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Spintronic devices based on pure spin currents have drawn a lot of attention during the last few years for low energy device design. One approach to generate pure spin currents is to combine a metallic or insulating ferromagnetic layer with a non-magnetic metallic layer with a large spin-orbit coupling. A recent controversy has arisen in the possible role of magnetic proximity effects at ferromagnetic/non-magnetic interfaces, which can hamper the understanding of pure spin current generation mechanisms. While magnetic proximity effects have been frequently observed at ferromagnetic metal/non-magnetic interfaces, there are only a few studies on ferromagnetic insulator/non-magnetic interfaces. Regarding the use of ferromagnetic insulators, the focus has been mainly on yttrium iron garnet (YIG). However, investigation of induced magnetic moments at YIG/Pt interfaces has engendered contradictory results. Here, we propose to study insulating ferrites for which electronic and magnetic properties can be modulated. Magnetic proximity effects have been investigated at $MnFe_2O_4$/Pt, $CoFe_2O_4$/Pt, and $NiFe_2O_4$/Pt interfaces by X-ray circular magnetic dichroism (XMCD) measurements at the Pt L_3 edge. Although hybridization with Pt seems to be different among the ferrites, we do not detect any XMCD signal as the signature of an induced magnetism in Pt. We have then studied the Fe_3O_4 ferrite below and above the Verwey transition temperature. No XMCD signal has been measured in the insulating or conducting phase of Fe_3O_4. This suggests that the absence of magnetic proximity effects at ferrite/Pt interfaces is not linked to the insulating character or not of the ferrites. *Published by AIP Publishing.* https://doi.org/10.1063/1.4987145

Generating a pure spin current without charge flow is a hot topic in spintronics for potential low energy consumption devices. Pure spin currents can be generated by the spin Seebeck effect (SSE)[1,2] or spin Hall effect (SHE) or detected by inverse spin Hall effects (ISHEs).[3] Conventional systems to produce pure spin currents are ferromagnetic/non-ferromagnetic (FM/N-FM) bilayers where the ferromagnetic (FM) thin layers are metallic or insulating and the non-ferromagnetic (N-FM) layer is a metal with a large spin-orbit coupling. In almost all experiments, a thin Pt layer is used. While Pt offers the advantage of a large spin-orbit coupling, magnetic proximity effects at the FM/Pt interface might occur and thus hamper the detection of the pure spin current by electrical measurements.[4] The main reason is that in such a case, in addition to ISHE and SSE effects, the induced magnetic moments in Pt thin films shall also lead to a transverse voltage contribution due to anomalous Hall and/or Nernst effects.

While magnetic proximity effects at ferromagnetic metal/non-ferromagnetic metal (FMM/N-FM) interfaces have been widely investigated,[5–8] experiments on the ferromagnetic insulator (FMI)/N-FM interface are sparse. Clear X-ray circular magnetic dichroism (XMCD) signals have been observed in FMM/N-FM (where FMM is typically Co, Fe, or Ni and NMN is Pd, Pt, Au, etc.), but there are few and disparate results on FMI/Pt interfaces. Recent experiments on $Y_3Fe_5O_{12}$/Pt bilayers have been performed but have led to contradictory results[9,10] and are still debated.[11] In yttrium iron garnet (YIG)/Pd systems, in which the signal from the gadolinium gallium garnet substrate less affects the X-ray absorption spectra at the L edges of the heavy elements, no XMCD signal has been detected at the Pd energy edge.[12] Here, in order to provide a clearer insight, we report on magnetic proximity effect studies at ferrite/Pt interfaces. Ferrites such as XFe_2O_4 (X = Mn, Co, and Ni) are insulating ferrimagnets whose magnetic and electronic properties can be varied in a controllable way. It is anticipated that they shall be complementary to YIG as promising systems to generate pure spin currents in spintronic devices[13–17] and even increase the accessible frequency range toward higher values. Their interesting advantage is that by changing the divalent cation (Mn, Co, and Ni), the magnetic moment, energy gap, and exchange energy can be tailored. Our objective is thus to investigate the magnetic proximity effects at ferrite/Pt interfaces by X-ray absorption near edge spectroscopy (XANES) and X-ray circular magnetic dichroism (XMCD) measurements at the Pt L_3 edge. XMCD is the most direct experimental technique to probe induced magnetic moments since quantitative information such as spin and orbital moments can be obtained using magneto-optical sum rules. The ferrites studied are $MnFe_2O_4$, $CoFe_2O_4$, and $NiFe_2O_4$.

$MnFe_2O_4$(111), $CoFe_2O_4$(111), and $NiFe_2O_4$(111) thin films (~15–40 nm) have been grown by molecular beam epitaxy on sapphire [α-Al_2O_3(00001)] substrates. Details on growth conditions and sample characterization can be found elsewhere.[18] In the present study, we have performed conventional characterization to study the structural and magnetic properties by reflection high-energy electron diffraction

during the growth, *in-situ* X-ray photoemission spectroscopy, and magnetometry. In particular, it allows us to determine the X/Fe ratio as well as the valence of the 3*d* elements. Advanced characterization has been performed previously such as X-ray absorption spectroscopy and XMCD at 3*d* elements (Mn, Co, Ni, and Fe) L_{23} edges in order to properly identify the spinel structure of different thin films. Cobalt and nickel ferrites have mainly an inverse spinel structure,[18] whereas manganese ferrite has a normal spinel structure.[19] As induced magnetism is expected to occur at the interface and spread over a few atomic layers only,[5] we have investigated the potential induced magnetism in 2 nm thick Pt films grown *ex-situ* by sputtering deposition. The surface roughness of Pt thin films has been measured by AFM, showing a root mean square roughness of ∼0.1 nm. A Co(10 nm)/2 nm Pt reference sample was also investigated for comparison. Co/Pt is a well-known system for which a clear XMCD signal at Pt L_{23} edges has already been observed.[8]

XANES and XMCD experiments have been performed at the ESRF ID12 beamline. Since the L_3 edge XMCD signal is expected to be larger than at the L_2 edge, we focus in this study on Pt L_3 edges. Measurements have been performed at both 10 K and 290 K. Grazing incidence magnetic fields up to 3 T have been applied in order to saturate the ferrite's magnetization (see supplementary material). Total fluorescence yield mode detection was used. To measure XMCD, the photon helicity (circular left and right) and the magnetic field were systematically flipped.[20]

Normalized XANES L_3 Pt edge spectra recorded at 290 K for the three different ferrites and the Co/Pt reference sample are shown in Fig. 1. Although Pt XANES spectra of ferrite samples present the same fine structure as those of the Co/Pt reference sample, indicating similar crystallinity, we observe slight differences in white line intensity, suggesting different electronic structures. In particular, $MnFe_2O_4$/Pt has a higher white line (WL) intensity. In comparison, the WL intensity of a metallic Pt foil is less than 1.3.[21] A WL intensity larger than 1.3 is usually associated with oxidation of Pt; for example, a $PtO_{1.6}$ compound has a WL intensity larger than 2.[22] Moreover, it has been observed, for example, in Pt

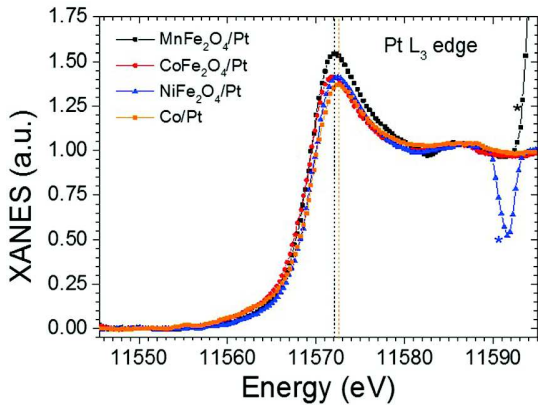

FIG. 1. Normalized Pt L_3 edge XANES spectra recorded at 290 K for $MnFe_2O_4$/Pt (black), $CoFe_2O_4$/Pt (red), and $NiFe_2O_4$/Pt (blue) samples. Spectra of the Co/Pt reference sample (orange) are also shown for comparison. Asterisks point out diffraction peaks. Black and orange dashed lines indicate the maximum of XANES intensity for the $MnFe_2O_4$/Pt and Co/Pt samples highlighting the energy shift of the white line (WL).

based catalysis studies that Pt oxidation usually induces a shift of the white line to higher energy (see, for instance, Refs. 23 and 24). Note, however, that in the case of $MnFe_2O_4$/Pt, we rather observe a shift to lower energy (∼0.6 eV). It has been shown in granular Co/Pt multilayers that Pt XANES spectra can be modified by hybridization at the Co/Pt interface.[25] An increase in the WL intensity as the one observed for $MnFe_2O_4$/Pt means that the Pt 5*d* band is less filled as a possible consequence of a charge transfer from Pt to $MnFe_2O_4$. This hypothesis would also explain the shift towards lower energies of the WL due to a modification of the Pt Fermi level. For $CoFe_2O_4$, we observe a similar WL energy shift but without an increase in its intensity. The stronger difference observed for $MnFe_2O_4$ could be explained by the fact that it has a smaller energy gap (0.08 eV).[26] On the other hand, $NiFe_2O_4$ which has the largest theoretical energy gap (0.98 eV) has a spectrum closer to the Co/Pt reference sample. This could reflect the fact that the hybridization mechanism between ferrite/Pt and Co/Pt is certainly different. Localized orbitals for ferrites and localized and delocalized bands for Co could be involved in the hybridization. Thus, these XANES measurements reveal different behavior between ferrites, suggesting a different hybridization at ferrite/Pt interfaces.

As for the proximity effect, we now discuss the XMCD measurements. In Fig. 2(a), we present the XMCD signals at the Pt L_3 edge obtained at 290 K for the three different ferrites and the Co/Pt reference sample. Whereas we observe a clear XMCD signal for Co/Pt, we do not observe any indication of induced magnetic moments for the ferrites/Pt samples. In Fig. 2(b), we plot XMCD spectra at 10 K for the three ferrites and together with the Co/Pt reference sample. Similar conclusion without any XMCD signal is obtained at room temperature, which allows to us rule out the presence of an interfacial compound with a magnetic transition at low temperature. The absence of magnetic proximity effects in our ferrite/Pt samples is in agreement with XMCD or X-ray resonant magnetic reflectivity measurements performed on the $CoFe_2O_4$/Pt (Ref. 27) or $NiFe_2O_4$/Pt (Ref. 28) bilayer. However, Amamou *et al.* have recently observed anisotropic magnetoresistance effects in the $CoFe_2O_4$/Pt bilayer, suggesting the magnetic proximity effect.[29] In Fig. 2(c), we plot XANES and XMCD spectra at Pt $L_{2,3}$ edges for the Co/Pt reference sample. By applying magneto-optical sum rules[30,31] using the method developed for Pt layers,[32] we deduce spin and orbital moments of 0.197 μ_B/atom and 0.042 μ_B/atom. With the XMCD noise level in ferrite/Pt samples being about 50 times lower than the XMCD signal in the Co/Pt sample, we can estimate that if any residual induced magnetic moment takes place, it should be at most about 5×10^{-3} μ_B/Pt which is close to the magnetic moment of paramagnetic Pt foils at 2 T [$\sim 2.2 \times 10^{-3}$ μ_B/Pt (Ref. 21)].

These experiments show that magnetic proximity effects between the investigated ferrites and Pt do not occur (or are too weak to be detected). We have then investigated Fe_3O_4/Pt bilayers. This system offers the advantage that Fe_3O_4 (magnetite) thin films are well-known ferromagnetic oxides which have the particularity to exhibit the Verwey transition.[33] Hence, possible induced magnetic moments can be investigated below and above the metal-insulator transition. We have performed XANES and XMCD measurements

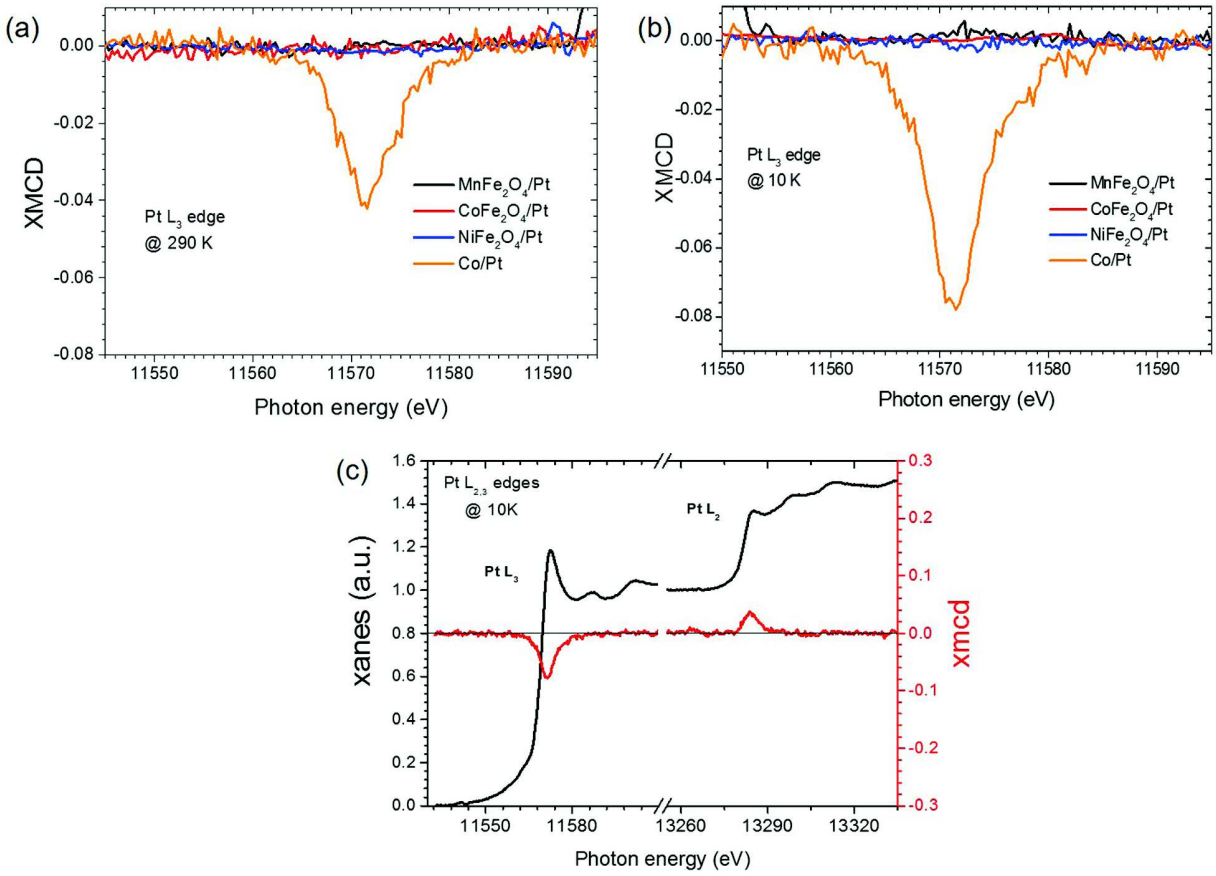

FIG. 2. Pt L_3 edge XMCD spectra recorded at 290 K (a) and 10 K (b) for $MnFe_2O_4$/Pt (black), $CoFe_2O_4$/Pt (red), and $NiFe_2O_4$/Pt (blue) samples. XMCD spectra of the Co/Pt reference sample (orange) are also shown for comparison. (c) XANES and XMCD spectra at Pt $L_{2,3}$ edges recorded at 10 K for the Co/Pt reference sample.

at the Pt L_3 edge on a Fe_3O_4(38 nm)/Pt(2 nm) sample. Fe_3O_4(111) thin films have been grown by molecular beam epitaxy,[18] and the Pt layer was grown in the same conditions as those for the ferrite/Pt samples. In Fig. 3, we display XANES and XMCD spectra recorded well below (10 K) and well above (290 K) the Verwey transition which occurs at ~120 K in our thin films.[34] The WL intensity is about 1.35 and is similar to the Co/Pt reference sample shown in Fig. 1. Hence, the WL intensity does not indicate Pt oxidation. Counterintuitively, the XANES spectrum of Fe_3O_4 is closer to the $NiFe_2O_4$ one than the $MnFe_2O_4$ and $CoFe_2O_4$ ones.

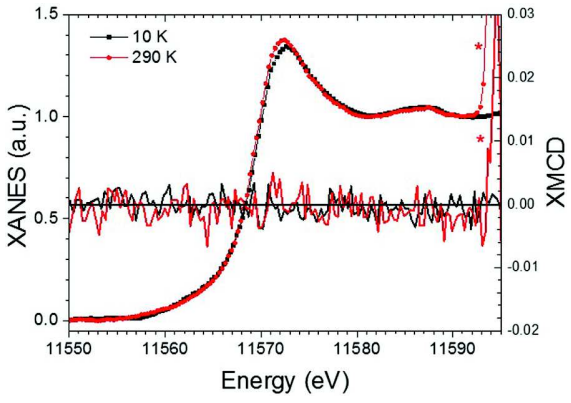

FIG. 3. Normalized Pt L_3 edge XANES and XMCD spectra of the Fe_3O_4/Pt sample recorded at 10 K (black) and 290 K (red). Asterisks point out diffraction peaks.

With $NiFe_2O_4$ having the largest energy gap, this would indicate that different hybridization mechanisms at ferrite/Pt and magnetite/Pt interfaces take place. The main result is that no XMCD signal is observed at the Pt L_3 edge whether below or above the Verwey transition ruling out magnetic proximity effects in both the insulating and conducting phases of Fe_3O_4.

These results raise the question of possible induced magnetic moments between a magnetic oxide and a nonmagnetic metal. While there are a large number of reports on induced moments on 4*d* and 5*d* elements when in contact with 3*d* ferromagnetic metals,[5–8] up to now, most of the ferromagnetic oxide/Pt interfaces in high quality samples as the ones studied here do not show magnetic proximity effects. We give a clear confirmation of this for Pt interfaced with $MnFe_2O_4$, $CoFe_2O_4$, $NiFe_2O_4$, and Fe_3O_4. This remains valid at low temperature and independent of the insulating or conducting state of the ferrite.

In conclusion, we have searched for induced magnetic moments at several ferrite/Pt interfaces by XANES and XMCD measurements at the Pt L_3 edge. No XMCD signals as fingerprints of induced magnetic moments in Pt have been detected for the three different insulating ferrites ($MnFe_2O_4$, $CoFe_2O_4$, and $NiFe_2O_4$). However, slight changes in XANES spectra and in particular a shift towards lower energies of the WL suggest different hybridization at the ferrite/Pt interfaces that remain to be fully understood. In particular, a clear charge transfer occurs between Pt and $MnFe_2O_4$ which has

the lowest energy gap. XMCD measurements were also performed on Fe_3O_4/Pt below and above the Verwey transition. On either sides of the metal-insulator transition, no induced moment was observed. This suggests that the absence of magnetic proximity effects at ferrite/Pt interfaces is not linked to the insulating character of the ferrites. We hope that our systematic investigation will trigger theoretical studies allowing to settle if the absence of induced magnetic moments at ferrite/Pt interfaces is a general rule and identify the possible role of defects and disorder in establishing magnetic moments or not since anisotropic magnetoresistance effects have been recently observed in the $CoFe_2O_4$/Pt bilayer,[29] suggesting the magnetic proximity effect.

See supplementary material for magnetic characterization of ferrite thin films.

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