Static magnetic proximity effect in Pt/\(\text{NiFe}_2\text{O}_4\) and Pt/Fe bilayers investigated by x-ray resonant magnetic reflectivity

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The spin polarization of Pt in Pt/\(\text{NiFe}_2\text{O}_4\) and Pt/Fe bilayers is studied by interface-sensitive x-ray resonant magnetic reflectivity to investigate static magnetic proximity effects and, therefore, proximity induced anomalous Nernst effect contributions in longitudinal spin Seebeck effect measurements. The asymmetry ratio of the reflectivity was measured at the Pt \(L_2\) absorption edge using circularly polarized x-rays for opposite directions of the magnetization at room temperature. The results of 2% asymmetry ratio for Pt/Fe bilayers are independent of the Pt thickness between 1.8 nm and 20 nm. By comparison with ab initio calculations, the maximum magnetic moment per spin polarized Pt atom at the interface is determined to be \((0.6\pm0.1)\mu_B\) for Pt/Fe. For Pt/\(\text{NiFe}_2\text{O}_4\) the asymmetry ratio drops below the sensitivity limit of 0.02\(\mu_B\) per Pt atom. Therefore, we conclude, that the longitudinal spin Seebeck effect observed in Pt/\(\text{NiFe}_2\text{O}_4\) is not influenced by a proximity induced anomalous Nernst effect.

In spintronics\(^3\) and spin caloritronics\(^2\) pure spin currents can be generated in ferromagnetic insulators (FMI) by spin pumping\(^3\) spin Hall effect\(^3\) and spin Seebeck effect\(^3\). Since these spin currents play an important role in spintronic applications, an understanding of the generation, manipulation and detection of spin currents is an important topic of research. A common spin current detection technique uses a non-magnetic metal (NM) thin film grown on a ferromagnet (FM). The inverse spin Hall effect\(^3\) converts the spin current into a transverse voltage in the NM. Pt is commonly used as NM due to its large spin Hall angle\(^3\), but has generated some controversy in the interpretation because of its closeness to the Stoner criterion, which can induce, e.g., Hall- or Nernst effects due to the proximity to the FM\(^3\).

For a quantitative evaluation of the spin Seebeck effect (thermal generation of spin currents) one has to exclude or separate various parasitic effects. It is reported\(^3\) that in transverse spin Seebeck experiments a spin current is generated perpendicular to the applied temperature gradient which is typically aligned in-plane. For ferromagnetic metals (FMM) with magnetic anisotropy, the planar Nernst effect\(^3\) can contribute\(^3\) due to the anisotropic magnetothermopower. Furthermore, out-of-plane temperature gradients due to heat flow into the surrounding area\(^11\) or through the electrical contact\(^12\) can induce an anomalous Nernst effect (ANE)\(^13\)\(^15\) or even an unintended longitudinal spin Seebeck effect as recently reported\(^16\).

The longitudinal spin Seebeck effect (LSSE)\(^17\) describes a spin current which is generated parallel to the temperature gradient, which is typically aligned out-of-plane to drive the parallel spin current directly into the NM material. For FMM or semiconducting ferromagnets an ANE can also contribute to the measured voltage\(^18\). Furthermore, for NM materials close to the Stoner criterion a static magnetic proximity effect in the NM at the NM/FMI interface can lead to a proximity induced ANE\(^3\). If an in-plane temperature gradient is applied, a proximity induced planar Nernst effect should also be considered\(^10\).

One technique to separate the LSSE from the proximity induced ANE was proposed by Kikkawa et al\(^19\)\(^20\). Here, in-plane and out-of-plane magnetic fields in combination with different directions of the temperature gradient are used. This technique can easily be applied to NM/FMI systems, since no additional ANE from the FMI is expected, and only LSSE and proximity induced ANE can occur. For FMM (or semiconducting ferromagnets) attached to a NM this technique has to be extended in order to separate the proximity induced ANE of the NM from the LSSE and ANE of the FMM.

X-ray magnetic circular dichroism (XMCD) has been used (fluorescence detection) to investigate magnetic proximity in Pt attached to the magnetic insulator \(\text{Y}_3\text{Fe}_5\text{O}_{12}\). Geprägs et al. did not observe any evidence for a spin polarization in 3 nm Pt\(^21\) and in 1.6 nm Pt\(^22\), while Lu et al.\(^23\) detected an average magnetic moment of 0.054\(\mu_B\) at 300 K and 0.076\(\mu_B\) at 20 K in 1.5 nm Pt.

While XMCD only gives the mean polarization of the Pt film, x-ray resonant magnetic reflectivity (XRMR)\(^24\) is directly sensitive to the spin polarization at the interface due to the interference of reflected light from the Pt surface and the Pt/FM interface. The magnetic dichroism for circularly polarized light reflected by the spin polarized interface results in a slightly different x-ray re-
fectivity (XRR) for varying magnetization directions due to a change of the optical constants of the spin polarized material. In particular, in magnetic materials the refractive index \( n = 1 - \delta + i\beta \) with dispersion and absorption coefficients \( \delta \) and \( \beta \) changes with \( \pm \Delta \delta \) and \( \pm \Delta \beta \) for different magnetization directions (\( \pm \)). The dispersion and absorption are connected via the Kramers-Kronig relation.

In recent LSSE/ANE\(^{18,26}\) and spin Hall magnetoresistance studies\(^{18} \) on Pt/\( \text{NiFe}_2\text{O}_4 \) (NFO) bilayers, we separated LSSE and ANE by measurements with and without Pt. The electrically semiconducting NFO allows a comparison of the temperature-dependent conductivity with spin Seebeck coefficients. In this report, we focus on XRMR measurements of Pt/NFO to identify or exclude additional proximity induced ANE effects which have not been taken into account before.

We prepared NFO films of up to 1\( \mu \)m thickness on \( 10 \times 5 \) mm\(^2 \) \( \text{MgAl}_2\text{O}_4(001) \) (MAO) substrates by direct liquid injection chemical vapor deposition (DLI-CVD)\(^{18,20}\). Furthermore, we deposited Fe on MAO as reference sample with Pt on top. Both Pt and Fe were deposited by dc magnetron sputtering in a 1.5 \( \times 10^{-3} \) mbar Ar atmosphere.

XRMR was measured at room temperature at the resonant scattering and diffraction beamline P09 of the third-generation synchrotron PETRA III at DESY (Hamburg, Germany)\(^{23}\). The sample and magnet system were mounted on the 6-circle diffractometer in the P09 first experimental hutch (P09-EH1) and the reflectivity curves were taken in a \( \theta - 2\theta \) scattering geometry. The external magnetic field was applied in the scattering plane and parallel to the sample surface using a four coils electromagnet constructed at Bielefeld University. Circularly polarized x-rays were generated by two diamond plates at the eight-wave plate condition mounted in series. The degree of polarization was \( (99 \pm 1)\% \) for right and left circular polarization as determined from a polarization analysis with a Au(111) analyzer crystal.

For detecting the Pt polarization, we used left circularly polarized x-rays with the photon energy of 11567.5 eV (Pt L\(_3\) absorption edge) and changed the magnetic field direction after having confirmed that right circularly polarized x-rays changes the sign of the XRMR asymmetry ratio. An external magnetic field of \( \pm 85 \text{ mT} \) was applied for each angle of incidence \( \theta \) while the reflected intensity \( I_{\pm} \) was detected. The dependence of the non-magnetic reflectivity \( I = I_{+} + I_{-} \) on the scattering vector \( q = \frac{4\pi}{\lambda} \sin \theta \) (\( \lambda \): wavelength) was fitted using the recursive Parratt algorithm\(^{23}\) and a Néov-Croce roughness mode\(^{23}\) using the analysis tool \( \text{iXRR} \). The magnetic asymmetry ratio \( \Delta I = I_{+} - I_{-} \) was simulated with \( \text{ReMagX} \)\(^{31}\) using the Zak matrix formalism\(^{33}\) and additional magnetooptic profiles for the change of optical constants with the position vertical to the film stack.

To obtain the magnetic moment of the Pt, we calculated the absorption coefficients at the L\(_3\) edge of Pt for various fixed spin moments with \( \text{FDMNES} \)\(^{33}\) in the full-multiple-scattering mode. The computed absorption spectra were fitted to experimental values far below and above the edge with the CHOOCH program\(^{34}\), which also produced the dispersion data by a Kramers-Kronig transformation. We checked that \( \Delta \delta \) and \( \Delta \beta \) are directly proportional to the magnetic moment of the Pt.

In Fig. (1a) the averaged XRR intensity \( I(q) \) of Pt/Fe/MAO shows Kiessig fringes, with an oscillation length \( \Delta q_{\text{Pt}} \) due to the interference of reflected light from the Pt/Fe and the Fe/MAO interfaces. The XRR analysis reveals an Fe layer thickness of 9.1 nm with a roughness of 0.4 nm. The Pt film introduces additional Kiessig fringes with the oscillation length \( \Delta q_{\text{Pt}} \), which give a Pt thickness of 3.4 nm and a roughness of 0.2 nm for Pt and MAO substrate. During the experiment, the sample was saturated magnetically as deduced from magnetooptic Kerr effect (MOKE) measurements shown in Fig. (1b).

XRMR from Pt/NFO/MAO (Fig. (1c)) does not exhibit oscillations with \( \Delta q_{\text{NFO}} \) due to the large thickness of the NFO layer. Therefore, only Kiessig fringes from the Pt layer can be observed. Since the NFO exhibits a very low MOKE, vibrating sample magnetometry (VSM) and LSSE measurements were performed (cf. Fig. (1d)). The results reveal a magnetic moment in magnetic field direction of 70\% saturation for the magnetic field of \( \pm 85 \text{ mT} \).
The absorption of the Pt(3.4 nm)/Fe(9.1 nm) sample at the Pt L\textsubscript{3} edge is presented in Fig. 2. The experimental data obtained by fluorescence fit closely to the simulation. The whiteline intensity (ratio of absorption maximum and edge jump) is 1.31, which indicates a mainly metallic state for Pt (1.25 for metallic Pt, 1.50 for PtO\textsubscript{1.36}, 2.20 for PtO\textsubscript{1.6}[33]).

The asymmetry ratio of the Pt/Fe sample has its maximum near the absorption maximum of the Pt L\textsubscript{3} edge (11567.5 eV) and vanishes at energies of more than 30 eV below and above. Therefore, influences from other absorption edges can be excluded. Assuming a magnetic moment of 0.2 µ\textsubscript{B} per Pt atom we calculated a maximum Δβ of 0.4 \times 10\textsuperscript{-7} which is located 1 eV below the maximum absorption of Pt in accordance with the literature[33]. Since we performed XRMR measurements at the absorption maximum (11567.5 eV), dashed vertical line in Fig. 2, we assume a ratio Δβ/Δδ of 3.4 (black crosses in Fig. 2) in the simulations of the asymmetry ratio.

Fig. 3(a) presents the XRMR data for Pt(3.4 nm)/Fe(9.1 nm) at 11567.5 eV. The blue dots and red stars denote the reflected intensity \(I_\pm\) for positive and negative external magnetic field, respectively. An oscillation of \(ΔI(q)\) can be observed as shown in Fig. 3(b) with an amplitude of about 2%. The asymmetry ratio can be fitted using the magnetooptic profile of Δδ and Δβ shown in the inset of Fig. 3(b) while keeping the ratio Δβ/Δδ = 3.4 constant. The thickness and roughness of the layers are kept fix (taken from the XRR fit in Fig. 1). The magnetooptic profile is generated by a Gaussian at the Pt/Fe interface convoluted with the roughness profile of the layers. We obtain a FWHM value of the magnetooptic profile of (1.1 ± 0.1) nm, which can be interpreted as the effective thickness of the spin polarized Pt layer at the interface to Fe.

By comparison of the magnetooptic profile with the ab initio calculations we deduce a magnetic moment of (0.6 ± 0.1) µ\textsubscript{B} per Pt atom, which can also be found for spin polarized Pt in the literature[32]. Compared to the results of Gepr"ags et al.[21] we observe a larger magnetic moment for our reference sample. With XMCD, they detected an average magnetic moment of 0.0325 µ\textsubscript{B} in Pt(10 nm)/Fe(10 nm). Assuming the spin polarized Pt is located in a 1.1 nm layer, one obtains 0.0325 µ\textsubscript{B} \times 1.1 nm ≈ 0.3 µ\textsubscript{B} per Pt atom from these XMCD results.

We also investigated Pt(x)/Fe(9.8 nm) for x = 1.8 nm, 5.9 nm and 20 nm. The experimental XRR results and the simulations are presented in Fig. 4(a), (c) and (e). The corresponding asymmetry ratios are shown in Fig. 4(b), (d) and (f). For all Pt/Fe samples we observe an amplitude of about 2%, independent of the Pt thickness. This result shows the benefits of XRMR as the asymmetry signal stems from the spin polarization at the interface. The XRR model in Fig. 4(g) and the magnetooptic profiles in Fig. 4(h) are used for the simulations. We again obtain magnetic moments of (0.6 ± 0.1) µ\textsubscript{B} for
the sample with 5.9 nm and 20 nm Pt, while we observe a smaller magnetic moment of $(0.2 \pm 0.1) \mu_B$ for the sample with 1.8 nm Pt.

For Pt/NFO we obtain a whiteline intensity of 1.33 which is comparable to the value 1.31 for Pt/Fe and again confirms the mainly metallic Pt state in our samples. However, this value is slightly larger than the whiteline intensities of the Pt layers in the study of Gepr¨ ags et al.\textsuperscript{21,22} which were lower than 1.30, and it is lower than the value of the Pt layer in the study of Lu et al.\textsuperscript{23} Their whiteline intensity can be determined to be 1.47 which points to partly oxidized Pt when compared with 1.50 for PtO$_{1.36}$.

In Fig. 5, the XMRM measurement of Pt/NFO is presented. For comparison, the measured asymmetry ratio $\Delta l(q)$ and a simulated asymmetry ratio are shown in Fig. 5(b). Here, the magnetooptic profile of the spin polarization at the Pt/Fe interface (cf. Fig. 5(a)) was used for simulating a similar spin polarization in the Pt/NFO sample. Due to the different optical constants for NFO compared to Fe, the amplitude of $\Delta l(q)$ would be larger for Pt/NFO compared to Pt/Fe using the same magnetooptic profile. The oscillations obtained by this simulation are clearly not visible in the experimental data.

In order to increase the sensitivity, we measured the reflectivity from $q = 0.2 \, \AA^{-1}$ up to $q = 0.6 \, \AA^{-1}$ (two Kessig fringes) and took the average from 52 experiments. The XMRM curves in Fig. 5(c) still have a vanishing $\Delta l(q)$ (cf. Fig. 5(d)) without any oscillations. A simulated asymmetry ratio assuming 2% of the Pt/Fe spin polarization leads to the lower detection limit and can be converted into a maximum magnetic moment in Pt on NFO of $0.02 \mu_B$ per Pt atom using the Pt/Fe calibration and taking into account that NFO is 70% magnetized for $\pm 85 \, \text{mT}$ (cf. Fig. 5(d)). Therefore, a static magnetic proximity effect in Pt/NFO can be neglected down to that limit.

In conclusion, we investigated the spin polarization of Pt in Pt/Fe and Pt/NFO bilayers using XMRM. We observed an asymmetry ratio of 2% for the Pt/Fe samples independent of the Pt thickness. Simulations lead to a maximum magnetic moment of $(0.6 \pm 0.1) \mu_B$ per Pt atom. The results demonstrate that XMRM is directly sensitive to the spin polarization at the Pt/FM interface. For Pt/NFO samples no asymmetry was found. Therefore, a static magnetic proximity effect and proximity induced ANE can be excluded in our LSSE investigations on Pt/NFO bilayers.

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