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Positive exchange bias of EuO_{1-x} films

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ABSTRACT

We have investigated the magnetic properties of oxygen-deficient europium monoxide EuO_{1-x} films prepared on (0 0 1)-orientation Si single crystal substrate *via* laser-MBE. Stoichiometric EuO and reduced EuO_{1-x} films are deposited by adjusting the annealing conditions of Si wafers pre-deposition. An enhanced Curie temperature (T_C) from 69 K to 150 K is observed by introducing oxygen vacancies to EuO, which is due to the formation of magnetic polarons. The EuO_{1-x} films exhibit positive exchange bias when the films enter the Heisenberg ferromagnetic phase at a lower temperature, which suggests that an antiferromagnetic coupling between the magnetic polarons and Eu^{2+} 4*f* spins which is ordered in the typical Heisenberg ferromagnet.

1. Introduction

Europium chalcogenides (EuX, X = O, S, Se, and Te) are magnetic semiconductors that are of great signification for spintronics and magneto-optical applications [1]. Novel spintronic couples an electron's spin with its charge and can have the greatly promise applications of nonvolatile logic circuits and microprocessors, high-density memory device with faster data processing speed [2,3]. EuO, a Heisenberg ferromagnetic semiconductor with a narrow bandgap of 1.12eVand a Curie temperature T_C of 69 K, is of particular interest [1]. It is known that the seven unpaired 4*f* electrons of Eu^{2+} form an exact half-filled 4*f* subshell, and the Eu^{2+} moments are coupled to each other to become ferromagnetically aligned below T_C. So EuO is a rare example of ferromagnetic semiconductor with a localized magnetic moment of $7.0\mu_B$ [1]. Not only does doped-EuO exhibit a high spin polarization close to 100% due to enormous exchange splitting of its conduction band [4], it also can be conductance-matched with Si [4,5] or chemical doping with trivalent rare-earth atoms such as Gd, La, or Lu [6–8]. Moreover, topological Hall effect and anomalous Hall effect have been observed in a number of EuO films suggesting EuO may belong to the interesting group of topologically driven materials with strong spin-orbit coupling [9,10]. For example, Ohuchi et al. found that magnetic skyrmions may be present in the Heisenberg ferromagnet of EuO as evidenced by the topological Hall effect [9].

Additional research have reported that the T_C of EuO can be enhanced significantly, and the increase of T_C may be originated from the enhanced exchange coupling by donor states and/or conduction electrons by electron doping *via* oxygen vacancies or trivalent rare-earth ions [11–14]. We have found in our previous studies that the doped electrons may form magnetic polarons with the nearby Eu^{2+} 4*f* spins in reduced EuO_{1-x}, which is the origin of the magnetic ordering above 69 K [15,16]. A model of magnetic polaron can provide a direct and better explanation for the "double dome" feature seen in the *M vs T* curve than the alternative models. Below 69 K, there appears an antiferromagnetic (AFM) coupling between the magnetic polarons and Heisenberg ferromagnet as suggested in experimentally observed inverted hysteresis loops [15,16]. It turns out that these magnetic polarons imbedded in the Heisenberg ferromagnet may manifest themselves as magnetic Skyrmions [9,10].

In this paper, we prepared the EuO_{1-x} films on (0 0 1)-Si substrate *via* laser assisted molecular beam epitaxy (laser-MBE) technique and investigated the magnetic properties of these thin films. The enhanced *Tc* is observed in EuO_{1-x} originating from the formation of the magnetic polarons due to electron doping by oxygen vacancies. Magnetic hysteresis loops exhibit positive exchange bias (loops shift toward positive field after cooling in a magnetic field), which is a clear evidence for AFM coupling between the magnetic polarons and the Eu^{2+} spins ordered in the Heisenberg ferromagnet.

2. Experimental details

The stoichiometric and oxygen-deficient europium oxide films on Si (1 0 0) wafers were prepared using the laser-MBE method. The Si wafers from MTI Corp. were firstly chemically etched with 5% diluted hydrofluoric acid (HF) and then rinsed with deionized water to remove the native oxide SiO_x layer, and finally immediately placed in the vacuum chamber after cleaning with acetone. The targets were high-quality Eu (99.9%) metal (purchased from Alfa Aesar). The pulsed

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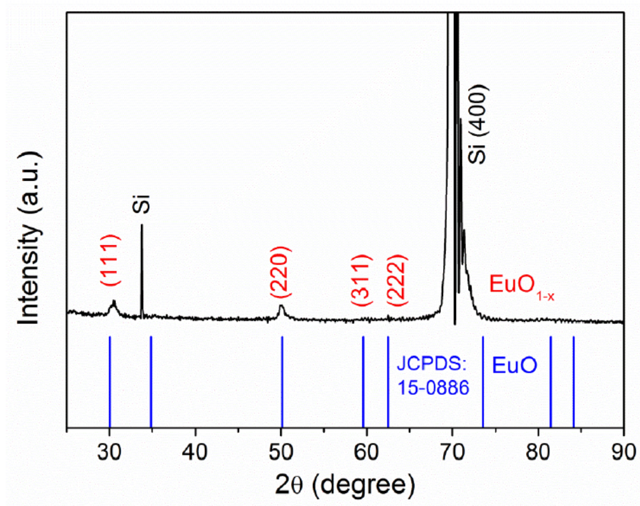

Fig. 1. X-ray diffraction pattern of a EuO_{1-x} film. Blue bars in the lower panel indicate the standard XRD peak positions of EuO from JCPDS: 15-0886.

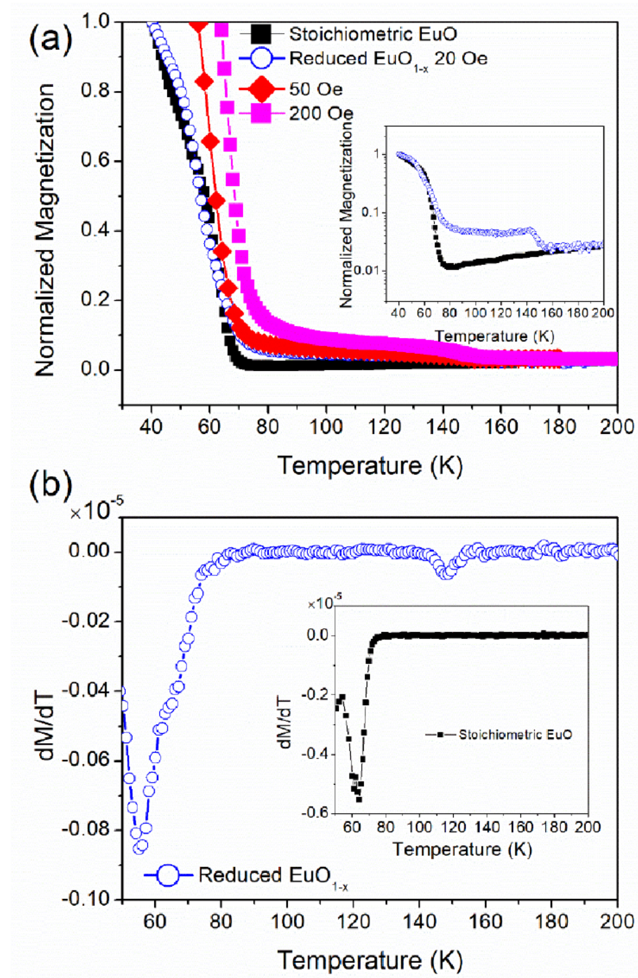

Fig. 2. M-T curves under different in-plane field after zero-field cooling or field cooling. (a) Magnetization as a function of temperature of EuO and oxygen-deficient EuO_{1-x} films. Inset: Logarithmic scale of normalized magnetization as a function of temperature. (b) Derivative of the magnetization as a function of temperature of EuO (inset), and oxygen-deficient EuO_{1-x}.

excimer laser uses KrF (λ = 248 nm, Compex 201) and produces a laser beam with the output of 100 mJ of intensity and 3 Hz of repetition rate at a substrate temperature of 150 °C during the deposition. After the deposition of the 20 nm films, the films were *in situ* annealed for 20 min., followed by covering a SnSe (15 nm, a non-magnetic material) capping layer on obtained EuO films at room temperature to prevent the degradation of EuO films and the formation of Eu^{3+}. On the other hand, before the deposition for oxygen-deficient EuO_{1-x} film, the single-crystal Si substrates were annealed at 700 °C in vacuum of 10^{-7}Torr in order to further remove the adsorbed oxygen from the surface of the wafers. The stoichiometric EuO film was grown using laser-MBE under the same conditions without the annealing process.

X-ray diffraction of the films was measured using X' Pert XRD spectrometer (PANalytical, Netherlands) with Ni-filtered Cu K_α radiation of λ = 1.5406 Å. The DC magnetic properties were collected using the vibrating sample magnetometer (VSM option) in a PPMS from Quantum Design Inc. (USA).

3. Results and discussion

Fig. 1 displays the θ-2θ X-ray scan spectra of obtained EuO_{1-x} films on surface-treated Si substrate, indicating the fcc rock salt crystal structure (Fm3m) of reduced EuO_{1-x} film. No impurity phase is observed in the EuO_{1-x} films, where the corresponding substrates were annealed at 700 °C for 25 min. It is difficult to form single crystal EuO film on Si substrate due to the large interfacial lattice misfit. The stacking planes are mainly aligned with the (1 1 1) and (2 2 0) orientations, somewhat different from the usually observed (1 1 1) and (1 0 0) planes [17]. The XRD shows that the polycrystalline oxygen-deficient EuO_{1-x} is of high-quality and textured. And the lattice constant of this oxygen-deficient EuO_{1-x} film is a = 5.0769 Å, smaller than that of EuO single crystal (a_{EuO} = 5.1439 Å, PDF#15-0886).

The temperature dependence of the magnetization was used to determine the Tc of the films. Fig. 2 shows the temperature-dependence magnetization $M(T)$ curves of EuO and EuO_{1-x} which the field is applied in-plane and H = 20 Oe. The films exhibit a ferromagnetic (FM) onset at 69 K for the stoichiometric EuO (similar to that of EuO single crystals) [4,18]. However, for oxygen-deficient EuO_{1-x} films, the Tc is enhanced to as high as150 K from the normalized magnetization M –T curve. Although the measured moment is relatively small above 69 K and the so-called "double-dome" feature is not as pronounced in our reduced EuO_{1-x} films, one still sees clearly the onset of the magnetic ordering near 150 K, which suggests that the film is lightly oxygen deficient [15]. Here we change the plot to the logarithmic scale of magnetization to reveal more details of the temperature dependence of magnetization behaviors, as illustrated in the inset of Fig. 2(a). The double-dome feature is much clearer. These properties can be seen clearly in Fig. 2(b), in which the dM/dT is exhibited as the relation of temperature T. EuO shows one dip at ~65 K. While the dip in the $dM/dT \sim T$ curve may not be an accurate estimate of the Curie temperature of our films, it is possible that the T_C of the films are slightly lower than 69 K because of the surface-induced effects due to the reduction of the amount of nearest neighbors, surface band bending, as well as the partial depopulation of the 4f states of Eu [12]. T_C has been found to decrease with decreasing film thickness in both experimental and computational studies [12,19]. The reduced EuO_{1-x} films have two dips in the dM/dT curve: a dominant one around 60 K and the other just below 150 K.

Fig. 3(a) and (b) show the typical temperature dependence magnetic hysteresis loops (M-H at T = 20–80 K) for the EuO film. Characteristically ferromagnetic can be observed clearly from the M-H loops. The coercive fields (~40 Oe) for stoichiometric EuO film at 20 K is typical for high quality EuO films [4,18]. The saturation magnetization is significantly reduced with increasing temperature. Fig. 3(c) and (d) show the M-H curves at different temperatures (from 20 K to 120 K) for the EuO_{1-x} film. Although the M-H curves are similar to those of stoichiometric EuO at low temperature, there are major

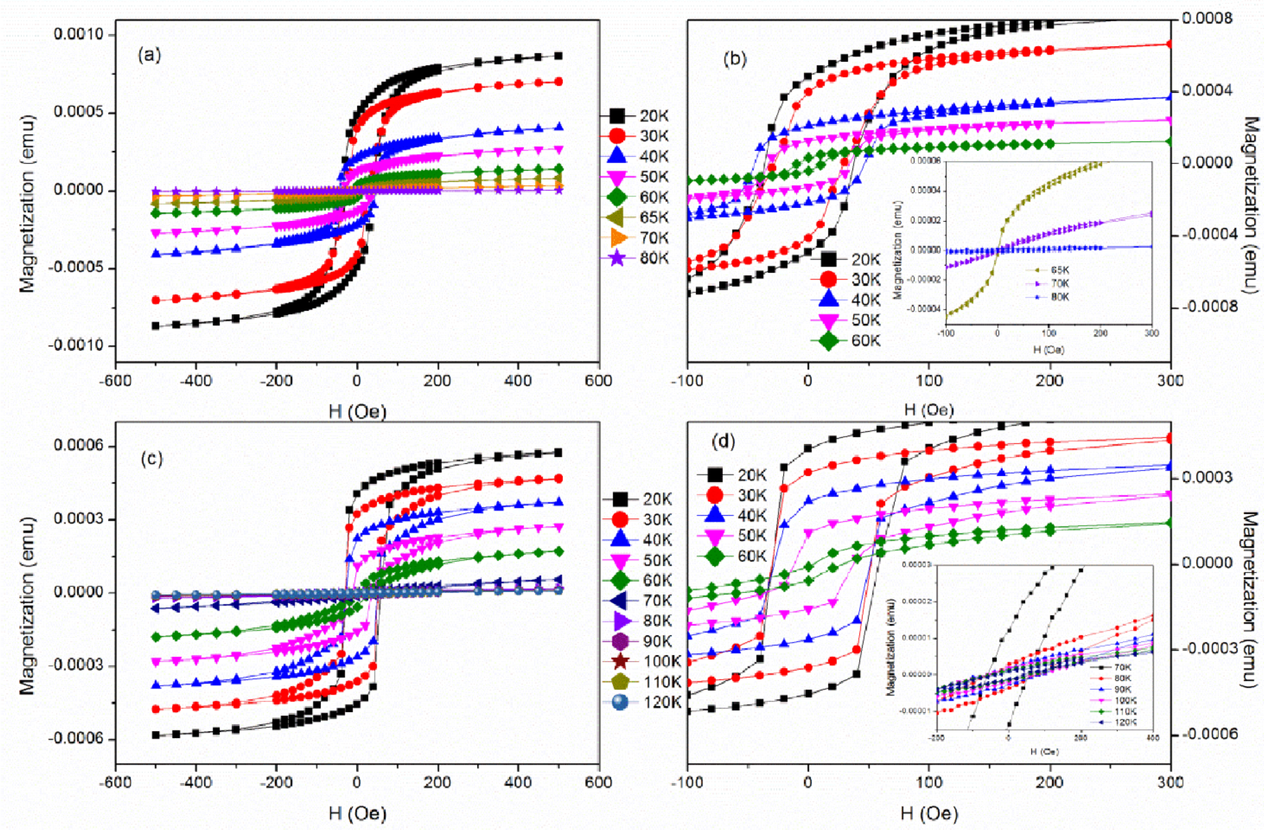

Fig. 3. In-plane M-H curves at different temperatures. (a) Magnetization as a function of applied field over the temperatures range from 20 to 80 K for EuO. (b) Details of the M-H curves in the low field region for EuO. (c) M-H curves at different temperatures for the lightly reduced EuO_{1-x} film. (d) Details of the M-H curves in the low field region for EuO_{1-x}.

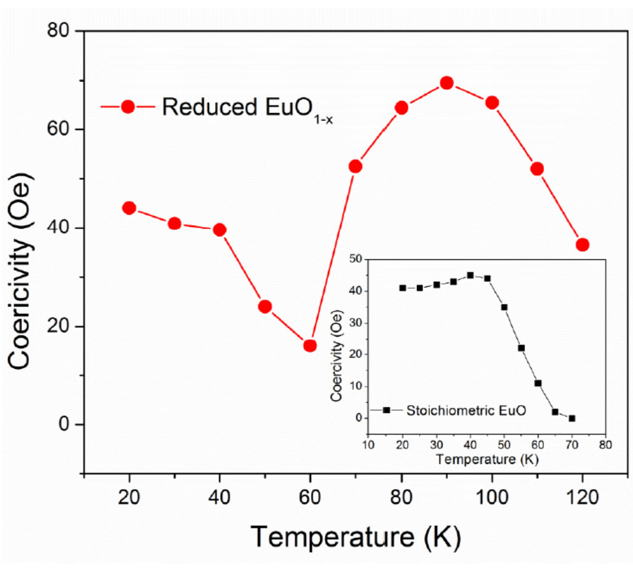

Fig. 4. Coercivity of EuO and EuO_{1-x} films as a function of temperature.

differences at high temperatures ($T > 69$ K). Apparent open M-H loops are observed throughout the entire temperature range shown. The coercivity of reduced EuO_{1-x} goes down initially with the increase of temperature below 69 K, reaching a minimum near 69 K, then rapidly increases to the peak with increasing temperature, and finally decreases again until the sample becomes paramagnetic. Fig. 4 is the plot of the coercivity H_C extracted from Fig. 3 as the function of temperature. The hysteresis and variation of H_C have been observed before [15,16] and are consistent with the formation of magnetic polarons at high temperatures in EuO_{1-x}. The dependence of the coercivity on the temperature for EuO_{1-x} films is similar to those reported in hard/soft FM composites with an exchange-spring behavior [20]. Indeed, the two systems are very similar in $Pr_{1-x}Ca_xCoO_3$, there is an unusual form of magnetoelectronic phase separation where long-range ordered ferromagnetism coexists spatially with short-range ferromagnetism with strong coupling between the two. This high temperature short-range ferromagnetically ordered state is of magnetic polaron in origin according to the authors. In electron-doped EuO system, the increased T_C also originates from the formation of magnetic polarons. The carriers are trapped by donor states and polarize the 4*f* electrons around the carriers, which forms bound magnetic polarons. These magnetic polarons have fairly large diameters (Here the estimated polaron diameter is around 5 nm, see Ref. [16]) due to the high dielectric constant of EuO and overlap to a certain degree to form a ferromagnetically ordered state below 150 K. Since the Eu local spins are fully aligned only at the very low temperature, the magnetic polaron state can be stable below 69 K extending over quite a large temperature range and co-exists with the long-range low temperature Heisenberg ferromagnet. The magnetic polaron model has been proposed for EuO both experimentally [21] and theoretically [22–24]. Experimental evidence for the presence of magnetic polarons in electron-doped EuO has been presented in many other reports, e.g., low-energy muon spin relaxation [25], NMR [26], optical absorption [27], Raman scattering [28], infrared magneto-optical imaging [29] and electron paramagnetic resonance [30] studies.

Exchange bias is usually associated with heterogeneous systems composed of ferromagnetic (FM) and antiferromagnetic (AFM) spin structures, when the system is cooled down from high temperature in a

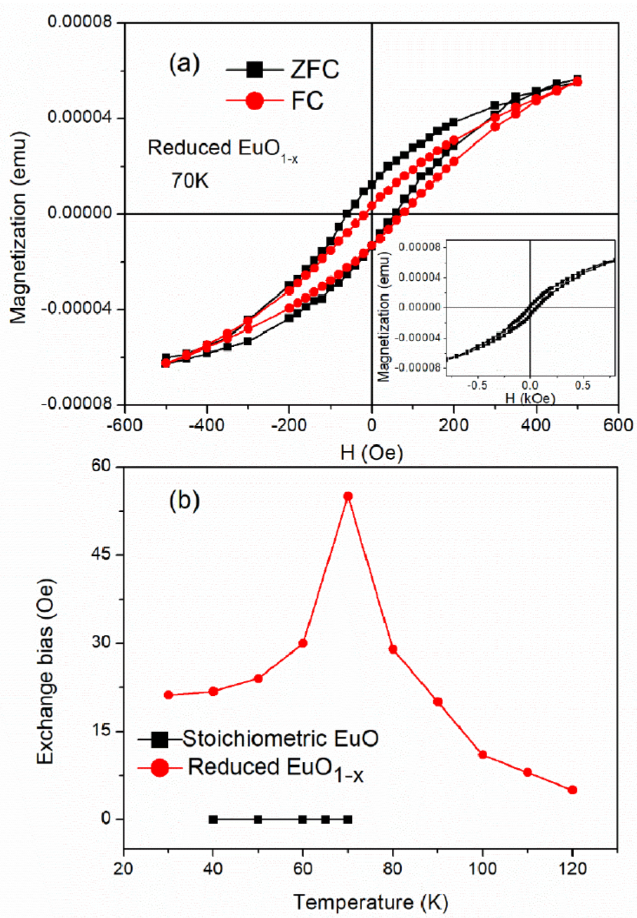

Fig. 5. (a) The hysteresis loops at 70 K measured after ZFC and FC processes for the reduced EuO_{1-x} film. Inset is the M-H loop after FC process at H = 50 Oe in-plane field, showing the exchange bias is about 50 Oe. (b) Temperature dependence of the exchange bias field in EuO and EuO_{1-x} films.

magnetic field. The common explanation is the interfacial exchange coupling between FM and AFM. Therefore, we measured the *M-H* hysteresis loops of reduced EuO_{1-x} film at different temperatures after field-cooling process (FC). Different from the normal hysteresis loops centered at zero field for zero-field-cooling (ZFC), a right-shift of the loop is observed when the reduced EuO_{1-x} film is cooled down from 300 Kin a field of H = 20 Oe, as shown in Fig. 5(a). This is indicative of exchange bias in EuO_{1-x}. What is also to be noted is that the loop is shifted toward positive field. While the commonly known exchange bias in a ferromagnet/antiferromagnet system is negative (loop shifting in the opposite direction of the cooling field), positive exchange bias is rare. For samples consisting two ferromagnetic components, positive exchange bias is an indication of AFM coupling between the two [31,32]. Our data provides strong direct evidence that there exists AFM coupling between the Eu spins ordered in the Heisenberg ferromagnet and the magnetic polarons. This AFM coupling is also the reason for the inverted hysteresis loops observed around 70 K in a different sample reported before [15]. Fig. 5(b) shows the temperature dependence of the exchange bias field in the film. The exchange bias peaks sharply at 70 K. As the temperature decreases from 70 K, the magnetization of the Heisenberg ferromagnet increases rapidly, and the exchange bias decreases accordingly since it is inversely proportional to the magnetization [33]. At temperatures higher than 70 K, the spontaneous magnetization of the Heisenberg magnet disappears but some remains possibly sustained by the applied magnetic field, which also reduces the exchange bias. It should be noted that, in a magnetic field, the ferromagnetic clustering and/or ferromagnetic ordering in EuO structure can persist to about 30–40 K above the Curie temperature [34].

The reason for the AFM coupling is as follows. According to the physical model of magnetic polaron [16], the conduction band (Eu 5*d* and 6*s*) in electron-doped EuO_{1-x} structure has already undergone somewhat exchange split near 69 K, resulting in the majority states are lowered than normal structure although they have not overlapped the defect level (that can happen when the temperatures is far below 69 K and the insulator-to-metal transition occurs), which is formed by trapping the doping electrons and located in the bandgap of EuO structure. The hybridization between the conduction band and the defect states is favorable for the doped-electrons to align their spins in the direction of the majority states, that is, in the same direction as those Eu spins ordered in the Heisenberg ferromagnet [35]. Considering that the Eu^{2+} 4*f* orbital is half-filled, the doped electron donating from the oxygen vacancies in reduced EuO_{1-x} bound to the defect level will align the spins of the adjacent Eu^{2+} ions to be antiparallel to its own spin, thereby forming a magnetic polaron, according to the Hund's rule-like coupling. This can result to the characteristically AFM coupling between the magnetic polarons (which Eu also attributes to the mostly moment) and the Eu moments in the Heisenberg ferromagnet. Our experiment verifies that the magnetic polarons are stable over a certain temperature range below 69 K.

Recently, magnetic Skyrmions have been reported in EuO below 69 K via the detection of topological Hall effect [9,10] and first-principles calculation [36]. It is entirely possible that the magnetic polarons evolve into topologically non-trivial magnetic Skyrmions instead of staying as topologically trivial polarons *via* broken time reversal symmetry or spatial inversion symmetry when the host becomes ferromagnetically ordered. The positive exchange bias may attribute to the AFM coupling between the magnetic Skyrmions/polarons and their ferromagnetic host.

4. Conclusion

In summary, we have investigated the abnormal magnetic properties of the oxygen-deficient EuO_{1-x} thin films which are grown by laser MBE. A positive exchange bias has been found experimentally, which is attributed to the AFM coupling between the magnetic Skyrmions/polarons and their ferromagnetic host. The positive exchange bias is a direct indication for the presence novel spin texture in the EuO_{1-x} films and offers a bulk measurement to experimentally detect such spin textures.

Acknowledgments

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