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Ce-doped EuO: Magnetic properties and the indirect band gap

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We have prepared and investigated thin films of EuO doped with the rare-earth element cerium. X-ray diffraction, scanning electron microscopy, and energy dispersive x-ray spectroscopy were used to determine the quality of these films prepared by pulsed laser deposition. Ce doping leads to an enhanced Curie temperature near 150 K, close to that seen for oxygen-deficient EuO_{1-x}. However, the magnetization of Ce-doped EuO exhibits differences from that observed for Gd-doped and oxygen-deficient samples. The high-resolution angular-resolved photoemission from Ce-doped EuO reveals filling of conduction-band states near the X point. This indicates that the band gap in EuO is indirect, and that at 2% doping Ce-doped EuO_{1-x} is at least semimetallic. © *2011 American Institute of Physics*. [doi:10.1063/1.3544478]

Europium monoxide (EuO) is a well-known ferromagnetic semiconductor. Stoichiometric EuO has a Curie temperature (T_C) of 69 K and a band gap of ~1.12eV.[1,2] There are some spectacular phenomena for this material with electron doping, such as a metal-to-insulator transition and colossal magnetoresistance, where the resistivity change can exceed 8–10 orders of magnitude.[3,4] The Curie temperature can also be enhanced significantly by electron doping via rare-earth atoms[5–7] or oxygen vacancies.[6–9] Recent studies have shown that the conduction band of EuO is spin split by ~0.6 eV in its ferromagnetic state, which leads to an almost 100% spin polarization of the electrons close to the conduction band.[10]

Epitaxial or strongly textured EuO (100) films can be grown on a Si (100) wafer with high-quality interface by reactive thermal evaporation of Eu or molecular beam epitaxy.[11] Our previous study demonstrates that high-quality EuO films can be grown using pulsed laser deposition (PLD) with metal targets.[8] Both stoichiometric and oxygen-deficient europium oxide films can be prepared by controlling the annealing conditions of the Si wafers.

In this paper, we have succeeded in preparing EuO, EuO_{1-x}, and $Eu_{0.98}Ce_{0.02}O_{1-x}$ films on Si (100) wafers via PLD. X-ray diffraction (XRD) and scanning electron microscopy-energy dispersive x-ray spectroscopy (SEM-EDX) were used to investigate the films and showed they have the fcc rock salt crystal structure with and without the doping of the rare-earth element cerium (Ce). Ce doping changes the lattice constant and leads to the enhancement of the Curie temperature to 150 K, close to that of oxygen-deficient EuO_{1-x}.[8] There are differences in the magnetization curves that suggest that the effects of Ce doping differ from that caused by oxygen vacancies.

The EuO films and Ce-doped EuO films were prepared using PLD in a vacuum of 10^{-5} Torr with flowing H_2 at room temperature. Before the deposition, the Si wafers were annealed at 750 °C under pure H_2 gas in order to remove the native SiO_2 surface layer from the wafers. Annealing times of 30 and 50 min resulted in stoichiometric and oxygen-deficient films, respectively. The PLD targets were either an Eu (99.9%) metal or a mixture of Eu (99.9%) and Ce (99.9%) metals, and the purity of the H_2 gas used during the deposition is 99.995%. The composition of the grown Ce-doped EuO was confirmed by EDS to be $Eu_{0.98}Ce_{0.02}O_{1-x}$. XRD data were collected using a Philips X'Pert diffractometer using Cu $K\alpha$ radiation. The combined photoemission and inverse photoemission studies were carried out as described elsewhere,[12] while angle-resolved high resolution photoemission studies were used to map the wave-vector-dependent density of states in the vicinity of the Fermi level, following a recipe also described elsewhere.[13]

As shown in Fig. 1, the XRD pattern of $Eu_{0.98}Ce_{0.02}O_{1-x}$ is consistent with a film having the fcc rock salt crystal

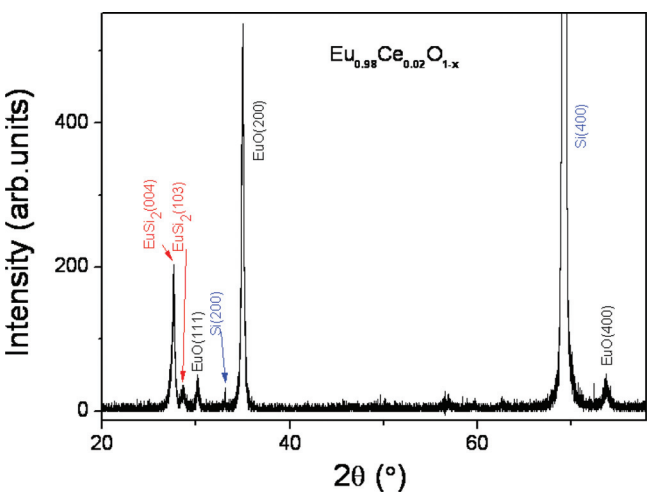

FIG. 1. (Color online) XRD patterns of $Eu_{0.98}Ce_{0.02}O_{1-x}$ film.

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TABLE I. Comparison of lattice constants and Curie temperatures for EuO, EuO_{1-x}, $Eu_{0.96}Gd_{0.04}O$,[a] $Eu_{0.96}Gd_{0.04}O_{1-x}$,[a] and $Eu_{0.98}Ce_{0.02}O_{1-x}$.

	EuO	EuO_{1-x}	$Eu_{0.96}Gd_{0.04}O$	$Eu_{0.96}Gd_{0.04}O_{1-x}$	$Eu_{0.98}Ce_{0.02}O_{1-x}$
Dominant orientation	⟨200⟩	⟨200⟩	⟨111⟩	⟨200⟩	⟨200⟩
Lattice constant (nm)	0.5131	0.5106	0.5118	0.5091	0.5105
Curie temperature (K)	70	150	120	145	150

[a]Reference 8.

structure expected of EuO. It shows that the stacking planes are mostly aligned with the ⟨200⟩ orientation as reported from prior works.[5,11] The XRD provides a good indication that the Ce-doped EuO film is of high quality and strongly textured. There is evidence of silicide formation as peaks of $EuSi_2$ were observed in the film.

Table I compares the lattice constant and Curie temperature of five different samples we have investigated. The lattice constants a determined from the (200) peaks for $Eu_{0.98}Ce_{0.02}O_{1-x}$ are consistent with the presence of Ce. While $a = 0.5131$ nm for EuO, this value decreases to 0.5105 nm for $Eu_{0.98}Ce_{0.02}O_{1-x}$ because of the smaller Ce^{3+} radius and oxygen deficiency. Because the doping level for Ce used here is a little lower than the Gd doping level, and because the radius of Ce^{3+} is a little larger than that of Gd^{3+}, the lattice constant of Ce-doped EuO_{1-x} is larger than that of Gd-doped EuO_{1-x}.

Figure 2 shows the magnetization versus temperature $M(T)$ curves of EuO, EuO_{1-x}, and $Eu_{0.98}Ce_{0.02}O_{1-x}$ measured in a field of $H = 500$ Oe. The ferromagnetic transition of the stoichiometric EuO is ~70 K, whereas both EuO_{1-x} and $Eu_{0.98}Ce_{0.02}O_{1-x}$ exhibit a very-much-enhanced Curie temperature (T_C) of 150 K. The distinct "double-dome" shape in $M(T)$ and higher T_C of EuO_{1-x} are characteristic of oxygen-deficient EuO. Similar results on EuO_{1-x} were observed by others, e.g., Borukhovich *et al.*[9] Although these two films have similar T_C, for $Eu_{0.98}Ce_{0.02}O_{1-x}$, the shape of $M(T)$ is different from the double-dome feature one sees with EuO_{1-x} films prepared by the same methods. For EuO_{1-x}, there are two noticeable changes in the magnetization, particularly the differential magnetization (the change in magnetization with temperature), at around 70 and 150 K. For $Eu_{0.98}Ce_{0.02}O_{1-x}$, there is no similarly distinctive drop in magnetization suggestive of a metamagnetic transition (a change from one type of ferromagnetism to another). These differences, between $Eu_{0.98}Ce_{0.02}O_{1-x}$ and EuO_{1-x} films, can be seen clearly in Fig. 3, in which the derivative of the magnetization dM/dT is shown as a function of temperature. With the dM/dT vs T plot, EuO has one peak at 70 K, which is obviously corresponding to its ferromagnetic transition. Both EuO_{1-x} and $Eu_{0.98}Ce_{0.02}O_{1-x}$ have two peaks in dM/dT, one dominant and the other smaller. The dominant peak occurs at 70 K and the smaller one at 150 K for EuO_{1-x}. On the other hand, for $Eu_{0.98}Ce_{0.02}O_{1-x}$, the dominant peak occurs at 150 K and the peak at 70 K is rather small. This suggests that most of the magnetic moments are ordered at temperatures as high as 150 K, in contrast to EuO_{1-x}.

It is known that the magnetization of EuO arises from the $4f^7$ electron configuration of Eu^{2+}. As suggested by Mauger and Godart,[1] carriers due to oxygen vacancies or doping with rare-earth elements can be excited into the conduction band, which will effectively enhance the magnetic coupling between Eu^{2+} $4f$ local moments via $5d$ conduction electrons due to the $4f$–$5d$ exchange interaction. This $4f$–$5d$ exchange interaction is responsible for the enhancement of T_C beyond 70 K. One expects similar values of the saturation magnetization both below and above 70 K based on this local moment model. An alternative model, based on the exchange splitting of the conduction electrons, predicts a smaller magnetization due to the on-site polarization of conduction

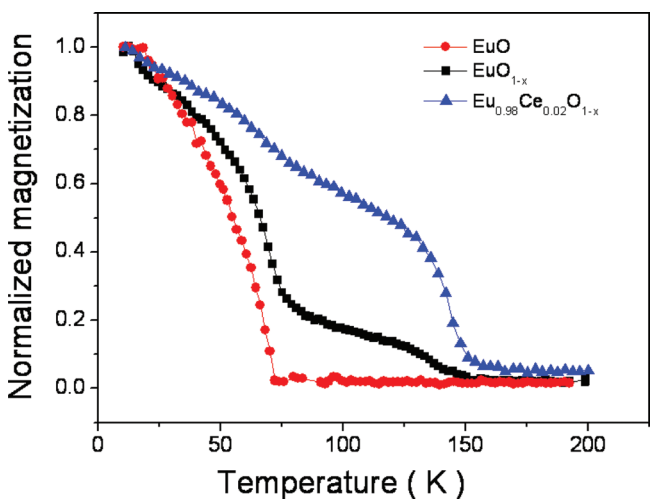

FIG. 2. (Color online) Magnetization as a function of temperature of EuO, EuO_{1-x}, and $Eu_{0.98}Ce_{0.02}O_{1-x}$ films grown by PLD in vacuum and under H_2 flow.

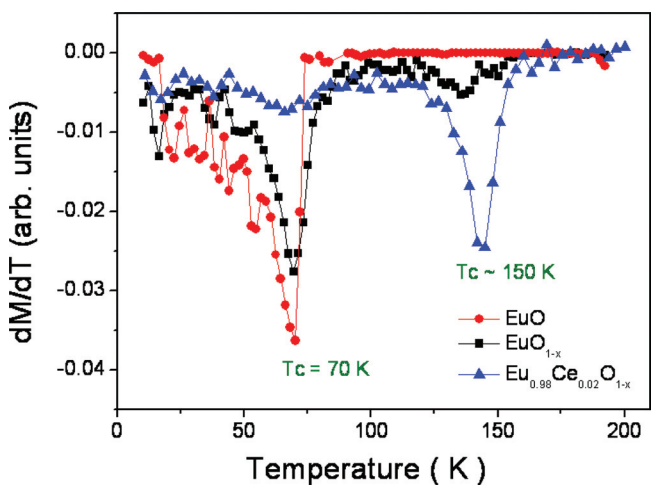

FIG. 3. (Color online) Derivative of the magnetization as a function of temperature of EuO, EuO_{1-x}, and $Eu_{0.98}Ce_{0.02}O_{1-x}$ films.

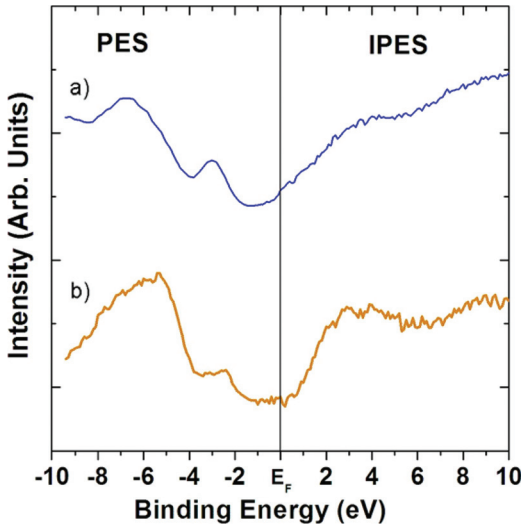

FIG. 4. (Color online) The combined photoemission (left) and inverse photoemission (right) of (a) EuO (100) and (b) $Eu_{0.98}Ce_{0.02}O_{1-x}$ (100).

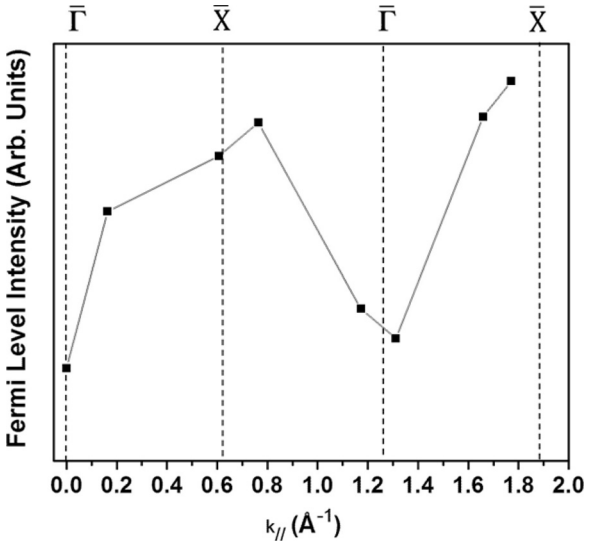

FIG. 5. The angle-resolved photoemission intensities at the Fermi level for $Eu_{0.98}Ce_{0.02}O_{1-x}$ (100), using a photon energy of 25 eV. The increase in intensity is indicative of electron pocket formation at the Brillouin zone edge along the Γ to *X* of the surface Brillouin zone.

electrons between 70 and 150 K with a much-reduced moment contribution from the Eu^{2+} moments until the temperature is reduced below 70 K.[14]

The magnetization curves of $Eu_{0.98}Ce_{0.02}O_{1-x}$ taken at 120 and 50 K show that saturation magnetization is similar. This behavior is unique to Ce-doped EuO and was not observed with Gd-doped EuO.[8] In our study of EuO_{1-x} and Gd-doped EuO, the saturation magnetization above 70 K was found to be significantly smaller than below 70 K.[8] Cerium is somewhat unique in that because of strong 4*f*–5*d* hybridization, there is an additional 4*f* local moment contribution to the electronic structure in the vicinity of the Fermi energy.[15–18] This Ce local moment contribution may aid to keep Eu^{2+} 4*f* local moments still aligned in EuO at 120 K, but from the data presented here, we can only speculate as the underlying mechanism is not clear.

Although the electronic structures of Ce-doped EuO and EuO do not appear to differ significantly in the combined photoemission and inverse photoemission studies (Fig. 4), the angle resolution photoemission studies of $Eu_{0.98}Ce_{0.02}O_{1-x}$ film indicate that there is filling of electron pockets, of an otherwise empty conduction band. As shown in Fig. 5, there is filling of electron pockets evident in the wave-vector-dependent photoemission density of states at the Fermi energy. This is not observed in the undoped EuO films. This filling of the conduction band minimum occurs at the Brillouin zone edge, indicating that the band gap in EuO is indirect.

In summary, we have prepared the high-quality europium oxide films with Ce doping on the Si (100) wafer via PLD. The T_C of $Eu_{0.98}Ce_{0.02}O_{1-x}$ film is significantly enhanced by Ce doping and oxygen vacancies to 150 K, similar to EuO_{1-x}, however, the magnetization $M(T)$ and $M(H)$ are remarkably different. Angular-resolved photoemission indicates that the band gap in EuO is indirect.

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