Metal-insulator transition temperature in EuO_{1-x} films as a function of exposure time in air

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Abstract

Oxygen-deficient Europium monoxide EuO_{1-x} shows a metal-to-insulator transition near the Curie temperature (T_C). A systematic transport study of EuO_{1-x} thin films as a function of exposure time in air reveals a gradually decreased T_C from 140 K to 70 K as the concentration of the oxygen vacancies decreases, which is accompanied by a drastic increase in the resistance. We also find an unusual enhancement of magnetic anisotropy in the transport measurements, which results from the strong spin-orbit coupling at the interface between the film and substrate and possible presence of spin-textures like skyrmions in EuO_{1-x}.

Introduction

Spin based device has become a certainty as a next generation memory device with high density, high speed, nonvolatile, and high energy efficient. Stoichiometric europium monoxide (EuO) which has both ferromagnetic and semiconducting properties with a band gap of 1.12 eV [1,2], undergoes ferromagnetic (FM) and metal-to-insulator transition at the Curie Temperature T_C of 69 K. Both the magnetic and transport measurements for Gd and La doped EuO show gradually increased T_C to 125 K [3-7], and the peak value of the resistance decreases with increasing doping concentration. In the ferromagnetic state, the exchange splitting of the conduction band of EuO is about 0.6 eV and creates nearly 100 % spin polarized electrons close to the conduction band edge [8]. For oxygen deficient, i.e EuO_{1-x}, thin films, which is equivalent to electron doping, magnetization versus temperature measurements reveals a characteristic “double doom” feature with one T_C near 70 K and a second enhanced T_C at about 140 K. Various models including He-like [4], bound magnetic polaron (BMP) [9], Kondo-lattice [10] and RKKY-interaction [11] models have been proposed to explain the enhanced T_C and metal-to-insulator transition. Although the exact mechanism has yet to be understood, magnetic measurements seems to suggest there exist two magnetic sub-lattices and favor the BMP model [12]. Depending on the

models used, below T_C the exchange-split conduction band shifts downward to overlap with the defect levels situated in the semiconducting band gap [13] resulting in the metal-to-insulator transition. In the BMP model, overlap of the magnetic polaron wavefunction leads to the metal-to-insulator transition. It is worth stressing that, for both stoichiometric and reduced EuO_{1-x}, T_C is reported to be the same at 70 K [5, 14] and in the latter case, followed by a second T_C near 140 K. It does not exhibit a continuous change from 70 to 140 K in magnetic measurements. Transport study on the metal-to-insulator transition in highly reduced EuO_{1-x} is scarce except for that [15] shows a peak in the resistivity near 100 K. There has been no experimental report on systematic enhancement in T_C from transport study on EuO_{1-x} so far.

Recently the interest in europium monoxide is stimulated with the observation of Topological Hall effect (THE) in EuO_{1-x}, which suggests the formation of 2D magnetic skyrmions [16]. Also, La doping has been found to play an important role in determining the phases, densities, sizes of the skyrmions in $La_x\ Eu_{1-x}O$ thin films [7].

In this paper, we report gradual enhancement in the T_C for a series of EuO_{1-x} from the transport measurements, which we explain based on the BMP model. In addition, we discuss an unusually large magnetic anisotropy for EuO_{1-x} resulting from the strong spin-orbit coupling at the interface of the film and substrate and possibly the presence of spin-textures like skyrmions in EuO_{1-x}.

Experiments

Thin film EuO_{1-x} samples were grown on a Si (001) substrate by Pulsed Laser Deposition (PLD). Si wafers were cleaned with distilled water, rinsed with acetone, and then kept in a vacuum chamber. The substrate was annealed at a temperature of 650^0C for 30 mins to remove the native SiO_2 surface layer from the wafers and films deposited at 350^0C. The Eu metal target (99.99 %) from American Element was kept at about 5 cm from the substrate and was ablated using a Nd:YAG laser with 266 nm wavelength and pulse energy of 350 mJ/pulse. The film was deposited for 30 mins with thickness around 80-100 nm without any capping layers. During sample preparation the PLD chamber pressure was kept at $P < 10^{-7}$ Torr.

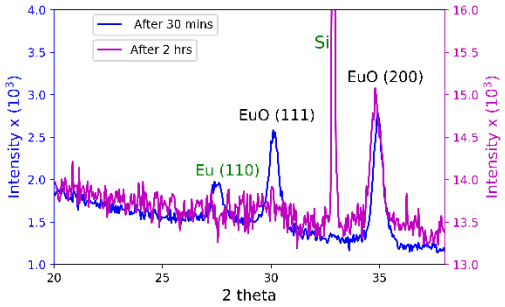


Fig:1. X-ray diffraction pattern for EuO_{1-x} thin films after different exposure times in air.

The magnetic and transport properties of the EuO_{1-x} thin films were examined using a Physical Property Measurements System (PPMS) from Quantum Design. The quality of the samples is monitored using x-ray diffraction (XRD). Figure 1 shows the XRD pattern of a sample studied in this work

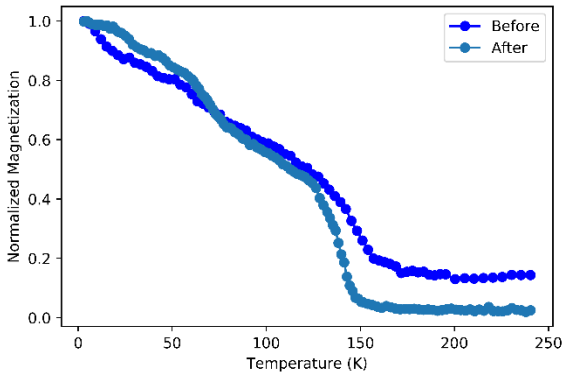


Fig:2. Temperature dependence of the normalized magnetization M measured at the beginning and after all the transport measurements (H = 500 Oe).

after it was exposed in air for about 30 mins (blue). It consists mainly peaks from EuO_{1-x} although an extra peak of Eu metal (110) is also visible. The presence of Eu metal is unavoidable and guarantees the samples are oxygen-deficient EuO_{1-x}. The magnetic measurements were carried out at the beginning and after all transport measurements were done. The effective total exposure time in air is about 2 hrs after all the transport and magnetic measurements. As seen in Fig. 1, after the measurements, the XRD pattern (purple) shows that the Eu metal peak is much reduced and largely gone.

Results and Discussion

The magnetization M of the EuO_{1-x} films was measured as a function of temperature with an in-plane magnetic field of 500 Oe. The double-dome feature of temperature-dependent magnetization with increased Curie temperature to around 140 K clearly shows that the samples are oxygen deficient as shown in Fig. 2 for both measurements done at the beginning and after the transport measurements. The measurement done at the beginning is on a piece cut from the same sample on which all transport and the second magnetic measurements were carried out. The elevated value of M above 150 K for the measurement done at the beginning is due to the excess amount of Eu metal present in the sample. The ferromagnetic ordering above 70 K originates from the antiferromagnetic coupling between the doped electrons and Eu 4f moments as explained by magnetic polaron model [12,17].

Longitudinal electrical resistance was measured as a function of temperature without an applied field using a four-probe method and gold wires directly bonded to the film surface using indium contacts. The first measurements were done as soon as the sample was grown, without much exposure to air. After the 1st measurement, 2nd, 3rd and 4th measurements were done for the same sample after exposing it in air intentionally for 30 mins between the measurements to oxidize the sample, which reduces the dopant concentrations. Figure 3 shows the resistance as a function of temperature obtained from the four measurements. The metal-to-insulator transition is clearly seen. Similar to Gd doped EuO [4,6,13,18] and in contrast for various non-stoichiometric Eu/O ratio [15], it shows a systematic decrease in the transition temperature with expose time in air as shown in fig. 3(a,b,c,d). The peak position is 138, 129, 90 and 83 K for the 1^{st}, 2^{nd}, 3^{rd} and 4^{th} measurements, respectively. This trend is accompanied by a drastic increase in the peak resistance from 80 ohms to 10^5 ohms. The systematic changes

seen as a function of the exposure time is related to the change in the electron doping level and can be explained on the basis of BMP model. Above the transition temperature, its semiconducting behavior arises from the variable range hopping of the magnetic polarons formed by the doped electrons of the oxygen vacancies. Below T_C, the overlap of the magnetic polaron wavefunctions leads to a global magnetization and metallic state. According to the BMP model, hopping conductance is expected for lower concentrations of

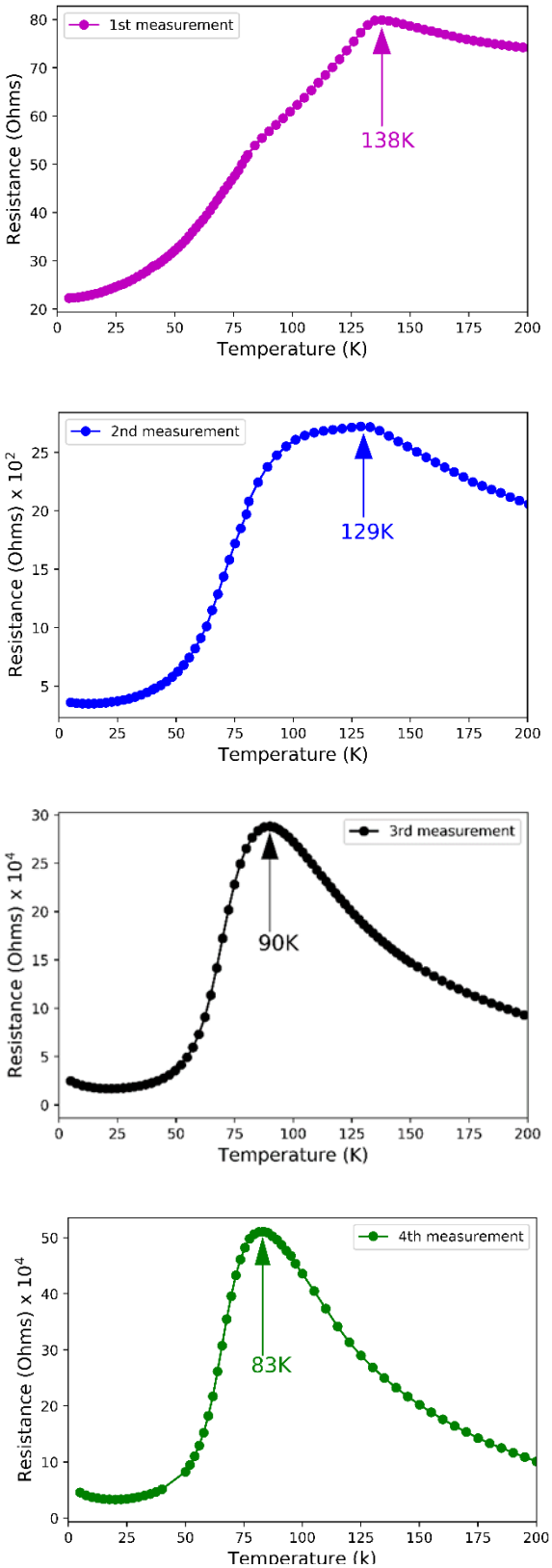
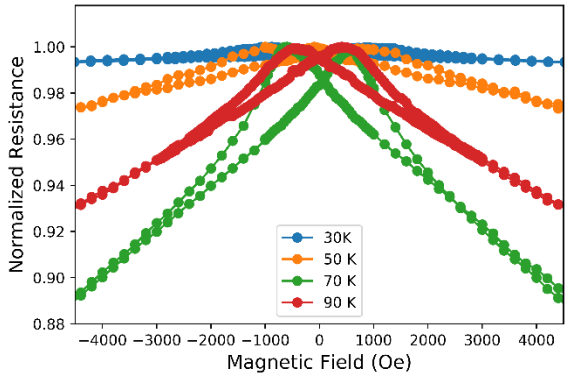


Fig: 3. Temperature dependence of the resistance for total expose time in air (a) 0 mins. (b) 30 mins. (c) 60 mins. (d) 90 mins.

dopants [14, 19]. As the concentration increases, the overlap of the polaron wavefunctions occurs at increasingly higher temperature leading to higher T_C and lower resistance. In terms of band structure, the exchange-split conduction band shifts downwards to overlap with the defect level of the doped electrons situated in the semiconducting band gap, which results in the metal-to-insulator transition. The observed lowering in the resistance is associated with the number of electrons activated from the oxygen vacancy states up into conduction-band [4,5].

At temperatures below 20 K, the upturn in the resistivity is observed in samples with less oxygen vacancies. It may be a result of the ending of the downshift of the spin-up conduction band below the T_C [10], which, as mentioned, is the origin of the metallic behavior. When the downshift ends and the conduction band no longer moves relative to the defect states, fewer electrons are

(a)



(b)

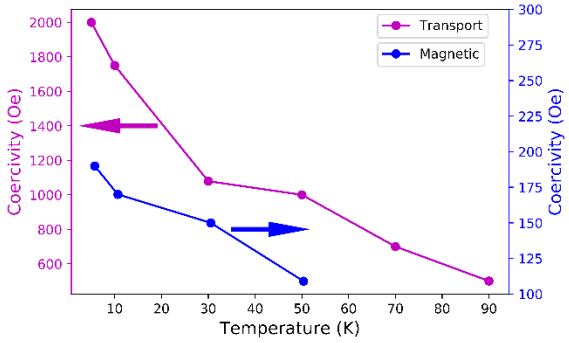


Fig: 4. (a) Normalized magnetoresistance curves at various temperatures. (b) Comparison of the out-of-plane coercive field between magnetic and transport measurements.

excited to the conduction band at lower temperature and the upturn is seen. This resistivity upturn is seen to diminish for the highly oxygen-deficient sample, see Fig. 3(a), where the overlap between the spin up conduction band and defect states is more complete.

As mentioned, the magnetic measurement, which was done after all the transport measurements, still shows enhanced Curie temperature around 140 K as a freshly prepared sample does. That is, even though the part of the sample probed by the transport measurements has already possessed a lower T_C via oxidation, the bulk of the sample (probed by the magnetic measurements) continues to exhibit the enhanced T_C at 140 K. This suggests the transport signals come from a different region of the sample than the bulk. We believe the transport properties described above originate from the part of the sample located at the interface between the film and substrate. It should be mentioned here

that the bulk of the sample, including the surface, has higher resistance than the interface region as the sample is exposed in air.

Indeed, magnetotransport study supports such a view point, which is interesting in its own right. Figure 4(a) shows the magnetoresistance (MR) when the applied field is out of plane normal to the film surface. The MR (%) is maximum at 70 K as expected from a colossal magnetoresistive (CMR) sample of EuO_{1-x}. In a previous report from our group on Pt/EuO_{1-x} heterostructure, the magnetic anisotropy was found much larger from the magnetotransport measurement compared to that obtained in the bulk magnetic hysteresis [20]. It was hypothesized that this is due to the formation of a metallic interface state between EuO and Pt that has much enhanced magnetic anisotropy than the EuO bulk due to the large spin-orbit coupling brought by Pt. Here for EuO_{1-x} films without Pt, we found a similar enhancement in the magnetic anisotropy, see Fig. 4(b), where the coercivities obtained from the magnetotransport and from the bulk magnetic measurements are compared. This suggests that the much enhanced magnetic anisotropy can be brought by strong spin-orbit coupling from the Eu in EuO_{1-x} itself. This strong spin-orbit coupling and the resulting magnetic anisotropy occur only at the interface thus are not detected by bulk measurements such as the magnetization measurement. Transport measurement, on the other hand, is sensitive to such a low resistance state. We will discuss the connection between this anisotropy and possible formation of 2D magnetic Skyrmions in a forthcoming paper.

Conclusions

In summary, we have observed enhanced Curie temperature up to 140 K in a highly reduced EuO_{1-x} thin film via its metal-to-insulator transition. The T_C decreases continuously when the sample is oxidized in air with time, which is accompanied with an increase in the sample's resistance. The magnetotransport of the film exhibits a much enhanced magnetic anisotropy compared to that obtained in bulk magnetic measurements. Combined with the fact that magnetic measurements show constant T_C at 140 K throughout this exposure time dependent transport study, we believe the measured transport properties originates from the interface between the film and substrate where spin-orbit coupling is strong. Indeed, it has been shown that EuO_{1-x} can have a strong spin-orbit coupling from photoemission spectroscopy, x-ray absorption and x-ray magnetic linear dichroism experiments [21-24]. The large magnetic anisotropy seen here is the first that shows europium's large spin-orbit coupling in a transport study, which we believe is amplified at the interface by possible changes in the crystal field, coordination numbers, valence and strains. Away from the interface, the exchange interaction between a doped electron and neighboring Eu magnetic moments that

forms BMP may be in a situation where it is independent of the doping concentration, which leads to a constant T_C near 140 K in the bulk measurement [12]. This bulk state retains a relatively small magnetic anisotropy as expected of a fcc crystal structure. The reason for the limited data available on its transport behavior until now may lie in the fact that the resistance of the samples is very high. On the other hand, the changed geometry, coordination and exchange interaction at the interface may stabilize the states revealed in the transport study presented here.

Acknowledgments

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The data that support the findings of this study are available from the corresponding author upon reasonable request.

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