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To cite this article: Pan Liu and Jinke Tang 2013 *J. Phys.: Condens. Matter* **25** 125802

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Received 1 December 2012, in final form 30 January 2013
Published 1 March 2013
Online at stacks.iop.org/JPhysCM/25/125802

Abstract

The investigation of a series of oxygen-deficient EuO thin films provided strong evidence that the doped electrons form magnetic polarons with the nearby Eu$^{2+}$ 4f spins; this is responsible for the enhanced Curie temperature observed near 140 K. Unlike in the previous magnetic polaron models proposed for the metal-to-insulator transition in EuO, the exchange coupling $J$ between the doped electron and its neighboring 4f spins is antiferromagnetic. The model explains satisfactorily the fact that the ordering temperature of the magnetic polarons occurs at $\sim 140$ K, independently of the oxygen vacancy concentration, and the contradiction that electron doping increases $T_C$ and yet reduces the red shift in the optical absorption. The magnetic polarons are coupled antiferromagnetically to the Eu$^{2+}$ local moments that are ordered in the Heisenberg ferromagnet below 69 K. This coupling was observable in the vicinity of 69 K. We discuss how, with increasing concentration of the oxygen vacancies, their behaviors evolve from those of isolated superparamagnetic polarons to those of percolating magnetic polarons with a finite coercivity.

(Esome figures may appear in colour only in the online journal)
RKKY model that includes the exchange of the conduction and oxygen vacancy defect electrons with the Eu spins failed to produce a measurable increase in the $T_C$ [14]. According to Arnold and Kroha’s model of an exchange-split conduction band [12], the existence of preformed local moments at the impurity levels inside the semiconducting gap is essential to explain the distinct double-dome shape of the $M$–$T$ curve. It should be mentioned here that numerous experiments have shown that oxygen deficiency alone, without doping localized moments, can be responsible for the unique double-dome feature [5–8], and the double-dome feature is observed for single-phase clean samples and is an intrinsic property of electron-doped EuO.

To explain the metal-to-insulator transition in EuO$_{1-x}$, a He-like model was first presented by Oliver et al [3]. They proposed a temperature-independent impurity level for the oxygen vacancies, which is below the conduction band at high temperatures but crosses the spin-up conduction band as the temperature is decreased. Another model, introduced by Torrance et al, is based on bound magnetic polarons (BMP) and assumes an exchange interaction between the doped electrons from the oxygen vacancies and the localized Eu spins [15]. Mauger has also studied the metal-to-insulator transition using the magnetic polaron model [16]. A Kondo-lattice model containing the impurity orbitals and their hybridization with the conduction band was formulated by Sinjukow and Nolting [17] in an attempt to explain the metal-to-insulator transition. Magnetic polarons themselves do not contribute to the enhancement in $T_C$ according to these models. Evidence for the presence of magnetic polarons has been shown in many experimental studies such as Raman scattering [18, 19], muon spin relaxation [20], optical absorption [21], and NMR studies [22]. Direct Raman spectroscopic evidence showed that the paramagnetic semiconductor-to-ferromagnetic metal transition in EuO is preceded by the formation of magnetic polarons [18]. Muon spin relaxation experiments demonstrated that magnetic polarons form in EuO around the doping centers at temperatures well above $T_C$ up to room temperature [20]. The local environment around the muon in the magnetic polaron was shown to be ferromagnetic. The existence of magnetic polaron states was interpreted as a possible origin of the spatial inhomogeneity of the electronic structure in electron-doped EuO films observed in infrared magneto-optical imaging [23]. The electric, magnetic, and electron paramagnetic resonance data were also analyzed using a bound magnetic polaron model [24].

In this paper, we argue that the $T_C$ enhancement in EuO$_{1-x}$ originates from the formation of the magnetic polarons. We have investigated the magnetic properties of a series of oxygen-deficient EuO thin films of different oxygen vacancy contents. The magnetic polaron model offers satisfactory explanations for the observed unique behaviors. We discuss how magnetic polarons form, evolve, and percolate as the concentration of the oxygen vacancies increases and how they interact with the Eu 4f local moments.

Thin film samples were grown by pulsed laser deposition (PLD) on Si substrates. Si wafers were cleaned with dilute HF acid, rinsed with acetone, and then immediately placed in the vacuum chamber. Before the deposition, the silicon wafers were annealed at a temperature of 750 °C under pure H$_2$ gas to further remove the native SiO$_2$ surface layer from the wafers. Changing oxygen vacancy concentration was realized by controlling the annealing time [8, 25, 26]. PLD sample preparation was carried out under a pressure of $10^{-5}$ Torr of H$_2$ gas of 99.995% purity. The target was Eu (99.9%) metal from Alfa Aesar, and the temperature of the substrates was kept at 300 °C during the deposition. More details about the sample preparation can be found elsewhere [8, 25, 27]. To prevent the degradation of the EuO$_{1-x}$ films when exposed to air, some films were protected using a Pt capping layer deposited in situ. The magnetic properties of both oxygen-deficient and stoichiometric EuO samples were examined using a physical properties measurement system (PPMS) from Quantum Design. X-ray diffraction (XRD) and scanning electron microscopy with energy dispersive x-ray spectroscopy (SEM–EDX) were used to investigate the films and verify they are of single-phase fcc rock salt crystal structure.

We have grown stoichiometric EuO thin films and three kinds of oxygen-deficient films with different concentrations of oxygen vacancies EuO$_{1-x}$. These films are named stoichiometric, and very lightly, lightly, and heavily reduced samples, respectively. Determining the exact amount of oxygen vacancies in the films is difficult. However, the lattice constants ($a = 0.5131$ nm, $0.5128$ nm, $0.5116$ nm and $0.5108$ nm for the stoichiometric, and very lightly, lightly, and heavily oxygen-deficient films, respectively) are consistent with the expected degree of reduction. The XRD patterns show that the stacking planes of the films are mostly aligned with the (200) lattice planes, as reported in prior works [6]. The normalized magnetizations $M$ as a function of temperature $T$ for different samples are shown in figure 2. For the stoichiometric EuO films, the Curie temperature is 69 K, as expected. The double-dome feature and enhancement of $T_C$ (≈140 K), on the other hand, can be obviously seen for the heavily reduced EuO$_{1-x}$ sample. For the lightly reduced EuO$_{1-x}$ samples, the magnetization for $T > 69$ K is much
smaller, although it is still apparent that the sample orders at around 140 K as seen in the slight jump in the magnetization below that temperature. But for the very lightly reduced sample, the M–T curve is essentially the same as that of stoichiometric EuO. We also plot the magnetization on a logarithmic scale as a function of temperature to reveal more details of the temperature dependence of the magnetization, as shown in the inset of figure 2. Clearly the onset of the magnetic ordering is near \( T = 140 \) K for the lightly and heavily reduced \( \text{EuO}_{1-x} \), with the apparent double-dome feature, but this is not seen for the very lightly reduced \( \text{EuO}_{1-x} \).

Figures 3(a) and (c) show the magnetization as a function of applied magnetic field \( H \) (M–H) at different temperatures (5 K < \( T < 120 \) K) for the lightly and very lightly reduced samples. Both samples are ferromagnetic over the entire temperature range shown. While the M–H curves are similar below the intrinsic Curie temperature of the stoichiometric EuO \( T_C = 69 \) K, there are differences for \( T > 69 \) K. For the lightly reduced sample, the M–H curves are characteristic of a ferromagnet with hysteresis loops and coercivities for \( T \) up to 120 K. Figure 4(a) shows the details of the M–H curves in the low field region for 40 K < \( T < 100 \) K. A unique feature was observed for the temperature dependence of the coercivity \( (H_C–T) \) curve shown in figure 3(b). The coercivity first decreases as the temperature increases when \( T < 69 \) K, reaches almost zero near 69 K, then increases to a maximum as \( T \) continues to increase, and finally decreases and becomes zero again as the sample becomes paramagnetic \( (T > 140 \) K; not shown). But for the very lightly reduced \( \text{EuO}_{1-x} \), there is no hysteresis and the coercivity is zero above 69 K (see figures 3(d) and 4(b)). As will be discussed later, this is indicative of superparamagnetic behavior typical of small magnetic particles or clusters. Another unique feature observed for both samples is the inverted hysteresis loops near the \( T_C \) of the stoichiometric EuO as shown in figures 5(b) and (d) at 68–70 K, which is not seen either below or above a narrow temperature region around 69 K (see figures 5(a) and (c)). The magnetization reverses its direction when the applied field is still positive as \( H \) is lowered from high positive field. The inverted hysteresis loops suggest that there are two subsets of magnetic moments which are coupled antiferromagnetically. This is accounted for by the presence of magnetic polarons, as discussed next.

For \( \text{EuO}_{1-x} \), the magnetization has different origins below and above 69 K. Below 69 K, the indirect exchange interaction between localized Eu\(^{2+}\) 4f spins is strong, which aligns their moments. We believe that above 69 K, the doped electrons are trapped in the defect levels associated with the oxygen vacancies and form magnetic polarons with the nearby Eu 4f spins. The unique \( H_c–T \) curve and inverted hysteresis loops near 69 K shown in figures 3(b), (d) and 5(b), (d) suggest that the coupling between the local Eu moments of the Heisenberg ferromagnet below 69 K and the moments of magnetic polaron is antiferromagnetic. The reason is as follows. Near 69 K, the conduction band is already exchange split and the majority states are lowered although they have not crossed the defect level, at least for temperatures not too far below 69 K. The hybridization between the defect states and the conduction band [17] favors the doped electrons aligning their spins in the same direction as the majority states, that is, in the same direction as those Eu local spins ordered in the Heisenberg ferromagnet. Since the 4f orbital of Eu\(^{2+}\) is half-filled, a doped electron bound to the defect level will align the spins of the neighboring Eu\(^{2+}\) ions antiparallel to its own spin to form a magnetic polaron (a Hund’s rule-like coupling). The net result is the antiferromagnetic coupling between the magnetic polarons (their moments mostly from Eu) and the Eu local moments ordered in the Heisenberg ferromagnet. The magnetic polarons exist even below 69 K (over a certain temperature range), but the much larger local moments of the Eu dominate the magnetization at low temperature. We wish to comment here that it is still a matter of debate whether the exchange coupling between the doped electron and its neighboring Eu\(^{2+}\) moments is ferromagnetic or antiferromagnetic. Although the coupling was mostly assumed to be ferromagnetic in previously mentioned papers, antiferromagnetic coupling has been investigated for magnetic polarons in [28, 29]. Hund’s rule-type couplings provide a possible origin for the antiferromagnetic coupling inside the magnetic polarons in EuO\(_{1-x}\) [29, 30].

For lightly reduced EuO\(_{1-x}\), we have explained in our previous paper [25] why the coercivity becomes zero near 69 K as shown in the \( H_c–T \) curve in figure 3(b). Briefly, a large field aligns the two subsets of the moments in the same direction. As the field is decreased to a critical value close to the coupling strength, the local Eu moments reverse their direction due to the antiferromagnetic coupling to the magnetic polarons, which gives rise to an inverted hysteresis loop. As the temperature increases, the magnitude of Eu local moments decreases to a critical level that is nearly the same as that of the magnetic polarons moments but with opposite direction; the \( M–H \) curve runs through the origin and \( H_c \) drops to zero. When the temperature increases further (\( T > 70 \) K),
Figure 3. (a) Magnetization as a function of applied field over the temperature range from 5 to 120 K for lightly reduced EuO\(_{1-x}\). (b) Coercivity obtained from (a) as a function of temperature. (c) Magnetization as a function of applied field for very lightly reduced EuO\(_{1-x}\). (d) Coercivity obtained from (c) as a function of temperature.

Figure 4. Details of the \(M-H\) curves in the low field region for 40 K < \(T\) < 100 K. (a) For lightly reduced EuO\(_{1-x}\) and (b) for very lightly reduced EuO\(_{1-x}\).

the magnetic polarons dominate the magnetization. Here, the magnetic polarons overlap and are coupled to each other, and the sample shows the behaviors of a normal ferromagnet with finite coercivity.

For the very lightly reduced EuO\(_{1-x}\), magnetic polarons also form and they form in exactly the same way. But because of the low oxygen vacancy concentration, these magnetic polarons are isolated and do not overlap like those in the lightly as well as heavily reduced EuO\(_{1-x}\). Without strong coupling between the magnetic polarons, they behave like superparamagnetic particles and exhibit no hysteresis above 69 K. When the temperature goes down near 69 K, the local moments of Eu start to align, and the antiferromagnetic coupling between the Eu local moments and these isolated magnetic polarons kicks in, which leads to the inverted hysteresis loop. Figure 6 shows the magnetization as a function of temperatures \((M-T)\) measured at different applied fields \((H)\) for the very lightly reduced EuO\(_{1-x}\). When a large field is applied, the double-dome feature becomes apparent, which was not seen in a low field. Since the isolated...
magnetic polaron model provides a good explanation for why most oxygen-deficient samples show the onset of the ferromagnetic ordering more or less near 140–150 K. The Curie temperature is primarily determined by the coupling strength within an individual magnetic polaron and is independent of the oxygen vacancy concentration. The concentration affects the number of the magnetic polarons and determines when the percolation of the magnetic polarons leads to a ferromagnetically ordered state across the entire sample with finite coercivity.

These magnetic polarons have a fairly large diameter due to the high dielectric constant of EuO. The effective Bohr radius of the orbiting donor electron can be calculated using

$$a_0 = \kappa_0 \hbar^2 / (m^* e^2),$$

where $\kappa_0$ is the background dielectric constant; for EuO, $\kappa_0 = 23.9$ [32]. $\hbar$ is Planck’s constant, $e$ is the electron charge, and $m^*$ is the effective mass of the doped electron, which is approximately half of the free electron mass in vacuum according to [16]. The estimated polaron radius is around 24.5 Å (diameter $d = 5$ nm). Assuming that the size of the magnetic polarons does not deviate from $a_0$ significantly according to [28, 33], they contain roughly $n = 1500$ Eu$^{2+}$ spins, which is expected to...
yield superparamagnetic behaviors. Knowing the ordering temperature of the magnetic polarons, \( T_C \approx 140 \) K, the constant of coupling \( J \) between the local Eu spins \( S_i \) and the spin of the donor electron \( s \) can be estimated for EuO. The exchange energy [15] is given by

\[
E = -J s \cdot S_i / n. \tag{2}
\]

The effective Weiss molecular field acting on \( S_i \) is \( J (S_i) / 2 \mu_0 H_B \) and on \( s \) it is the sum of all \( S_i \) in the polaron \( \sum_{\text{polaron}} J(S_i) / 2 \mu_0 H_B = J(S_i) / 2 \mu_0 H_B, \) where \( (S_i) \) and \( (S_i) \) are the average spins of the donor electron and Eu\( ^{2+} \), respectively. Using an analogy similar to that in [30] and applying the Brillouin functions that describe \( (S_i) \) and \( (S_i) \) near \( T_C \), we found \( k_B T_C = [(S + 1) S^2 / 2 n]^{1/2} J \). With \( T_C = 140 \) K, the absolute value of \( J \) was estimated to be 0.4 eV. \( J \) is negative, indicating the antiferromagnetic coupling originating from the Hund’s rules. Both the sign and value of \( J \) are drastically different from those in the previously discussed magnetic polaron models for EuO [15, 34], which typically give a \( J \) value of +0.1 eV, based on the 5d character of the orbiting electron and positive coupling.

Recent results of angle-resolved photoemission spectroscopy on Gd- and Ce-doped EuO show filling of electron pockets in an otherwise empty conduction band [8, 35], which troscopy on Gd- and Ce-doped EuO show filling of electron pockets in an otherwise empty conduction band [8, 35], which further suggests that a magnetic polaron is a more appropriate model than models based on exchange-split conduction bands or RKKY interaction for describing the magnetic ordering of EuO at above 69 K, although this is not to say that magnetic polarons do not exist in Gd- and Ce-doped EuO. In fact, magnetic polarons have been observed in the paramagnetic state of Gd-doped EuO [19] and used to explained the magnetic ordering [34, 36]. In addition, models based on exchange splitting of the conduction electrons have difficulty in producing the antiferromagnetic coupling and may require rare earth doping to achieve \( T_C > 69 \) K.

There has been a long standing unexplained contradiction that electron doping increases \( T_C \) but at the same time reduces the red shift in the optical absorption [37, 38]. The red shift is a result of the reduction of the band gap between the localized 4f\(^2\) and the 5d conduction band, since the latter is exchange split with a lowered majority band below 69 K. The smaller red shift with higher level of electron doping means a smaller exchange splitting of the conduction band, which is in contradiction to the increased \( T_C \). This is well explained in our model, considering that there exists antiferromagnetic coupling between the magnetic polarons and local Eu\(^{2+} \) moments, which reduces the effective field that exchange splits the conduction band.

In summary, investigation of a series of oxygen-deficient EuO thin films provided strong evidence that the doped electrons form magnetic polarons with the nearby Eu 4f spins, which gives rise to the ferromagnetic order near 140 K. With increasing concentration of the oxygen vacancies, behaviors from superparamagnetic isolated magnetic polarons to percolating magnetic polarons with finite coercivity were observed.

### Acknowledgments

This work was supported by the National Science Foundation (DPR-0852862 and CBET-0754821) and the US Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering, under Award DE-FG02-10ER46728.

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