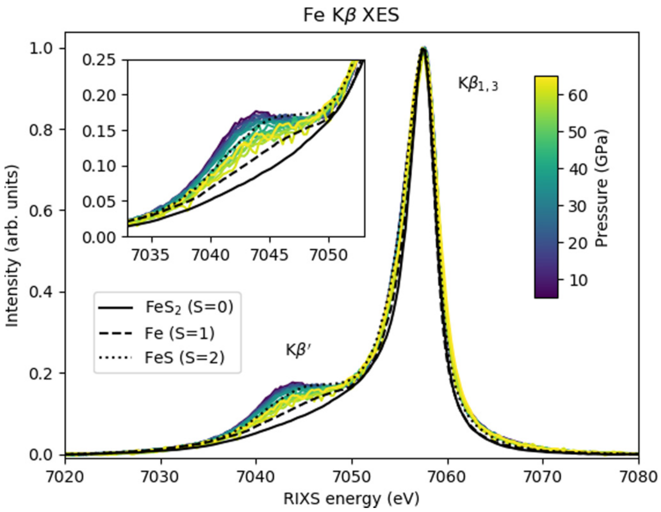

FIG. 2. Fe Kβ XES spectra as a function pressure; the inset shows a zoom of the satelite (Kβ') region. Reference spectra representative of $S = 0, 1, 2$ spin state and measured in FeS_2, Fe metal, and FeS are shown with black solid, dashed, and dotted lines from Ref. [20].

To first assess the nature of the high-pressure phase, we compare in Fig. 2 the emission spectra in $SrFeO_2$ with spectra measured in reference compounds borrowed from Ref. [20], the Fe(II) compounds FeS and FeS_2 with nominal spin states $S = 2$ and $S = 0$ and Fe metal with nominal $S = 1$. While the FeS_2 XES spectrum shows no distinct Kβ' feature, Fe metal exhibits a weak satellite, which seems very comparable to $SrFeO_2$ high-pressure spectra. This qualitatively confirms the intermediate spin state ($S = 1$) assignment of the high-pressure phase of $SrFeO_2$. The low-pressure spectra compare well with that of the $S = 2$ compound FeS although the satellite intensity is somewhat higher in $SrFeO_2$, likely due to the different Fe environment and degree of covalency.

The pressure dependence of the local spin moment S can be more quantitatively estimated by means of the integral absolute difference (IAD) method, which has been developed earlier [4,21]. Following Vankó *et al.* [4], the IAD values were computed by integrating the spectral difference $|\mathrm{XES}(P) - \mathrm{XES}(P = 0)|$ after normalizing the spectral intensity to the total area and aligning the spectra to the center of gravity. Figure 3 shows the IAD change [here expressed as $\max(\mathrm{IAD}) - \mathrm{IAD}(P)$] as a function of pressure. This pressure dependence is very comparable to the one obtained by other methods of evaluating S, including first moment analysis or satellite intensity, demonstrating its robustness. Using the reference spectra of Fig. 3, we have converted the IAD values onto an indicative spin scale represented by the right axis in Fig. 3. The IAD analysis confirms the pressure-induced transition from HS to IS states. We can obtain a rough estimate of the transition pressure P_c by fitting the IAD dependence

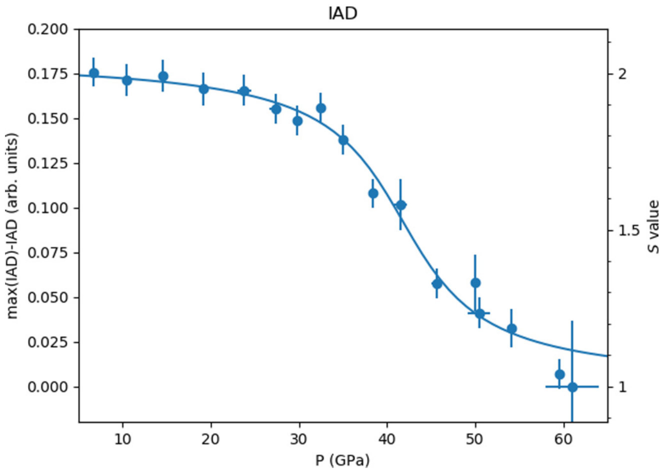

FIG. 3. Computed IAD as a function of pressure (circles) and arctan fit (solid line); the IAD is converted onto a indicative spin scale (right axis).

with an arctan function:

$$H/\pi\{\pi - \arctan[2/w(P - P_c) + \pi/2]\}$$

with H the step height and w the distribution width.

The fit shown in Fig. 3 with the solid line yields $P_c =$ 42 GPa, a value somewhat higher than the value of 33 GPa reported by Kawakami *et al.* [10]. The width w is estimated at 14 GPa (versus less than 5 GPa in Ref. [10]) which could be due to pressure gradient and phase mixing. These discrepancies are likely related to the use of difference pressure media. In this regard, the recently published work on the CoCrFeMnNi high-entropy alloys is particularly enlightening [22]. The results show that (1) the different pressure medium can considerably modify the fcc-hcp pressure transition in these materials and (2) nonhydrostatic media tend to lower the transition pressure by several 10 GPa. Thus, the use of a poorly hydrostatic medium in Ref. [10] may have in fact facilitated the structural change in SrFeO$_2$. This would explain why the pressure transition and likely the transition width are lower in Ref. [10] compared to the values reported in this work.

2. *XAS*

We now turn to the XAS results, which provide a local view of structural change across the pressure-induced spin transition. The Fe K edge x-ray absorption spectra were measured at two pressures across P_c in the low-pressure (LP) phase at 0 GPa and high-pressure (HP) phase at 45 GPa. Figure 4 (top panel) displays the two spectra on a relative energy scale $E - E_0$ with $E_0 = 7115.5$ eV. The spectra were corrected for self-absorption. For the sake of comparison, the XAS spectra were normalized in intensity to an edge jump of unity and aligned in energy so that the flex point falls at E_0. The spectra are composed of an intense pre-edge feature (0–5 eV) of mixed p-d character (as explained bellow) followed by an intense edge jump (5–20 eV) related to the p states due to dipolar transitions. The spectra undergo a drastic change with pressure marked by a shift of the pre-edge and post-edge features toward high energy along with a sizable broadening.

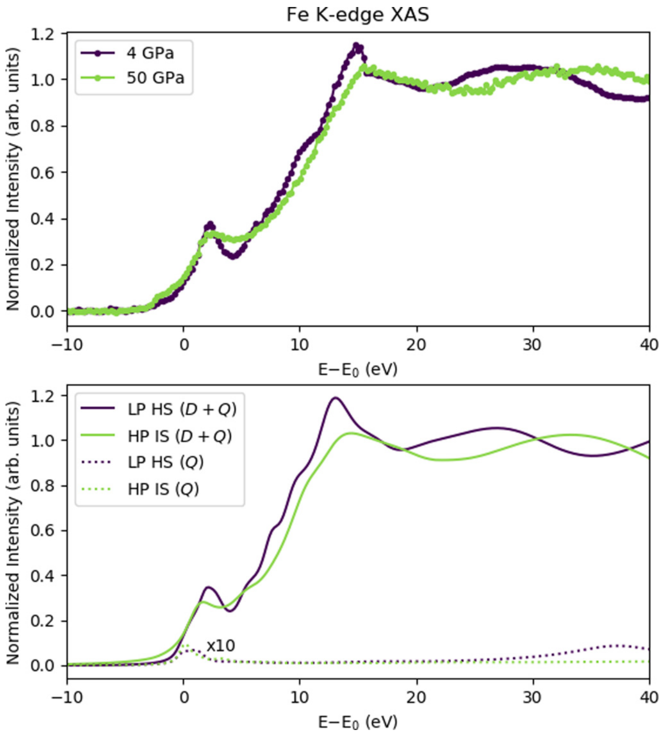

FIG. 4. (Top panel) Experimental Fe K edge XAS spectra in the low-pressure (LP) and high-pressure (HP) phases; (bottom panel) computed spectra using FDMNES in both LP and HP phases (solid lines). D and Q refer to the dipolar and quadrupolar contributions. For the sake of clarity, the latter (dashed lines) has been multiplied by 10.

To get deeper insight in the spectral changes, the experimental spectra are compared to the first-principle calculations (Fig. 4, bottom panel). The calculations were performed using the FDMNES code [23] on a 7 Å radius atomic cluster within the LDA approximation. The Hubbard U parameter was disregarded for the LP phase unlike more sophisticated calculations [24–26] as we are mostly interested in p states. This approximation is valid for the HP phase where a vanishing U is predicted at high pressure in Rahman *et al.* [24], in agreement with the observation of the gap closing around 50 GPa [10]. We used the structural parameters obtained at 0 GPa ($a = 3.991$ Å, $c = 3.474$ Å) and 45 GPa ($a = 3.744$ Å, $c = 3.002$ Å) obtained from Refs. [10,11] within the same space group $P4/mmm$ as illustrated in 1. We forced Fe to adopt a $3d^6$ electronic configuration with a high-spin (respectively intermediate spin) state in the LP (resp. HP) phase. The computation was carried out using self-consistent, non-muffin-tin potentials and including the spin-orbit effect and both dipolar (D) and quadrupolar (Q) contributions. To take into account the sharpening effect due to the PFY approach, the computed spectra were convolved by a Lorentzian with FWHM of 0.5 eV (thus below the 1s lifetime estimated at 1.3 eV).

The pressure-induced experimental changes are well reproduced by the calculations confirming that the observed spectral differences are driven by changes in the Fe electronic structure upon lattice compression. The quadrupolar

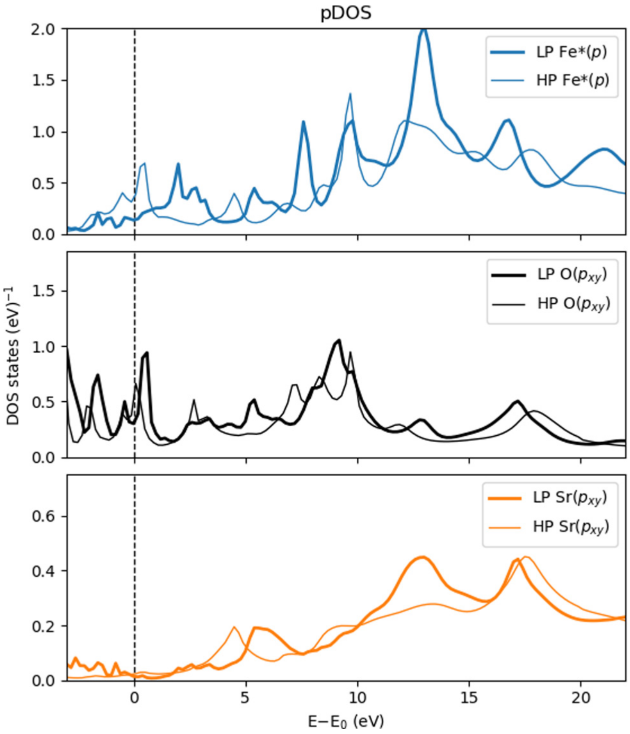

FIG. 5. (Top panel) Computed Fe*-*p* (top panel), O-*p* (middle panel), and Sr-*p* pDOS (lower panel) in the low-pressure (thick line) and high-pressure (thin line) phases.

contribution shown as a dashed line in Fig. 5 appears to be of minute intensity and located in a narrow energy window around E_0. This demonstrates that the overall spectrum including the pre-edge region is dominated by the dipolar component related to the Fe *p* states.

To evaluate the change of the electronic structure, we display in Fig. 5 the projected density of states (pDOS) of the absorbing Fe atom at low and high pressures. Our computed pDOS differs from previously reported works [10,24–26] as it takes into account the 1*s* core-hole left in the XAS final state (indicated by Fe*). Our purpose moreover is to focus on the changes observed in the empty *p* states, which are probed by XAS.

A comparison with Fig. 5 first confirms that the XAS spectra reflect the unoccupied Fe*-*p* pDOS. The Fe-*p* pDOS are further compared to the O-*p* or Sr-*p* pDOS shown in the lower panels in Fig. 5. While there is a clear overlap between the O-*p* states and Fe-*p* states, the former happen to be barely affected by the pressure-induced changes. Interestingly, the Sr-*p* pDOS show strong similarities with the Fe-*p* states with changes reminiscent of the Fe pDOS electronic changes at the transition, indicating that Sr plays an active role in the electronic structure.

III. CONCLUSIONS

We have studied the pressure-induced spin transition in $SrFeO_2$ with x-ray spectroscopy by combining Fe Kβ XES and XAS at the Fe K edge up to 60 GPa. The results provide a detailed picture of the Fe electronic changes across the magnetic transition from a local point of view. While Fe remains magnetic at 60 GPa, we can expect a second transition to another IS state or even a complete loss of magnetic moment at even higher pressure when the *d*-electrons become fully delocalized. This should motivate a continuation of this work towards the 100 GPa range. Finally, we notice that while the AFM state in the LP phase is well established, the FM nature of HP phase is still debated. Because XES is a local probe, it cannot discriminate between FM or other magnetic structures. But other probes of the long-range order such as x-ray magnetic dichroism at the Fe K edge could be attempted in the future.

To conclude, the persisting high spin state of Fe in $SrFeO_2$ up to high pressure reveals a remarkable chemical stability of the Fe state in the square planar environment. This is confirmed by the subsequent synthesis of $CaFeO_2$ reported in Ref. [12]. In spite of the cation substitution, $CaFeO_2$ has a square planar environment and high spin configuration too. The stability of the Fe state in these materials opens up possibilities for robust magnetic applications.

ACKNOWLEDGMENTS

We wish to acknowledge the SOLEIL Synchrotron for provision of beamtime (proposal 20181616). This work was supported by JSPS Core-to-Core Program (Grant No. JPJSCCA20200004).

[1] J.-F. Létard, P. Guionneau, and L. Goux-Capes, Towards spin crossover applications, *Spin Crossover in Transition Metal Compounds III*, Topics in Current Chemistry Vol. 235 (Springer, Berlin, Heidelberg, 2004), pp. 221–249.

[2] A. Mattila, J.-P. Rueff, J. Badro, G. Vankó, and A. Shukla, Metal-Ligand Interplay in Strongly Correlated Oxides: A Parametrized Phase Diagram for Pressure-Induced Spin Transitions, Phys. Rev. Lett. **98**, 196404 (2007).

[3] M. P. Pasternak, R. D. Taylor, R. Jeanloz, X. Li, J. H. Nguyen, and C. A. McCammon, High Pressure Collapse of Magnetism in $Fe_{0.94}$ O: Mössbauer Spectroscopy Beyond 100 GPa, Phys. Rev. Lett. **79**, 5046 (1997).

[4] G. Vankó, T. Neisius, G. Molnar, F. Renz, S. Karpati, A. Shukla, and F. M. F. de Groot, Probing the 3d spin momentum with x-ray emission spectroscopy: The case of molecular-spin transitions, J. Phys. Chem. B **110**, 11647 (2006).

[5] C. J. Pollock and S. DeBeer, Insights into the geometric and electronic structure of transition metal centers from valence-to-core x-ray emission spectroscopy, Acc. Chem. Res. **48**, 2967 (2015).

[6] J.-D. Cafun, J. Lejeune, F. Baudelet, P. Dumas, J.-P. Itié, and A. Bleuzen, Room-temperature photoinduced electron transfer in a Prussian blue analogue under hydrostatic pressure, Angew. Chem., Int. Ed. **51**, 9146 (2012).

[7] D. Papanikolaou, S. Margadonna, W. Kosaka, S.-i. Ohkoshi, M. Brunelli, and K. Prassides, X-ray illumination induced Fe(II) spin crossover in the Prussian blue analogue cesium iron hexacyanochromate, J. Am. Chem. Soc. **128**, 8358 (2006).

[8] B. W. Lebert, V. Balédent, P. Toulemonde, J. M. Ablett, and J.-P. Rueff, Emergent high-spin state above 7 GPa in superconducting FeSe, Phys. Rev. B **97**, 180503(R) (2018).

[9] Y. Wang, J. Ying, Z. Zhou, J. Sun, T. Wen, Y. Zhou, N. Li, Q. Zhang, F. Han, Y. Xiao *et al.*, Emergent superconductivity in an iron-based honeycomb lattice initiated by pressure-driven spin-crossover, Nat. Commun. **9**, 1914 (2018).

[10] T. Kawakami, Y. Tsujimoto, H. Kageyama, X.-Q. Chen, C. L. Fu, C. Tassel, A. Kitada, S. Suto, K. Hirama, Y. Sekiya *et al.*, Spin transition in a four-coordinate iron oxide, Nat. Chem. **1**, 371 EP (2009).

[11] Y. Tsujimoto, C. Tassel, N. Hayashi, T. Watanabe, H. Kageyama, K. Yoshimura, M. Takano, M. Ceretti, C. Ritter, and W. Paulus, Infinite-layer iron oxide with a square-planar coordination, Nature (London) **450**, 1062 (2007).

[12] C. Tassel, J. Pruneda, N. Hayashi, T. Watanabe, A. Kitada, Y. Tsujimoto, H. Kageyama, K. Yoshimura, M. Takano, M. Nishi *et al.*, CaFeO$_2$: A new type of layered structure with iron in a distorted square planar coordination, J. Am. Chem. Soc. **131**, 221 (2009).

[13] H. Kageyama, T. Watanabe, Y. Tsujimoto, A. Kitada, Y. Sumida, K. Kanamori, K. Yoshimura, N. Hayashi, S. Muranaka *et al.*, Spin-ladder iron oxide: Sr$_3$Fe$_2$O$_5$, Angew. Chem., Int. Ed. **47**, 5740 (2008).

[14] T. Yamamoto, C. Tassel, Y. Kobayashi, T. Kawakami, T. Okada, T. Yagi, H. Yoshida, T. Kamatani, Y. Watanabe, T. Kikegawa *et al.*, Pressure-induced structural, magnetic, and transport transitions in the two-legged ladder Sr$_3$Fe$_2$O$_5$, J. Am. Chem. Soc. **133**, 6036 (2011).

[15] J.-P. Rueff, Spin-transitions in metal oxides, in *Spin-Crossover Materials*, edited by M. A. Halcrow (John Wiley and Sons, New York, 2013), pp. 527–541.

[16] J.-P. Rueff, J. M. Ablett, D. Céolin, D. Prieur, T. Moreno, V. Balédent, B. Lassalle, J. E. Rault, M. Simon, and A. Shukla, The GALAXIES beamline at SOLEIL synchrotron: Inelastic x-ray scattering and photoelectron spectroscopy in the hard x-ray range, J. Synchrotron Radiat. **22**, 175 (2015).

[17] K. Hämäläinen, D. P. Siddons, J. B. Hastings, and L. E. Berman, Elimination of the Inner-Shell Lifetime Broadening in X-Ray Absorption Spectroscopy, Phys. Rev. Lett. **67**, 2850 (1991).

[18] J.-P. Rueff, C.-C. Kao, V. V. Struzhkin, J. Badro, J. Shu, R. J. Hemley, and H. K. Mao, Pressure Induced High-Spin to Low-Spin Transition in FeS Evidenced by X-Ray Emission Spectroscopy, Phys. Rev. Lett. **82**, 3284 (1999).

[19] F. M. F. de Groot, High resolution x-ray emission and x-ray absorption spectroscopy, Chem. Rev. **101**, 1779 (2001).

[20] A. Carlantuono, X-ray emission spectroscopy to retrieve the local spin moment in 3d transition metal compounds, Master's thesis, Politecnioc Di Milano, 2017, http://hdl.handle.net/10589/133061.

[21] J.-P. Rueff, M. Krisch, Y. Q. Cai, A. Kaprolat, M. Hanfland, M. Lorenzen, C. Masciovecchio, R. Verbeni, and F. Sette, Magnetism and structural α-ϵ phase transition in Fe monitored by x-ray emission spectroscopy, Phys. Rev. B **60**, 14510 (1999).

[22] F. Zhang, H. Lou, S. Chen, X. Chen, Z. Zeng, J. Yan, W. Zhao, Y. Wu, Z. Lu, and Q. Zeng, Effects of non-hydrostaticity and grain size on the pressure-induced phase transition of the CoCrFeMnNi high-entropy alloy, J. Appl. Phys. **124**, 115901 (2018).

[23] O. Bunău and Y. Joly, Self-consistent aspects of x-ray absorption calculations, J. Phys.: Condens. Matter **21**, 345501 (2009).

[24] M. Rahman, Y.-z. Nie, and G.-h. Guo, Electronic structures and magnetism of SrFeO$_2$ under pressure: A first-principles study, Inorg. Chem. **52**, 12529 (2013).

[25] H. J. Xiang, S.-H. Wei, and M.-H. Whangbo, Origin of the Structural and Magnetic Anomalies of the Layered Compound SrFeO$_2$: A Density Functional Investigation, Phys. Rev. Lett. **100**, 167207 (2008).

[26] J. M. Pruneda, J. Íñiguez, E. Canadell, H. Kageyama, and M. Takano, Structural and electronic properties of SrFeO$_2$ from first principles, Phys. Rev. B **78**, 115101 (2008).