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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. 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 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 \( \sim 1.12 \text{eV} \). 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. The Curie temperature can also be enhanced significantly by electron doping via rare-earth atoms or oxygen vacancies. Recent studies have shown that the conduction band of EuO is spin split by \( \sim 0.6 \text{eV} \) in its ferromagnetic state, which leads to an almost 100% spin polarization of the electrons close to the conduction band.

Epitaxial or strongly textured EuO films can be grown on a Si (100) wafer with high-quality interface by reactive thermal evaporation of Eu or molecular beam epitaxy. Our previous study demonstrates that high-quality EuO films can be grown using pulsed laser deposition (PLD) with metal targets. 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, and Eu0.98Ce0.02O1−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. 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 \( \text{H}_2 \) at room temperature. Before the deposition, the Si wafers were annealed at 750 °C under pure \( \text{H}_2 \) gas in order to remove the native SiO2 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 \( \text{H}_2 \) gas used during the deposition is 99.995%. The composition of the grown Ce-doped EuO was confirmed by EDS to be Eu0.98Ce0.02O1−x. XRD data were collected using a Philips X’Pert diffractometer using Cu Kα radiation. The combined photoemission and inverse photoemission studies were carried out as described elsewhere, 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.

As shown in Fig. 1, the XRD pattern of Eu0.98Ce0.02O1−x is consistent with a film having the fcc rock salt crystal...
structure expected of EuO. It shows that the stacking planes are mostly aligned with the (200) orientation as reported from prior works.\textsuperscript{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\textsubscript{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\textsubscript{0.98}Ce\textsubscript{0.02}O\textsubscript{1\texttextsubscript{x}} are consistent with the presence of Ce. While \(a = 0.5131\) nm for EuO, this value decreases to 0.5106 nm for Eu\textsubscript{0.98}Ce\textsubscript{0.02}O\textsubscript{1\texttextsubscript{x}} because of the smaller Ce\textsuperscript{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\textsuperscript{3+} is a little larger than that of Gd\textsuperscript{3+}, the lattice constant of Ce-doped EuO\textsubscript{1\texttextsubscript{x}} is larger than that of Gd-doped EuO\textsubscript{1\texttextsubscript{x}}.

Table I compares the lattice constants and Curie temperatures for EuO, EuO\textsubscript{1\texttextsubscript{x}}, Eu\textsubscript{0.96}Gd\textsubscript{0.04}O\textsubscript{1\texttextsubscript{x}}, Eu\textsubscript{0.98}Ce\textsubscript{0.02}O\textsubscript{1\texttextsubscript{x}}, and Eu\textsubscript{0.98}Ce\textsubscript{0.02}O\textsubscript{1\texttextsubscript{x}}.

<table>
<thead>
<tr>
<th>Dominant orientation</th>
<th>EuO</th>
<th>EuO\textsubscript{1\texttextsubscript{x}}</th>
<th>Eu\textsubscript{0.98}Gd\textsubscript{0.04}O</th>
<th>Eu\textsubscript{0.98}Ce\textsubscript{0.02}O\textsubscript{1\texttextsubscript{x}}</th>
<th>Eu\textsubscript{0.98}Ce\textsubscript{0.02}O\textsubscript{1\texttextsubscript{x}}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice constant (nm)</td>
<td>0.5131</td>
<td>0.5106</td>
<td>0.5118</td>
<td>0.5091</td>
<td>0.5105</td>
</tr>
<tr>
<td>Curie temperature (K)</td>
<td>70</td>
<td>150</td>
<td>120</td>
<td>145</td>
<td>150</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Reference 8.

![FIG. 2](Color online) Magnetization as a function of temperature of EuO, EuO\textsubscript{1\texttextsubscript{x}}, and Eu\textsubscript{0.98}Ce\textsubscript{0.02}O\textsubscript{1\texttextsubscript{x}} films grown by PLD in vacuum and under H\textsubscript{2} flow.

![FIG. 3](Color online) Derivative of the magnetization as a function of temperature of EuO, EuO\textsubscript{1\texttextsubscript{x}}, and Eu\textsubscript{0.98}Ce\textsubscript{0.02}O\textsubscript{1\texttextsubscript{x}} films.

EuO\textsubscript{1\texttextsubscript{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\textsubscript{0.98}Ce\textsubscript{0.02}O\textsubscript{1\texttextsubscript{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\textsubscript{0.98}Ce\textsubscript{0.02}O\textsubscript{1\texttextsubscript{x}} and EuO\textsubscript{1\texttextsubscript{x}} films, can be seen more 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\textsubscript{1\texttextsubscript{x}} and Eu\textsubscript{0.98}Ce\textsubscript{0.02}O\textsubscript{1\texttextsubscript{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\textsubscript{1\texttextsubscript{x}}. On the other hand, for Eu\textsubscript{0.98}Ce\textsubscript{0.02}O\textsubscript{1\texttextsubscript{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\textsubscript{1\texttextsubscript{x}}.
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.\textsuperscript{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.\textsuperscript{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.\textsuperscript{8} Cerium is somewhat unique in that because of strong 4f–5d hybridization, there is an additional 4f local moment contribution to the electronic structure in the vicinity of the Fermi energy.\textsuperscript{15–18} This Ce local moment contribution may aid to keep Eu$^{2+}$ 4f local moments still aligned in EuO at 120 K, but from the data presented here, we can only speculate as to 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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