XMCD Study of Magnetic Proximity Effects in FM(Co, Ni) – AFM(MnF₂, NiF₂) Heterostructures

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Present work is devoted to the study of magnetic proximity effects between metallic ferromagnetic layer and insulating antiferromagnetic epitaxial layers by using element selective X-ray magnetic circular dichroism (XMCD) technique.

1 Introduction

Interfacial interaction between different magnetic materials is known to give rise to new phenomena [1,2], e.g., appearance of unidirectional magnetic anisotropy in ferromagnet (FM) / antiferromagnet (AFM) systems, referred to as exchange bias, widely exploited in today’s device applications. In the present work, we study the proximity effects between metallic FM layer and insulating AFM layer by using X-ray magnetic circular dichroism (XMCD) at BL16A beamline of Photon Factory synchrotron. Our recent XMCD experiments [3] revealed that the cobalt FM layer induces a net magnetic moment at the interface with MnF₂ at 300 K - well above T_Néel for bulk MnF₂. Orientation of Mn²⁺ magnetic moments was found to be antiparallel with respect to FM magnetization [2]. In order to get a more detailed and general picture of the interfacial phenomena we have conducted series of experiments using different materials for FM (Co, Ni) and AFM (MnF₂, NiF₂) layers, which are presented here. Nickel was used instead of cobalt as a magnetically soft layer. NiF₂ was attractive because it is known to possess spin-canted weak ferromagnetism at low temperature in bulk.

2 Experiment

Ferromagnet/antiferromagnet Ni/MnF₂ and Co/NiF₂ heterostructures were grown on silicon wafers by molecular beam epitaxy. Schematic view of investigated heterostructures is presented in Fig.1. The MnF₂ and NiF₂ layers were grown onto CaF₂/Si(111). The Si(111) substrate is used to guide the growth of a CaF₂ buffer, which is (111) oriented and which in turn prevents chemical reactions with Si and drives the epitaxial growth of MnF₂ and NiF₂. MnF₂ grows in the orthorhombic α-PbO₂ type metastable phase, presenting a (111) surface orientation and island growth mode. In a similar manner NiF₂ grows in the orthorhombic CaCl₂ type metastable phase and presents (100) surface orientation. The bare fluorite surface consists of domains whose sizes are strictly dependent on the growth temperature. To study dependence on surface roughness, series of samples with different growth temperature (100-350 °C) was grown for this experiment.

Ferromagnetic layers of Co and Ni with coverage ranging between 2 and 6 nm were grown at room temperature from an e-beam bombardment cell. Co and Ni FM layers grow in a similar manner - AFM and SEM images show dense array of islands with diameters smaller than 5 nm and a density of approximately 8000μm⁻². RHEED patterns taken during the growth show that the film is polycrystalline. To prevent metal from oxidation, a 3 nm CaF₂ capping layer was deposited on top of the samples.

Element-selective absorption (XAS), magnetic dichroism (XMCD) and magnetic reflectivity (XRMR) measurements were performed both at room and liquid helium (T=22K) temperatures using a continuous-liquid-helium-flow-type cryostat. XAS spectra were measured in the highly surface sensitive total electron yield (TEY) mode by acquiring drain current from the sample as a function of the photon energy. The incidence angle of the beam was kept at 30°. XMCD spectra were obtained by calculating difference between XAS signals with parallel and anti-parallel alignment of the magnetization direction with respect to photon helicity vector. To minimize the apparatus-related magnetic field influence on the electron yield detection, the sample was negatively biased to a few tens of volts with respect to the ground. BL16A beamline is highly suitable for XAS and XMCD measurements as it provides fast helicity switching using two high-brilliance undulators.
3 Results and Discussion

Ni/MnF₂ heterostructures

The XAS and XMCD spectra for Ni/MnF₂ heterostructures are shown in Fig. 2. A clear XMCD signal with opposite signs at L₁ and L₂ edges was found at Mn edge only after sample cooling (22K). There is no presence of XMCD signal at 300K. As XMCD signals for Ni and Mn have opposite signs, we can conclude that the Mn magnetic moments are antiparallel aligned with respect to FM magnetization.

XAS and XMCD line shapes of Mn are similar to those observed earlier in Co/MnF₂ [3]: XAS spectra match the absorption of the Mn²⁺ ion calculated within the atomic multiplet theory, assuming the octahedral crystalline field with 10Dq=0.75 eV [3, 4]. On the other hand, Mn L₂,3 dichroism line shape (Fig. 2) reflects a reduced crystal field with respect to the bulk fluoride. This can be ascribed to the fact that the Mn ions contributing to the dichroism are localized at the interface region, where ligand field effects can be altered with respect to the bulk MnF₂. This suggests that the Ni/MnF₂ interface is chemically stable and no chemical reaction has occurred. The antiferromagnetic interaction between the Mn and Ni spins could be explained in terms of a superexchange coupling mediated by the fluorine ions at the interface region, similarly to the transition metal oxides.

It should be mentioned that in the case of Co on MnF₂ a net ferromagnetic moment induced by the FM layer exists in the AFM layer at the FM/AFM interface even at 300 K [3] - well above T_Néel for bulk MnF₂ (67 K). Meanwhile in the case of Ni on MnF₂ the induced moment is significantly smaller and can be seen in XMCD only at low temperatures. This behavior can be associated with the difference in the net magnetic moments per atom and magnetic anisotropy of cobalt and nickel.

After field cooling of Ni/MnF₂/CaF₂/Si(111) heterostructure, element spécifique hysteresis loop measured at Ni L₃ absorption edge demonstrated negative exchange bias with the bias field in the range of 50 Oe and coercivity field of 100 Oe. Fig.3. The measured H_{EB} values are compatible with results reported in the literature for similar systems [3]. Positive exchange bias shift was never detected in this study, up to the highest cooling fields applied to the system (1.2 T) as well as in the case of previously studied system Co/MnF₂ [3].

![Fig. 3: Element selective hysteresis loop of nickel measured at T=22 K after field cooling at H_{Ec}=1.2 T](Image)

As it was mentioned earlier, nickel layer is formed by nanoparticles below ~5 nm in size. For samples with different nickel exposure and consequently different particle size (with a nominal thickness of 2 and 6 nm) different nickel XMCD lineshape was observed (Fig. 4). This behavior differs from what was observed for cobalt particles, where the m/mₐ ratio coincides with the bulk value and varies for 2 and 6 nm thick FM layer.

<table>
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<tr>
<th>Ni layer thickness and corresponding m/mₐ ratio</th>
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<tbody>
<tr>
<td>2 nm Ni</td>
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<tr>
<td>6 nm Ni</td>
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<td>bulk Ni</td>
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This behavior differs from what was observed for cobalt particles, where the m/mₐ ratio coincides with the bulk value (0.07).

Co/NiF₂ heterostructures

XAS and XMCD spectra for Co/NiF₂ heterostructures are shown in Fig. 5. It was observed that the magnetized Co induces a net magnetic moment on Ni in the proximity...
of the interface well above Neel temperature. A clear XMCD signal with opposite signs at L$_3$ and L$_2$ edges was found at Ni edge. As XMCD signals for Co and Ni have the same sign, one can assume that the Co and Ni$^{2+}$ moments couple parallel, as opposed to the observed earlier antiparallel magnetisation alignment in Co/MnF$_2$ system [3].

Element specific magnetization curves for Co/NiF$_2$/CaF$_2$/Si(111) heterostructures were obtained by measuring Co and Ni L$_3$ absorption edges as a function of applied magnetic field (Fig.6). Hysteresis loops of Ni exhibit the same shape and width as those of cobalt, showing that Ni$^{2+}$ moments follow the magnetization of Co.

After field cooling Co/NiF$_2$ heterostructures demonstrate negative exchange bias with bias fields in range of (50..30 Oe).

The doublet structure at the L$_3$ and L$_2$ edges observed in NiF$_2$ XAS are the characteristic features of the Ni$^{2+}$ ion in the octahedral crystal field [4] indicating that NiF$_2$ surface is not changed by the proximity of the Co layer. In contrary the Ni L$_{2,3}$ XMCD lineshape shows structure, which is different from isolated Ni$^{2+}$ ion in the crystal field and looks more like a metallic nickel (Fig.2). Moreover it was observed that the value of induced magnetic moment is not changing with temperature. This can be ascribed to the fact that Ni ions at the interface can be in direct exchange with Co atoms. Another possibility is interdiffusion, loss of fluorination or nickel segregation, but XAS spectra in highly surface sensitive TEY mode show none of these characteristic features. Furthermore it is worth noting that no XMCD signal was detected for the bare NiF$_2$/CaF$_2$/Si(111) surface, therefore the existence of the ordered Ni moments must be due to the interfacial interaction between NiF$_2$ and Co.

It is obvious that the proximity effect is dependent on the interface area. Another interesting possibility was to observe the interlayer coupling between FM layers through thin AFM layer. For this reason we have grown a multilayered structure with 5 periods, schematically presented in Fig.4. FM and AFM layers with identical thicknesses equal to 2 nm were grown at 400K. The RHEED patterns during the growth were reproducible from layer to layer, indicating epitaxial quality of the heterostructure. Vivid Ni$^{2+}$ XMCD signal of the same sign as that of Co was observed. Element specific magnetization curves obtained at Co and Ni absorption edges (Fig.7) prove that Ni moments rotate and follow the magnetization of the Co upon field reversal. Interestingly after field cooling of the multilayered structure no exchange bias was observed. This fact can be associated with small thickness and volume of the AFM layer. Shape of the hysteresis loop did not indicate any special alignment between FM layers except FM one. Coercivity field is varied from 0.5 kOe @ 300K to 1.2 kOe @ 4K. Such multilayer structures can be attractive for further resonant X-ray and polarized neutron reflectivity investigations.

### 3 Conclusion

It was found that the magnetized Co layer induces a net magnetic moment at the interface with AFM at 300 K - well above $T_{\text{Neel}}$ for bulk NiF$_2$. Orientation of Ni$^{2+}$ magnetic moments was found to be parallel with respect to Co magnetization, on the contrary to antiparallel alignment in Co/MnF$_2$ system observed earlier [3]. In case of Ni FM layer on top of MnF$_2$, prominent proximity induced magnetization, coupled antiparallel to the FM, was observed only at low temperatures.
In general XMCD signal is more pronounced in AFM films with smaller crystallographic domains grown at lower temperatures, as compared to the films with higher crystalline quality grown at high temperature. No XMCD signal was observed in the case of inverted structures with fluoride layer grown on top of FM. This can be related with polycrystalline nature of AFM layer grown on top of thick FM layer at 300K. Growing at higher temperatures is undesirable since it results in change of FM layer morphology.

Acknowledgement
The study was carried at PF out along the 2011G592 proposal. The authors wish to kindly acknowledge the BL16A beamline staff (Prof. Kenta Amemiya and Dr. Masaaki Sakamaki) for precious technical assistance during the experiments. The authors appreciate financial support from the European Commission via project ONDA FP7-PEOPLE-2009-IRSES-247518.

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