Influence of structure and cation distribution on magnetic anisotropy and damping in Zn/Al doped nickel ferrites

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(Dated: August 23, 2019)

An in-depth analysis of Zn/Al doped nickel ferrite with a nominal composition of Ni0.65Zn0.35Al0.8Fe2.3O4 was conducted to gain insight into the magnetic properties interesting for applications in spintronics. The material is insulating, ferromagnetic at room temperature and has a low magnetic damping with additional strong magneto-elastic coupling. A growth optimisation for reactive magnetron sputtering is performed and the sample system is analysed for crystal structure, chemical composition and static as well as dynamic magnetic properties. Thus a correlation between strain, cation distribution, magneto-crystalline anisotropy and damping is evidenced. XMCD and XMCD(H) measurements at the L3,2 edge of Ni and Fe are performed to complement integral SQUID magnetometry and identify their magnetic contributions to the hysteresis. In particular, a strong influence of the lattice site occupation of Ni2+ and cation coordination of Fe3+ on the intrinsic damping is found. Furthermore, the vital role of the incorporation of Zn2+ and Al3+ is evidenced by comparison with a control sample of slightly altered nominal stoichiometry. A strain-independent improvement of the magnetic anisotropy and damping by adapting the cation distribution is demonstrated.

I. Introduction

In spintronics one aims to obtain pure spin currents as an additional degree of freedom in logic circuits aside from electric charges [1]. By spin pumping [2] it is feasible to induce a spin current from ferromagnetic materials into adjacent non-magnetic layers. To ensure pure spin currents and exclude charge currents ferromagnetic insulators are the materials of choice. However, ferromagnetic insulators with low intrinsic magnetic damping are sparse [3]. The most commonly used material for magnetoelectric devices is yttrium iron garnet (YIG) [4, 5]. YIG has two major drawbacks, i.e. the complex garnet structure, which is almost exclusively grown on gadolinium gallium garnet (GGG) substrates and its weak magnetoelastic response. It could be replaced by cubic Zn/Al doped nickel ferrite (NiZAF) thin films grown on MgAl2O4, which were reported to have comparably favourable magnetic properties [6] as YIG: ferromagnetic at room temperature and a low intrinsic damping. Furthermore, the static magnetic analysis shows a soft magnetic behaviour with a low coercive field, which makes the material interesting for high frequency applications. An advantage of NiZAF over YIG is the strong magnetoelastic coupling. The combination of these properties makes it especially suitable for applications in magnetoelectric and acoustic spintronics. NiZAF is based on nickel-ferrite NiFe2O4, which grows in the cubic inverse spinel crystal structure, i.e. Ni occupies octahedral (NiOh) and Fe sits in a 1:1 ratio either at tetrahedral FeTd or octahedral FeOh lattice sites. By doping with Zn and Al, which substitute Ni and Fe, respectively, the structural and magnetic properties are tuned. Previous work on the single ion model of ferrite magnetism [7] shows a negative impact of tetrahedrally coordinated Ni with a valency of 2+ (Ni2+Fe) on the magnetic damping due to unquenched orbital moment. This effect has not been found for octahedrally coordinated Ni2+Fe. Since Zn2+ prefers the tetrahedral sites it prevents Ni2+ from occupying these sites and therefore, predominantly Ni2+Fe3+ is formed. Growth of highly strained NiFe2O4 thin films [8] showed an increase in damping caused by defects. Thus, to reduce the strain that also shows an influence on magnetic anisotropy smaller Al3+ cations are added to substitute for Fe3+. A doping percentage of 0.8 was reported to be the best compromise between magnetostriction and saturation magnetisation for bulk polycrystalline NiZAF [8]. Substituting ferromagnetic with non-ferromagnetic elements in NiZAF results in a lower saturation magnetisation MS ∼ 110 kA/m as well as Curie temperature TC ∼ 450 K [8] compared to undoped NiFe2O4 with MS up to 300 kA/m and a significantly higher Curie temperature of TC = 860 K [9]. In turn, NiZAF gains a smaller ferromagnetic resonance (FMR) line-width ∼ 0.82 mT resulting in a Gilbert damping parameter of α ∼ 3 × 10−3 [8] in comparison to a line-width Bpp = 35 mT of NiFe2O4 [9]. Furthermore, in contrast to HE = 100 mT [9] for undoped NiFe2O4 a reduced coercive field of ∼ 0.2 mT [9] has been reported. Zn/Al doping of NiFe2O4 is therefore an advantageous trade off since low damping and coercivity are the relevant quantities for applications in spintronics.

In this work NiZAF was fabricated using reactive mag-
netron sputtering (RMS) and studied for the correlation between strain, magnetic anisotropy, cation distribution and intrinsic damping. This investigation indicated that already a moderate increase of the strain leads to a significantly increased magneto-crystalline anisotropy, which results in an enhanced intrinsic damping. From a comparison between experimental X-ray magnetic circular dichroism (XMCD) spectra and multiplet ligand field theory simulations, Ni$^{2+}$ and Fe$^{2+}$ are identified as another cause for an enhancement of anisotropy. Finally, the cation distribution of a control sample with slightly different nominal stoichiometry revealed the tuneability of the magnetic properties of NiZAF by site occupation independent of strain.

II. Experimental Details

Zn/Al doped nickel ferrite thin films were epitaxially grown with RMS in an UHV chamber with a base pressure of $2 \times 10^{-9}$ mbar from a target with a nominal composition of Ni$_{0.65}$Zn$_{0.35}$Al$_{0.8}$Fe$_{1.2}$O$_4$. As a substrate for the thin film growth double side polished single crystalline spinel [MgAl$_2$O$_4$(001)] was chosen. A variation of the growth conditions was done for a heater temperature range of 810$^\circ$C to 850$^\circ$C and an Ar:O$_2$ ratio from (10:0)sccm to (10:0.2)sccm. The data of the growth optimisation including a thickness variation and annealing can be found in a data repository [11]. The best results were achieved with the highest possible heater temperature of $T_H = 850$ $^\circ$C corresponding to a sample temperature of $\sim 525$ $^\circ$C, an Ar:O$_2$ ratio of (10:0)sccm to (10:0.1)sccm, a magnetron power of 30 W and a working pressure of $4 \times 10^{-3}$ mbar. Additionally, a control sample with a slightly altered nominal stoichiometry of Ni$_{0.64}$Zn$_{0.46}$Al$_{0.62}$Fe$_{1.28}$O$_4$ was fabricated for comparison. For the growth of this sample a sample temperature up to $\sim 600$ $^\circ$C could be achieved.

The structural characterisation of the samples was done with X-ray diffraction (XRD) measurements by a Panalytical X’Pert MRD and a Seifert XRD3003 recording $\omega - 2\theta$ scans and symmetric as well as asymmetric reciprocal space maps (RSM). The surface roughness was characterised with an atomic force microscope (AFM). The interface on an atomic scale was checked with transmission electron microscopy (TEM) using a Jeol JEM-2200 FS. Furthermore, the chemical composition was obtained with energy dispersive X-ray spectroscopy (EDX) in the TEM system. The static magnetic properties were measured with integral superconducting quantum interference device (SQUID) magnetometry by a MPMS-XL5 system from Quantum Design applying the magnetic field in the film plane (IP) as well as out-of-plane (OOP). The magnetic behaviour in a field range of $\pm 5$ T from room temperature (RT) down to 2 K and the temperature dependence of the magnetisation up to 300 K are measured. The data were background corrected for the contribution of the diamagnetic substrate and known artefacts were carefully avoided [12, 13]. The dynamic magnetic properties were analysed with conventional X-band ferromagnetic resonance (FMR) at room temperature researching the polar and azimuthal angular dependence of resonance position and line-width. Finally, X-ray absorption (XAS) and XMCD spectra at the Ni and Fe L$_3$ edge were measured at the X-Treme beamline at the Swiss Light Source (SLS) [14] to complement the integral SQUID magnetometry and investigate the element selective contributions to the hysteresis by recording XMCD(H) curves. The XMCD spectra were obtained in total electron (TEY) and fluorescence yield (TFY) with $20^\circ$ grazing and normal incidence at RT and a field of 6.8 T. Due to self-absorption in the TFY leading to a reduced intensity, only the TEY spectra are shown here. Furthermore, in Fe oxides, re-absorption results in negative absorption spectra at the Fe L$_3$ edge (further data can be found in a repository [11]). The XMCD(H) curves are measured in a field range of $\pm 6.8$ T in TEY and TFY at RT at the maximum of the XMCD peaks sensitive to the site occupancy of the cation in the crystallographic structure. Due to a higher signal to noise ratio, the TFY curves at normal incidence are used for characterisation. The raw data of the measurements can be found in a data repository [16].

III. Structural Properties

The crystalline structure of the material is routinely analysed with symmetric $\omega - 2\theta$ scans using XRD. Results for two samples with different thicknesses are shown in Fig. 1(a). Both samples have the same (004) reflection at 42.67$^\circ$ with respect to the substrate and show Laue oscillations. The film reflection with a small full width half maximum (FWHM) around 0.13$^\circ$ for the 70 nm sample results in a perpendicular lattice parameter of $a_{\perp} = 8.47 \pm 0.01$ Å. The symmetric RSM along (004) and the asymmetric RSM along (115) are shown in Fig. 1(b) and Fig. 1(c), respectively. The reflection from the MgAl$_2$O$_4$ substrate corresponds to a lattice parameter of $a_{\parallel} = 8.09$ Å, which has a lattice mismatch of $\sim 2\%$ with bulk NiZAF ($a_0 = 8.24$ Å) [8]. The asymmetric scan reveals an in-plane lattice parameter of $c/\alpha = 1.047 \pm 0.001$ confirming a clearly strained material. Additionally, the unit cell volume of the strained material is 554 Å$^3$, which is equal to a reduction of the unit cell volume by only $\sim 1\%$ with respect to the bulk. Even though the samples are significantly strained, they maintain an excellent crystal quality evidenced by the well pronounced Laue oscillations visible in the line scan as well as the RSM indicating a homogeneous crystal growth for a thickness of up to 70 nm.

In Fig. 2(a) the high resolution cross-section TEM image along [100] shows a smooth interface transition between film and substrate on an atomic scale. No indi-
cation for dislocations or defects can be found in the measurements on various length scales, further proving the excellent structural quality of the coherently strained material. However, the enhanced contrast in the film indicates a higher strain, which corroborates the findings of the RSM (see Fig. 1(b)). A clear separation between film and substrate is visible by looking at the sample interface on a larger scale, depicted in Fig. 2(b). Additional annealing had no influence on the structural quality nor the magnetic properties further supporting a low-defect material, in contrast to previous works on epitaxially grown spinel ferrite thin films [9, 17].

The analysis of the chemical composition with EDX in the TEM system (not shown, see repository [11]) revealed a ratio of (Fe : Ni : Zn) (1 : 0.55 : 0.22). In comparison to the nominal values of (Fe : Ni : Zn) (1 : 0.54 : 0.29) (all values are normalised with respect to the Fe amount in the material) a clear reduction of Zn content is observed. The deficiency in Zn can be explained by its high volatility, which is even more enhanced by the high growth temperatures [18]. Unfortunately no reliable value for the aluminium concentration in the material can be given due to the difference in atomic number in comparison to the other metals.

FIG. 1: Structural properties of NiZAF measured with XRD by means of a 70 nm sample, (a) shows a symmetric $\omega - 2\theta$ scan in comparison with a 16 nm sample, (b) depicts a symmetric RSM along (004) and (c) depicts an asymmetric RSM along (115).

FIG. 2: Surface and interface properties of a 70 nm NiZAF sample. In (a) a high-resolution cross section TEM image shows the interface of film and substrate on an atomic scale, in (b) the growth on a larger scale and (c) depicts an AFM scan of the surface.
In Fig. 2(c) an AFM image of the surface in a 550 × 550 nm² area is shown. A flat surface with neither cracks nor holes and a low average maximum roughness peak height $R_{\text{p}} = 40$ pm as well as a root mean square roughness of $R_{\text{q}} = 24$ pm is found. This is further supported by the highest deviation being 2 nm in size, which corresponds to approximately 2 monolayers of film. The flat structureless surface is ideal for growing heterostructures making NiZAF a perfect choice for spin pumping devices with an insulating ferromagnetic material.

FIG. 3: Static magnetic properties obtained from integral SQUID magnetometry. (a) shows the hysteresis at 300 K and 2 K with an inset giving a closer look at the open hysteresis at low fields and (b) the hystereses at various temperatures from 2 K to 300 K with an inset sketching the coercive fields $H_c$ over the temperature. In (c) the temperature dependence of the magnetisation from 2 K to 400 K at 10 mT is depicted. An estimation of the Curie temperature is given in the inset.

IV. Magnetic Properties

The static and dynamic magnetic behaviour of the material is measured with SQUID magnetometry and FMR, respectively. In Fig. 3(a) a hysteresis at 300 K and 2 K is shown. The inset depicts the RT hysteresis in more detail around zero field. For low temperatures the typical increase of remanence and coercivity is observed. The volume of the film is taken into account for the magnetisation values by thickness determination from the Laue oscillations (see Fig. 1(a)) and area measurements of the sample. Accordingly, a saturation magnetisation of $M_S = 118 \pm 12$ kA/m is obtained from the hysteresis at RT. This value coincides with the saturation in the bulk material $\sim 120$ kA/m and previous values for thin films $\sim 120$ kA/m. Furthermore, a small coercive field of $H_c = 1.2$ mT at 300 K can be seen in the inset, which is further evidence for a low-defect material. Additionally, by measuring the hystereses at various temperatures from 2 K to 300 K (see Fig. 3(b)) a temperature dependence of the coercive field is obtained. A steady increase from $H_c = 1.2$ mT at 300 K up to $H_c = 40$ mT at 2 K was determined, as can be seen in the inset of Fig. 3(b). The Curie temperature of $T_C = 375 \pm 2$ K was estimated from the M(T) curve at 10 mT shown in the inset of Fig. 3(c). Even though the Curie temperature is reduced, if compared with pulsed laser deposited (PLD) prepared samples with $T_C = 450$ K, ferromagnetic applications at RT are still feasible.

In addition, the directional dependence of the static magnetic properties was studied. A comparison of two IP hystereses along [100] to [110] shown in Fig. 4(a) suggests magnetically isotropic material in the film plane without a distinct preference for either direction. In contrast to cubic bulk NiZAF a shift of the easy axis from [111] to [110], for thin films grown with PLD as well as RMS, is evidenced. The difference in saturation field between IP and OOP on the other hand is clearly visible in Fig. 4(b). A large uniaxial OOP anisotropy field of $B_{\text{aniso}} > 3$ T is obtained, which cannot be solely explained by shape anisotropy, which is at most $B = \mu_0 M_S = 0.15$ T. This high value for the anisotropy in the material is unexpected, since NiFe$_2$O$_4$ with lower crystal quality shows no OOP anisotropy except for shape [10]. The large OOP anisotropy contributions originate from the magneto crystalline anisotropy given by the environment of the highly strained inverse spinel crystal structure. This is supported by previous work on less strained Zn/Al doped nickel ferrite $(c/a = 1.035)$ with a smaller out-of-plane anisotropy $(B_{\text{aniso}} > 1$ T) in Ref. [6]. At first sight the major change in anisotropy from $B_{\text{aniso}} > 1$ T to $B_{\text{aniso}} > 3$ T seems to be caused by a small change in the c lattice parameter from $a_{\perp} = 8.36$ Å to $a_{\perp} = 8.47$ Å. Furthermore, the high OOP anisotropy field of more than 3 T is confirmed by XMCD(H) measured in TFY of normal incidence at RT, which are shown in Fig. 3(c). At present, only the comparison of the different contributions to the average with respect to the SQUID data is
FIG. 4: Directional dependence of the static magnetic properties obtained from integral SQUID magnetometry at RT, (a) shows a comparison between [100] and [110] direction and (b) between IP and OOP. The directions with respect to the sample are shown in the inset of (a). Additionally, the XMCD (H) of FeOdh, FeTds, Ni and an average of all three in comparison with the integral IP and OOP SQUID measurements are plotted in (c).

FIG. 5: Dynamic magnetic properties obtained from conventional FMR, (a) shows the polar angular dependence from 0° to 180° and (b) the azimuthal angular dependence from 0° to 360° for the resonance position as well as the line-width. The inset in (a) depicts the smallest FMR line measured at f = 9.5 GHz in the easy axis.

of importance and the XMCD spectra will be discussed in more detail further below. The average of the element selective hystereses shows the same behaviour as the OOP M(H) curve of the integral SQUID measurements.

FMR measurements have been performed with a conventional X-Band resonator based set-up at RT to obtain the dynamic magnetic behaviour of the material. The FMR line at $f = 9.5$ GHz in the inset of Fig. 5(a) has a resonance position of $B_0 = 36.2 \pm 0.2$ mT with a line-width $B_{pp} = 12.0 \pm 0.2$ mT. Measurements on the bulk material indicated line-widths four times higher ($B_{pp} = 43$ mT [8]). The easy and hard axis pointing in-(0°) and out-of-plane (90°), respectively, are obtained from the polar angular dependence of the material shown in Fig. 5(a). The similar increase of the line-width near the hard axis is caused by dragging effects [19]. An analysis of the in-plane azimuthal angular dependence shown in Fig. 5(b) indicates an in-plane easy axis along [110]. However, the difference between [110] and [100] of 2 mT suggests only a weak in-plane anisotropy consistent with IP SQUID measurements in Fig. 4(a). Previous work showed a stronger preference for [110] with an in-plane anisotropy of $\sim 10$ mT for a lesser strained material ($c/a = 1.035$) grown by PLD [6]. Furthermore, the fourfold symmetry of the angular dependence depicts the underlying cubic crystal structure. Additionally, the difference in resonance position between [100] and [010] indicates an additional small uniaxial IP anisotropy contribution of $\sim 1$ mT. As known for thin film ferromagnets, this is most likely induced by step anisotropy of the underlying substrate (miscut angle $\sim 0.5\degree$).

A home-built short-circuited multi-frequency FMR set-
VI. Cation distribution

The cation distribution as well as the occupation of lattice sites of the several elements contributing to the magnetic and structural properties of NiZAF are of special interest due to the reported influence on the intrinsic damping. The possible coordination in the case of an ideal inverse spinel crystal structure, as it is given for undoped NiFe₂O₄, is shown in Fig. 3(a). Half the Fe³⁺ occupies octahedral, the other half tetrahedral, whereas Ni²⁺ only sits at octahedral sites. Ideally, Zn²⁺ would substitute for Ni²⁺ and the smaller Al³⁺ goes to Fe³⁺ sites according to the nominal composition of Ni₀.₆₅Zn₀.₃₅Al₀.₈Fe₁₂O₄ maintaining the inverse spinel. For experimental evidence, total electron yield XAS and XMCD spectra in 2⁰ grazing incidence at the Ni and Fe L₃,₂ edge shown in Fig. 3(b) are obtained. Respective simulations are done with CTM4XAS [22] using multiplet ligand field theory. The chosen parameters are adapted from nickel ferrite [22], which shows similar XAS spectra and resulting XMCD curves. Scaling percentages for the Fpd, Fdd, and Gpd Slater integral reductions of 70 % and 80 %, respectively are used to consider interatomic screening and mixing. For the octahedral coordination a crystal field splitting of 10Dq = 1.2 meV and a positive exchange field of J = 48 meV is used to fit the obtained Curie temperature of $T_C = 375 \pm 2$ K (see Fig. 3(c)). [22]. The tetrahedral coordination is simulated with a splitting of 10Dq = −0.6 meV and a negative exchange field $J = -48$ meV. Charge transfer is not taken into account, because no influence on the absorption spectra has been found [21]. Furthermore, the instrumental and intrinsic broadening is included by a Gaussian function of $\sigma = 0.25 e V$ and a Lorentzian function with a range of $\Gamma[0.3 e V$ to $0.5 e V]$, respectively. Note that the simulation is shifted in photon energy to fit the experimental data.

A comparison between the experimental and simulated XAS and XMCD spectra at the Ni L₃,₂ edge (see Fig. 3(b)) suggests percentages of 94 % Ni²⁺, 15 % Fe³⁺, and 6 % Ni³⁺, showing a slight deviation from the inverse spinel crystal structure. This assumption is supported by evaluation of the simulation matching the experimental XAS and XMCD spectra of Fe (see Fig. 3(c)). The Fe contributions are more complex, since not only Fe³⁺ occupying Oh and Td sites but also Fe²⁺, was identified in the experimental data. The best match between experiment and simulation was determined by relying on the main peaks of the XMCD at the L₃ edge as shown in Fig. 3(d). Percentages of 33 % Fe²⁺, 45 % Fe³⁺, and 22 % Fe³⁺ are obtained. From this, a mixed state between the inverse and normal spinel crystal structure is apparent, as has been evidenced for thin film nickel ferrites in earlier works [6, 24]. The element selective magnetic contributions from Ni and Fe directly infer the occupation of Zn and Al. According to the single ion model of ferrites [7], Ni²⁺ does not enhance the damping, but Ni³⁺ contributes by an unquenched orbital momentum. Less than 6 % Ni³⁺ suggest still too little amounts of Zn²⁺ incorporated in the material, since Zn²⁺ favours the occupation of tetrahedral sites thus reducing the amount of Ni²⁺ [3]. This has already been suggested by the EDX measurements showing a significant reduction of Zn content compared to the nominal composition of the target. Additionally, the strong imbalance between octahedral and tetrahedral coordinated Fe as well as the high amount of Fe²⁺ suggest a deficiency of Al. This is further supported by Ref. [8] due to the significant impact of the Al percentage of bulk NiZAF on the magnetic properties, in particular the coercive field. The high amount of octahedral coordinated Fe can be explained by too little Al, since Al³⁺ favours octahedral incorporation [8]. Furthermore, less Al³⁺ doping in the bulk material results in a broader FMR line-width [8] underlining its influence on the magnetic damping. Additionally, the large amount of ~ 33 % Fe²⁺ has a negative impact on the damping due to hopping [Fe²⁺ → Fe³⁺ + e] [6, 7]. The results are in good agreement with the previous analysis of the material system and give an explanation on the atomic level for the increased intrinsic damping. The main cause are a small number of Ni³⁺ due to a low incorporation of Zn²⁺ and large amounts of Fe³⁺. Furthermore, a deficiency of Al³⁺ is inferred from the imbalance between tetrahedral and octahedral coordinated Fe³⁺ suggesting a mixed spinel crystal structure.
VI. Governing Mechanism

To determine the governing mechanism for tuning the magnetic properties a control sample with a slightly altered nominal stoichiometry of \( \text{Ni}_0.64 \text{Zn}_{0.46} \text{Al}_{0.62} \text{Fe}_{1.28} \text{O}_4 \) was fabricated. In Fig. 7(a) a comparison between data and simulation of the XAS and XMCD spectra at the Ni L\(_{3,2}\) edge is depicted resulting in percentages of 2.5\% Ni\(^{2+}\)\(_{\text{Td}}\) and 97.5\% Ni\(^{2+}\)\(_{\text{Oh}}\). A reduction of more than 50\% in tetrahedral coordinated Ni suggests an improved incorporation of Zn\(^{2+}\). This already indicates a better agreement with the ideal inverse spinel crystal structure than in the previous sample (see Fig. 6(b)). However, structural analysis shows a comparably excellent crystal quality with well pronounced Laue oscillations and a within error bars similar or even slightly increased perpendicular lattice parameter of \( a_{\perp} = 8.49 \pm 0.01 \text{Å} \) instead of \( a_{\perp} = 8.47 \pm 0.01 \text{Å} \) (see inset of Fig. 6(a)). Furthermore, the correlation between data and simulation of the XAS and XMCD spectra at the Fe L\(_{3,2}\) edge shown in Fig. 6(b) confirms the results obtained for Ni. The simulation is fitted with respect to the primary peaks of the XMCD at the L\(_{3}\) edge, since the magnetic information of the material is mainly contained in the XMCD spectra. Percentages of 28\% Fe\(^{2+}\)\(_{\text{Oh}}\), 28\% Fe\(^{3+}\)\(_{\text{Oh}}\) and 44\% Fe\(^{3+}\)\(_{\text{Td}}\) are calculated indicating a more even distribution of Fe in the inverse spinel crystal structure in contrast to previous values (see Fig. 6(c)). From this a better incorporation of the Al\(^{3+}\) in the crystal structure can be inferred, even though the nominal value is less in the control sample (0.66 compared to 0.80). Additionally, the reduction of Fe\(^{2+}\)\(_{\text{Oh}}\) suggests a positive impact on the intrinsic magnetic damping due to less opportunity for hopping. This interpretation is confirmed by the improved magnetic properties of the material indicated by an increase in Curie temperature by 20 K up to \( T_C = 395 \pm 2 \text{K} \) as shown in Fig. 7(c). The inset of Fig. 7(c) depicts an FMR line with a higher resonance position of \( B_0 = 57.7 \pm 0.2 \text{mT} \) and a smaller line-width of \( B_{pp} = 7.0 \pm 0.2 \text{mT} \) than before (see inset of Fig. 5(a)) confirming the improved magnetic damping. Since the resonance position depends on the magneto crystalline anisotropies of the material this shift coincides with the findings of a decreased OOP anisotropy of \( B_{\text{aniso}} > 2 \text{T} \) (shown in Fig. 7(d)). Furthermore, a smaller coercive field of \( H_c \sim 0.2 \text{mT} \) at 300K depicted in the inset of Fig. 7(d) indicates less
FIG. 7: Analysis of a control sample showing the TEY XAS and XMCD spectra in grazing incidence of 20° at RT and simulations done with CTM4XAS [21] at (a) the Ni L\textsubscript{3,2}, and (b) the Fe L\textsubscript{3,2} edge. The inset in (a) depicts a symmetric $\omega - 2\theta$ scan. In (c) the M(T) at 100 mT from 2 K to 390 K with an inset showing the FMR line at 9.5 GHz is given. A comparison between IP and OOP orientation of M(H) curves at RT is shown in (d) with an inset depicting the hysteresis around zero field.

defects and a transition to an even softer magnetic material than previously determined (see Fig.3 b)). At temperatures as low as 100 K similar values for the coercivity as in previous samples of $H_c = 1.2 \text{mT}$ are reached. The increase of the saturation magnetisation to $M_S = 195 \pm 20 \text{kA/m}$ at RT (not shown, see repository [11]) in comparison to $M_S = 118 \pm 12 \text{kA/m}$ can be explained by the nominal higher amount of ferromagnetic Fe. Although the strain remained the same or has even slightly increased, by improving the cation distribution the magnetic anisotropy and damping could be reduced remarkably. These results demonstrate the relevance of the cation distribution, in particular the amount of Ni\textsuperscript{2+}Td and Fe\textsuperscript{2+}Oh as another major criteria for the optimisation of the magnetic properties. So far, only the influence of Al on bulk NiZAF [8] has been studied, however this investigation showed the importance of tuning both the Al and the Zn content. Therefore, for a full understanding of this complex material system the determination of the whole parameter space of Al and Zn concentration together with the site occupancy in NiZAF thin films is vital.

VII. Conclusion

In this work growth of Zn/Al doped nickel ferrite with excellent crystal quality was achieved by reactive magnetron sputtering from a target with nominal composition of Ni\textsubscript{0.65}Zn\textsubscript{0.35}Al\textsubscript{0.8}Fe\textsubscript{1.2}O\textsubscript{4}. A thorough growth optimisation was conducted, which yielded the following results for the material system of nickel ferrites. Although the material is highly, but coherently strained, evidenced by a tetragonal distortion of $c/a = 1.047 \pm 0.001$, no indication for defects or dislocations can be observed from structural analysis. A comparison with bulk [8] shows a shift of the in-plane magnetic easy axis from [111] to the [110] for thin films grown with PLD [6] or RMS. However, the small in-plane anisotropy of $\sim 2 \text{mT}$ shows an almost uniform magnetisation within the film plane.

Comparison with a sample of slightly altered nominal stoichiometry highlighted a significant influence of the cation distribution on the magneto-crystalline anisotropy and the intrinsic magnetic damping. A reduction of Ni\textsuperscript{2+}Td by more than 50\% infers a better incorporation of Zn\textsuperscript{2+}Td leading to a decrease in coercivity from $H_c = 1.2 \text{mT}$ to $H_c = 0.2 \text{mT}$ at RT. Furthermore, 5\% less Fe\textsuperscript{2+}Oh resulted in a smaller line-width of $B_{pp} = 7.0 \pm 0.2 \text{mT}$ in con-
contrast to \( B_{pp} = 12.0 \pm 0.2 \text{ mT} \). Additionally, a decrease in the magneto crystalline anisotropy resulted in a reduction down to an OOP anisotropy \( B_{\text{aniso}} \) of 2 T by at least 1 T. This further explains the shift of the resonance position from \( B_0 = 36.2 \pm 0.2 \text{ mT} \) to \( B_0 = 57.7 \pm 0.2 \text{ mT} \). Moreover, the Curie temperature increased by 20 K to \( T_C = 395 \pm 2 \text{ K} \). In general, an improved incorporation of the cations is evidenced by the ratio of Td to Oh coordinated Fe. Even though, the nominal amount of Al\(^{3+}\) is less in the control sample.

In addition to these findings, a dependence on the deposition method is evident, since growth by thermal PLD \( ^6 \) shows a better stoichiometric transfer than RMS. An adjustment of the stoichiometry by adding small amounts of Zn and Al could result in a lower magnetic damping and ordered anisotropy in this tunable material by improved cation occupation. Especially, since the change in stoichiometry to Ni\(_{64}\)Zn\(_{0.4}\)Al\(_{0.6}\)Fe\(_{2}\)O\(_{4}\) leads to an improvement in the cation distribution favouring softer magnetic properties.

To conclude, by fabrication of NiZAF thin films with RMS, samples with a higher strain than previously reported were obtained. In contrast to initial assumptions, strain is not the sole mechanism to control the magnetic properties in this complex material system. In addition, the cation distribution, i.e., the amount of Fe\(^{3+}\)\(_{\text{Oh}}\) and Ni\(^{3+}\)\(_{\text{Td}}\) was found to have a major impact on the magnetic anisotropy and damping independent of strain. A strong influence on the Curie temperature and the coercivity is apparent as well. Studies on bulk NiZAF evidenced the crucial role of the Al concentration. However, the thorough analysis on NiZAF thin films in this work, reveals that the magnetic properties can be further improved by tuning the concentration and lattice occupation of the Zn dopants.

Acknowledgement

The authors gratefully acknowledge funding by FWF project ORD-49. The X-ray absorption measurements were performed on the EPFL/PSI X-Treme beamline at the Swiss Light Source, Paul Scherrer Institut, Villigen, Switzerland. Further acknowledgement to Werner Ginzinger for TEM sample preparation.

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