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Magnetization modulation by ferroelectric polarization switching is reported for the ferromagnetic-ferroelectric EuO/$BaTiO_3$ heterostructure. The value of the magnetization critical exponent β is consistent with the expected Heisenberg-like ferromagnetism of EuO and reported Curie temperature. The critical exponent is seen to decrease with increased magnetic coupling. The results are discussed in the context of data obtained earlier for epitaxial $La_{0.67}Sr_{0.33}MnO_3/BaTiO_3$ heterostructures, where magnetization increases and critical exponent β also declines with ferroelectric polarization pointing away from ferromagnetic layer. The observed similarity between two systems illustrates an importance of charge doping in magnetoelectric coupling, which can be modulated by ferroelectric polarization reversal. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4803492]

Europium chalcogenides (EuX, X = O, S, Se, and Te) have been studied since 1961 and typically classified as 3D Heisenberg ferromagnets.[1–7] This class of materials contains some of the very few ferromagnetic (FM) insulators with a simple rock salt lattice structure. In particular, EuO has an accessible Curie temperature[7] (T_c) of 69 K that is seen to be sensitive to lattice strain.[8–12] The EuO system contains localized magnetic moments of 4*f* moments[13–15] and in the ferromagnetic state exhibits very large magneto-optical effects.[16] Metal-to-insulator transition and colossal magneto-resistance have been reported in EuO systems with electron doping.[14,17–20]

Much effort has been put into investigating the influence of the substrate on the magnetic properties of EuO[2–6,11,12,21,22] including changes to the Curie temperature (T_c) and critical exponents. Ferroelectric (FE) substrates are unique due to the potential for electric modulation, coming from the ferroelectric polarization reversal, which can be considered as a form of extrinsic electrostatic doping at the FM-FE interfaces.[23] Not surprisingly, magneto-electric coupling at the FM/FE interfaces is attracting both theoretical and experimental interest.[23–27] In this context, the study of the magnetic properties of EuO, including the critical exponents, on a ferroelectric substrate is of especial interest because EuO as an insulator has few free carriers. On the other hand, the sizeable energy dispersion of Eu 4*f* state[18,28] is inconsistent with the Heisenberg model.[28] To investigate the magnetic properties of EuO under extrinsic doping, we have investigated EuO/$BaTiO_3$/$SrTiO_3$ (EuO/BTO/STO) heterostructures.

The 100 nm EuO films were deposited using pulsed laser deposition (PLD)[15,17,18,29] at 10^{-5} Torr pressure on the barium titanate ($BaTiO_3$, or BTO) films grown on the $La_{0.67}Sr_{0.33}MnO_3/SrTiO_3$(001) (LSMO/STO) substrates (LSMO thickness was 10 nm). It has been shown previously[30] that growing compressively strained $BaTiO_3$ films on $SrTiO_3$ substrates enhances the resulting polarization and aligns it normal to the surface. In our studies, thickness of $BaTiO_3$ was chosen to be 48 unit cells (~19 nm) to ensure stable and switchable polarization. The composition of the grown EuO films was confirmed using an Oxford Instruments INCAx-act EDS detector (Model #51-ADD0025). XRD data were collected by Philips X'Pert diffractometer using Cu Kα radiation. The magnetic properties were measured with a physical properties measurement system (PPMS) from Quantum Design.[12,15,29] As seen in Figure 1, the 100-nm-thick EuO films are textured along (100). The results obtained for the EuO/$BaTiO_3$ samples are here compared with the data obtained previously using epitaxial $BaTiO_3$ films on $La_{0.67}Sr_{0.33}MnO_3/SrTiO_3$ (LSMO/STO) substrates.[23]

For the purpose of this work, upward FE polarization (P_{up}) is defined as the polarization pointing away from the FM material: in the case of the EuO/BTO system, this is defined with respect to the EuO layer. When the direction reverses, and the polarization direction is towards the FM material, this corresponds to the downward polarization (P_{down}). The ferroelectric polarization was switched from

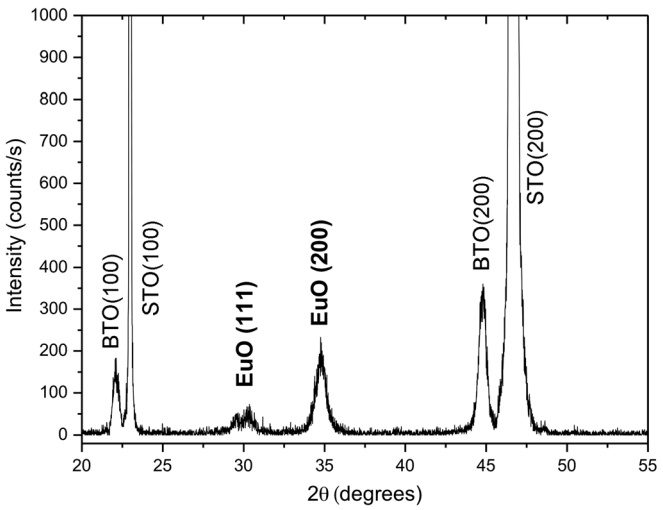

FIG. 1. The XRD patterns of the EuO thin films grown on BTO/STO substrates.

"up" to "down" with an applied voltage in excess of 400 V, in excess of the coercive voltage of the BTO films, as noted in prior work.[23] In all cases, the $La_{0.67}Sr_{0.33}MnO_3$ was used as a conducting electrode to allow electrical control of polarization in the BTO layer. In the case of the EuO/BTO heterostructure, the effect underlying LSMO electrode provided little additional magnetization, as was established through the comparative studies with the LSMO/BTO structures.

Figure 2 shows the temperature dependence of magnetization for EuO/BTO and BTO/LSMO heterostructures. The magnetization curves clearly change for both EuO (Figure 2(a)) and LSMO (Figure 2(b)) with the change in the polarization direction of the ferroelectric BTO layer. In Figure 2(a), the magnetization plots of the EuO/BTO heterostructure indicate a ferromagnetic Curie temperature (T_c) of ~70 K even in the constant magnetic field H = 200 Oe of the measurement. This value is close to the value of $T_C = 69.3$ K, commonly reported for EuO.[15,29] This is further confirmation that our EuO is stoichiometric.

A change in the Curie temperature is expected for both EuO and LSMO with extrinsic doping, which in turn should change with ferroelectric polarization reversal. Prior studies reported an increase in Curie temperature for EuO with electron doping (n-type doping of the EuO).[12,29] As seen in Figure 2, there is no significant change in the critical magnetization temperature neither for LSMO (Ref. 23) nor for EuO with polarization reversal in BTO. The EuO has the thickness of about 100 nm so that the extrinsic doping at the EuO/BTO interface is restricted to the interface region. Since EuO is an insulator, there is limited compensating charge and only a small effect of the interface on the whole EuO layer magnetization can be expected. In other words, we expect the EuO layer T_c to be barely perturbed, as discussed in detail below. However, the magnetization curves are different for two polarization FE states for both the EuO/BTO and LSMO/BTO heterostructures. For the EuO/BTO heterostructure, should there be any contribution from the LSMO layer, it should actually act to diminish the net apparent EuO magnetization change with ferroelectric polarization. The presence of the LSMO layer within the EuO/BTO heterostructure does not completely compensate or erase the magnetization gain in the EuO when the ferroelectric polarization is away from the ferromagnetic EuO layer.

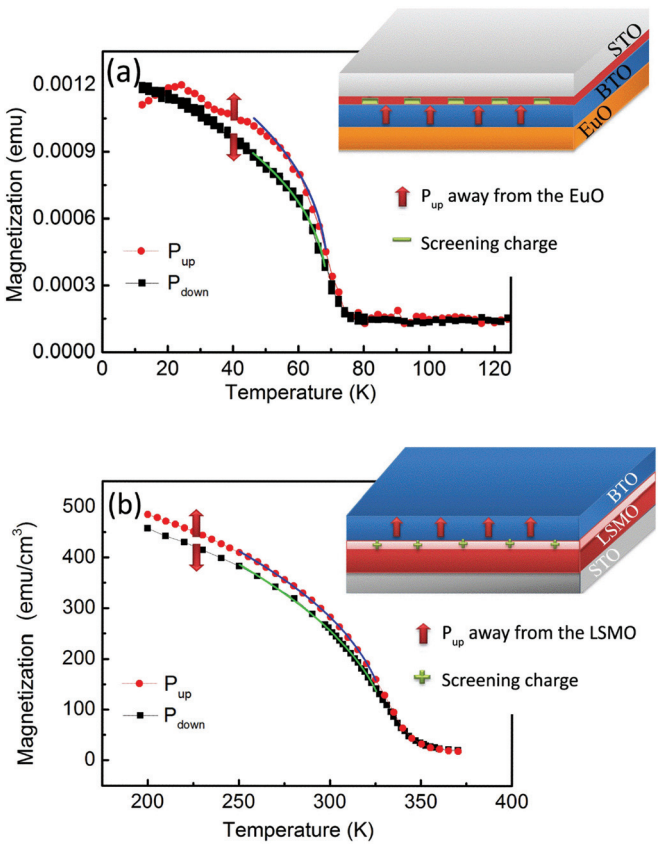

FIG. 2. The temperature dependence of magnetization of the ferromagnetic/ferroelectric heterostructures. The directions of red arrows in inset sandwich structures show the BTO polarization directions. (a) Magnetization and fitting curves of the EuO/BTO heterostructure for opposite polarization directions. From fitting temperature range 46 K-68 K, critical exponents $\beta = 0.36$ (for P_{up}) and $\beta = 0.39$ (for P_{down}) were obtained corresponding to the fitting curves (blue and green solid lines), respectively. (b) Magnetization and fitting curves of the BTO/LSMO heterostructure (reported in Ref. 23) for opposite polarization directions. The inset is the schematic illustration of FM/FE heterostructure with BTO in the P_{up} state (away from the LSMO layer). Fitting of the LSMO magnetization curves in the 250 K to 325 K temperature range (solid lines) yield the values of critical exponents 0.43 (for P_{up}) and 0.48 (for P_{down}).

For both the EuO/BTO and LSMO/BTO heterostructures, when the BTO polarization is in the P_{up} state (the ferroelectric polarization is away from the ferromagnetic layer), the magnetization is larger than that for the P_{down} state (the polarization is towards the ferromagnetic layer). The P_{up} state induces positive screening charges in LSMO/BTO interface (schematically illustrated in Figure 2(b)). On the other hand, for the same P_{up} state, there is a negative charge at the EuO/BTO interface, as charges are hindered from flowing through insulating EuO to the interface. The net negative charges at the EuO/BTO interface produce extrinsic doping effect on EuO. Because EuO is insulating, it is very possible that the mechanisms leading to extrinsic charge doping of the ferromagnetic layer are different for LSMO/BTO and EuO/BTO systems.

It has been known that the nearest neighbor (NN) exchange interaction J_1 and the next-nearest neighbor (NNN) exchange interaction J_2 are the main contributions to the magnetic coupling in the EuO system.[4,12,15] Previous studies shown that if n-type doping in EuO was introduced, the interaction J_1 will increase.[12,29,31] From Bloch's $T^{3/2}$ law[32]

$$M(T) = M(0)\left[1 - \frac{\alpha}{S}\left(\frac{k_B T}{2SJ}\right)^{3/2}\right],$$

where $M(0) = Ng\mu_B S$ is the zero-temperature magnetization. From this law, it is clear that the ferroelectric polarization at the EuO/BTO interface can increase the interaction J leading to the increasing of magnetization $M(T)$, as seen in Figure 2(a).

While valid only when T is very close to T_C, $M(T)$ is proportional to $(T_C - T)^{\beta}$ and it is safe to assume that when $(T_C - T)/T_C < 1$, there is an inverse relationship between $M(T)$ and critical exponent β. Thus, if the P_{up} FE state leads to doping of EuO and an increase in the magnetization, due to the increase in the interaction J_1, then the critical exponent β should decrease. On the other hand, for the P_{down} FE state,

TABLE I. Comparison of the EuO critical exponents β obtained by different methods.

EuO	Methods	β
Film	Magnetization when P_{up}	0.36[a]/0.43[b]
Film	Magnetization when P_{down}	0.39[a]/0.47[b]
Bulk	Bulk magnetization	0.368 (Ref. 2)
Bulk	Nuclear magnetic resonance	0.366/0.378 (Ref. 3)
Bulk	Faraday rotation	0.370 (Ref. 4)
Bulk	Neutron scattering	0.36 (Ref. 5)
	Theory (Series expansions)	0.38 (Ref. 6)
Mean Field	Theory	0.5 (Refs. 33 and 35)
3D Heisenberg	Theory	0.365 (Refs. 33 and 35)

[a]This work with the fitting was obtained by selecting data range about 46 K-68 K. The corresponding T_c is 69.6 K/69.3 K for P_{up}/P_{down} with R^2 value of 0.99428/0.99225, respectively.
[b]This work with the fitting was obtained by selecting data range about 46 K-70 K. The corresponding T_c is 71.0 K/70.8 K for P_{up}/P_{down} with R^2 value of 0.99113/0.99007, respectively.

while J_1 and the magnetization should decrease, the critical exponent β should increase.

To test the premise that the interface charge changes the interaction J_1 of the FM layer, the temperature dependence of magnetization curves was fit to the standard[33] $M(T) \propto (T_c - T)^{\beta}$. It is known that the temperature range has a profound effect on the extracted critical exponent value,[34] but the trend remains clear. In the EuO/BTO system, the critical exponents extracted from the magnetization curves for the BTO polarization P_{up}/P_{down} for a temperature range of 46 K-68 K and 46 K-70 K are $\beta = 0.36/0.39$ and $\beta = 0.43/0.47$, respectively. As seen in Table I, when the fitting magnetization curves for the temperature range of 46 K–70 K, the extracted critical exponents β are similar to the expectations from the mean-field theory but very different from the critical exponents previously measured for bulk EuO, which should resemble a typical Heisenberg magnet, if the Eu 4*f* dispersion is ignored.[18,28] If the data are analyzed for the reduced temperature range of 46 K–68 K, the deviation of the critical exponent β from Heisenberg model is small and the extracted Curie temperature (69.6/69.3 for BTO polarization P_{up}/P_{down}) is close to the expected value of $T_C = 69.3$ K for EuO,[15,29] and the quality of the fit is slightly better. Of key importance is that, as seen from comparison of data in Table I and Figure 2(a), the obtained critical exponent of the magnetization curve of the EuO/BTO system is smaller for the greater magnetization, which corresponds to the P_{up} polarization state of BTO.

A similar situation is found for the LSMO/BTO heterostructure. Figure 2(b) shows the magnetization curves of the LSMO/BTO system for opposite ferroelectric polarizations of BTO, where the LSMO thickness is 25 nm. The magnetization curves for LSMO corresponding to P_{up} and P_{down} polarization states of BTO, are characterized by different values of the critical exponent, 0.43 and 0.48, respectively (Table II). Again, it can be seen that as the magnetization increases due to an increase in the *J* coupling strength, the critical exponent decreases. Note that the Curie temperature of the LSMO remains about 375 K for both polarization directions.

TABLE II. Comparison of the LSMO critical exponent β obtained by different methods.

LSMO	Methods	β
$La_{0.67}Sr_{0.33}MnO_3$ film	Magnetization when P_{up}	0.43[a]
$La_{0.67}Sr_{0.33}MnO_3$ film	Magnetization when P_{down}	0.48[a]
$La_{0.7}Sr_{0.3}MnO_3$ bulk	Magnetization	0.37 (Ref. 35)
$La_{0.7}Sr_{0.3}MnO_3$ bulk	Neutron scattering	0.295 (Ref. 36)
$La_{0.7}Sr_{0.3}MnO_3$ bulk	Microwave absorption	0.45 (Ref. 37)
$La_{0.7}Sr_{0.3}MnO_3$ bulk	Magnetization	0.45 (Ref. 38)
$La_{0.8}Sr_{0.2}MnO_3$ bulk	Ferromagnetic antiresonance	0.45 (Ref. 34)
Mean field	Theory	0.5 (Refs. 33 and 35)
3D Heisenberg	Theory	0.365 (Refs. 33 and 35)

[a]This work.

For the LSMO system,[34–38] the value of critical exponent β is a subject of much debate, as summarized in Table II. Crystal quality, different chemical compositions of the manganite, and even the temperature range selected for fitting[34] (as also seems to be the case for the EuO/BTO system) can have noticeable effects on β.[34–38] For the LSMO/BTO system, our results show consistency with prior values obtained for the LSMO system, specifically with those that fit the mean field theory predictions.

The magnetization and critical exponent β were investigated in FM/FE heterostructures of EuO/BTO and LSMO/BTO. The reversal of the ferroelectric polarization changes the magnetization due to the charge doping effect. The critical exponent, β, decreases with the increase in the magnetization, which corresponds to the polarization P_{up} pointing away the FE/FM interface. The results show that extrinsic charge doping, due to an adjacent ferroelectric, affects the magnetization interaction J and critical exponent β in a manner consistent with Bloch's $T^{3/2}$ law.

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