Magnetic properties of Eu-Fe thin films

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We studied the formation of alloys and compounds of the Eu-Fe binary system, in the form of thin films, prepared using molecular beam epitaxy. Diffraction and photoelectron spectroscopy investigations revealed mixing of the elements during the annealing at relatively low temperature. Magnetic studies showed ferromagnetic behavior up to 400 K, and strong thermomagnetic effects and exchange bias indicating the presence of an antiferromagnetic phase and superparamagnetic particles. X-ray photoemission microscopy with dichroic contrast confirmed this hypothesis, showing two types of Eu-Fe alloys with various stoichiometries and showing ferromagnetically ordered particles of 100–500 nm in size. Ferromagnetic particles contain divalent Eu atoms, whereas the antiferromagnetic alloy is probably composed of the trivalent Eu atoms detected in the photoelectron spectra. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4797622>]

RareEarth_xTransitionMetal_y compounds with different stoichiometries have been extensively studied during the last decades, especially from the point of view of their interesting magnetic properties.¹ In RE–Fe binary alloys, the magnetic ordering temperature is influenced mostly by the type of RE atoms present, and is proportional to the magnitude of RE spin (T_C is the highest for Gd-Fe with the largest RE spin, and it decreases for Tb-Fe, Dy-Fe alloys).¹ The number of bulk form RE-Fe compounds is relatively large; nevertheless, it is limited to a few stoichiometries: RE₂Fe₃, REFe₃, RE₆Fe₂₃, RE₂Fe₁₇.² There is only limited information about the formation of stable compounds between iron and europium.³

The magnetic properties of europium are directly connected to its valency state; Eu³⁺ is non-magnetic ($J=0$), while Eu²⁺ has a large pure spin moment ($J=7/2$). Metallic europium is divalent, but in alloys or intermetallic compounds, Eu may be in a divalent, trivalent, or intermediate-valency state. The ability to control the Eu valency, and consequently to switch between the non-magnetic and magnetic states of Eu, led us to study the Eu-Fe system.

Similarly, as in the cases of Eu-(Mn, Cr),^{4,5} the Eu_xFe_y films were grown on Si or GaAs (with a 50 nm thick buffer layer of Mo) substrates in a wide x and y ranges (EuFe, EuFe₃, EuFe₅, Eu₂Fe₁₇) with a molecular beam epitaxy (MBE) deposition system. Two deposition modes—multilayer deposition and co-deposition were used. To form the Eu_xFe_y compounds, the films were annealed up to 500 K. Most films were then capped by a protective thin film (up to 3 nm) of Mo.

To examine the possibility of the formation of new ordered phases in the Eu-Fe system, we employed Reflection High Energy Electron Diffraction (RHEED) and X-ray Photoelectron Spectroscopy (XPS). Further structural characterization was carried out with the use of X-Ray Reflectivity (XRR) and X-Ray Diffraction (XRD). The magnetic properties were determined based on SQUID measurements and X-Ray Photoemission Microscopy (XPEEM).

Structural changes in the deposited layers were observed by RHEED, both after deposition and after the annealing process. In both cases, the films exhibit polycrystalline structure. Visible blurring of the rings indicates amorphization of the surface or some other dynamical processes. During the annealing process, observed changes in distances between diffused spots could indicate film texture changes, or that some additional strains occurred.

The X-ray reflectivity measurements (Fig. 1) showed that a uniform layer (see Fig. 1, inset), composed of a mixture of Eu and Fe, is formed on the top of Si/Mo substrate. Well-defined oscillations in the XRR patterns allowed for calculations (Reflectivity 2000 program) of the thickness of the films. It was found that they are in good agreement with the assumed ones; typically the calculated thicknesses were several angstroms smaller than the assumed ones. This would suggest that the Eu and Fe atoms are mixing, and form more closely packed structures in such mixtures.

Possible formation of new Eu_xFe_y phases has been verified through the XRD research. Unfortunately, no atomically ordered intermetallic phase could be resolved. Even in the low incident angle analysis mode, the only apparent diffraction peaks come from the substrate or the protective Mo coating.

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FIG. 1. Electron density profile (blue) calculated from the specular reflectivity (black and red) for the film with assumed stoichiometry EuFe_5 .

The photoemission spectra of core levels were systematically taken after the deposition of Eu-Fe multilayers or co-deposited layer and later during the annealing process. For all examined films in the Eu-Fe system, both Eu and Fe exhibit typical metallic behavior after deposition. Chemical shifts of the core levels (e.g., Eu $3d$ up to 8.9 eV and Fe $2p$ up to 0.2 eV) and relative changes in the Eu $4d/\text{Fe } 2p$ line area ratio monitored by the XPS during the annealing process indicate mixing between Eu and Fe layers. A relatively low content of oxygen was observed after the annealing process. For almost all examined films of the Eu-Fe system, valence transition from Eu^{2+} to Eu^{3+} was observed (see Fig. 2), however, for selected compositions, the Eu^{2+} was still observed by the low intensity contribution to the $3d$ and $4d$ spectra.

Magnetic properties of the annealed films were studied with the use of a SQUID magnetometer in the temperature range of 1.9–400 K and in fields up to 7 T. All the measured samples showed similar features (see Fig. 3)—ferromagnetic behavior up to the highest available temperature of 400 K and strong thermomagnetic effects. Typical for Eu-Fe system temperature dependence of magnetic moment (M-T), obtained in both zero-field cooled (ZFC) and field cooled (FC) modes, are different in nature than that observed in Eu-Mn or Eu-Cr systems.^{4,5} Here, the magnetic behavior is associated mainly with the iron atoms or their clusters. From magnetization measurements obtained with the use of Physical Property Measurement System (PPMS magnetometer), we estimate T_c to be at least 600 K. For higher temperatures, irreversible degradation of the films was observed.

The most important feature of the M-T curves obtained at applied field of 100 Oe is a strong thermomagnetic effect seen as irreversibility in FC and ZFC modes. The irreversibility can be attributed to the slowing of the spin relaxation times, which is caused by the distribution of the coercivity in

FIG. 2. Changes of Eu $3d$ core level during the annealing process for the EuFe_5 film.

FIG. 3. M-T curves obtained for films with assumed stoichiometries (a) EuFe_5 , (b) EuFe_3 , (c) EuFe , (d) Eu_xFe_y . Listed Eu/Fe ratios have been calculated from the XPS spectra obtained after the annealing process.

ferromagnetic particles. For the M-T curves obtained in measurements performed in ZFC mode, the magnetic moment increases more rapidly than for those performed in FC mode. This behavior is a typical characteristic of the blocking process for an assembly of superparamagnetic nanoparticles, but can be also linked to the spin glass materials.^{6,7} Frustration in the magnetic ordering can also lead for similar thermomagnetic effects.

Besides the irreversibility, there are a number of additional important features manifested in the M-T curves in both modes. One characteristic feature, which can be seen in M-T curves obtained in ZFC mode, is the presence of a broad maximum. The maxima in the M-T curves measured in the ZFC mode are related to the superparamagnetic unblocking process of single domain particles (in other words, it is related to the average blocking temperature of the particles). Most likely, the particles become superparamagnetic at temperatures above that observed maximum.

Looking more closely at M-T curves measured in FC mode, some additional features allow us to qualify two of the films as spin glass or super spin glass like materials. The films with the Eu/Fe ratio 0.82 and 1.4 have minima in the M-T curves in FC mode at 18 K and 22.3 K, respectively. This behavior is only observed in spin glass and super spin glass systems.^{6,7}

Another important feature is an unusual and rarely observed effect; the value of the magnetic moment measured in ZFC mode exceeds the one found in the FC mode. This

effect was observed for three films (see Figs. 3(b)–3(d)). Such an unusual effect was seen only in a very limited number of materials, for example, in amorphous flash-evaporated Pd-doped NiMn thin films.⁸ With regard to the results presented in Fig. 3, the model proposed in Refs. 8 and 9 could be introduced with the assumption that a layer of pure Fe or Eu-Fe mixture with some specified Eu/Fe ratio plays the role of the classical ferromagnetic phase, whereas the antiferromagnetic regions consist of a Eu-Fe mixture (with different Eu/Fe ratio) or pure Eu. The XRR results, however, show no separated Eu, Fe, or Eu-Fe layers, therefore, we attribute each particular region to relatively small (too small to give peaks in XRD diffraction pattern) Eu or Eu-Fe nanoparticles. This effect was the greatest for the co-deposited film (Fig. 3(d)), which might be an additional indication that the antiferromagnetic phase is rather uniformly distributed in the film.

The observed field dependence of the peak in M-T curves (Fig. 3(b)) in the ZFC mode as well as rather weak changes in the temperature dependence of the FC magnetization indicate a cluster spin glass like behavior, with some strong interactions between the particles.¹⁰ The separation of the FC and ZFC branches of the M-T curves obtained at 50 Oe and 100 Oe for the EuFe₃ film is still visible (Fig. 3(b)). The blocking temperature decreases as the field increases from 50 to 100 Oe. This essentially means that for higher applied fields, the effective spin reorientation barriers are lowered. Additionally, for measurements performed in the applied field of 50 Oe, in contrast to the one performed at 100 Oe, the M-T curves in ZFC mode are not above the one measured in FC mode. This would suggest that a 50 Oe external field is too low to see the impact of antiferromagnetically ordered regions on the FC and ZFC branches, as was observed for 100 Oe.

For all examined films, the hysteresis loops revealed a decreasing value of coercive field with increasing temperature. The exchange bias phenomenon was observed in the M-H hysteresis loops for all examined stoichiometries and for both deposition modes: multilayer deposition and co-deposition process. Exchange biasing in the uniform layer confirms the presence of antiferromagnetically ordered regions. We attribute the exchange biasing to the interaction between anti-ferromagnetically oriented regions originating from the Eu-Fe alloy, and a ferromagnetic Fe or Eu-Fe phase. Similarly, exchange biasing was observed in ferromagnetic Co layers with embedded antiferromagnetic CoO nanoparticles.¹¹ To confirm the origin of the exchange biasing, we studied the EuFe₅ film with the use of the XPEEM microscope at the PoLux beamline of the Swiss Light Source (SLS) synchrotron. The ELMITEC (PEEMIII) spectromicroscope was used, and measurements were performed at the room temperature. The photoemission images were registered for photon energies corresponding to the Fe L_{2,3} edge and Eu M_{4,5} edge for right and left circularly polarized light. The photoemission maps exhibit a clear heterogeneity of the film. There are regions (100–500 nm in size) rich in Eu embedded in the Eu_xFe_y matrix (Fig. 4). These regions show a clear dichroic effect obtained by subtraction of the RCP and LCP intensity maps obtained at the Eu M_{4,5} edge, while the Fe L lines hardly show any dichroism. This may be

FIG. 4. PEEM images of EuFe_{0.36} film obtained at the photon energies of Eu M_{4,5} (a) and Fe L_{2,3} (b) absorption edges and magnetic dichroism in photoemission (XPEEM images) obtained by subtracting the images acquired with left (LCP) and right (RCP) circularly polarized light energies corresponding to the Eu M_{4,5}, (c) field of view—10 μm.

related to strong Fe-Eu interactions, leading to ferromagnetic ordering within the Eu rich spots. These spots contain magnetic Eu²⁺ atoms, whereas the matrix is probably rich in non-magnetic Eu³⁺ atoms. The lack of dichroism in the Fe rich matrix means that this region is ordered antiferromagnetically. Taken together, this would explain the exchange biasing and freezing of the ferromagnetic particles observed for the ZFC mode. The ferromagnetic phase may have a well-defined Eu/Fe ratio, though it is not clear whether any atomically ordered phase is formed.

Even if the formation of new ordered Eu-Fe compounds was not observed, the Eu-Fe films still exhibit a few interesting properties. The RHEED, XRR, as well as XPS measurements indicate mixing between Eu and Fe layers. The valence transition of europium from Eu²⁺ to Eu³⁺ was observed for most samples. The magnetic properties, verified via SQUID, PPMS, and XPEEM, result from the presence of an antiferromagnetic phase and superparamagnetic regions composed from a mixture of Eu and Fe atoms with different Eu/Fe ratios.

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