# Is There an Intrinsic Limit to the Charge-Carrier-Induced Increase of the Curie Temperature of EuO?

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Rare earth doping is the key strategy to increase the Curie temperature ($T_C$) of the ferromagnetic semiconductor EuO. The interplay between doping and charge carrier density ($n$), and the limit of the $T_C$ increase, however, are yet to be understood. We report measurements of $n$ and $T_C$ of Gd-doped EuO over a wide range of doping levels. The results show a direct correlation between $n$ and $T_C$, with both exhibiting a maximum at high doping. On average, less than 35% of the dopants act as donors, raising the question about the limit to increasing $T_C$.

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Increasing the Curie temperature ($T_C$) of the half-metallic ferromagnetic semiconductor europium monoxide (band gap $E_{\text{gap}} = 1.12$ eV at 300 K [1]) is the key problem which has to be addressed to make this versatile material attractive for wide use. EuO offers the third strongest saturation magnetization of all known ferromagnets [2], one of the largest magneto-optic Kerr effects [3], pronounced insulator-to-metal transitions [4] as well as colossal magnetoresistive effects [5]. The recent demonstration of its half-metallic behavior and its structural and electronic compatibility with the technological relevant semiconductors silicon, GaN [6] and GaAs [7] make EuO a promising material for semiconductor-based spintronics. In addition, epitaxially strained EuO has been predicted to be ferroelectric and even multiferroic [8]. Despite these outstanding properties, the potential of EuO critically depends on the improvement of its Curie temperature of 69 K [9]. To address this challenge, several strategies have been proposed and are pursued, including the application of isostatic pressure [10,11], epitaxial strain [12], and charge carrier doping by either oxygen vacancies [13] or by substituting $Eu^{2+}$ with trivalent ions like $Fe^{3+}$ [14], $La^{3+}$, or $Gd^{3+}$ [15]. As the latter approach potentially offers the easiest way to substantially boost the $T_C$ of EuO, rare earth doping has been extensively studied [6,15–22]. For optimized doping concentrations $x$ in $Eu_{1-x}B_xO$, Curie temperatures have been reported to reach 170 K for $B = \text{Gd}$, $x = 0.04$ [21], and 180 K for $B = \text{Fe}$, $x = 0.077$ [23]. For doping concentrations exceeding these optimized values, however, the Curie temperature is progressively suppressed, giving rise to a maximum in $T_C$. Both the increase of $T_C$ and the existence of a maximum of the Curie temperature for optimized doping have been attributed to an indirect exchange interaction, mediated via the conduction electrons. This indirect exchange acts in addition to the direct Heisenberg exchange between the localized $4f$ magnetic moments of the Eu atoms and is supposed to become stronger with increasing carrier density. Several theoretical models have been introduced which describe this indirect exchange interaction and its effects on $T_C$ via an effective charge carrier doping [12,24,25]. In these models, the existence of a maximum of the Curie temperature is associated with a critical carrier density, above which magnetic instabilities [24] or antiferromagnetic ordering [12] reduce the indirect exchange. These models imply the existence of an intrinsic limit on how far the $T_C$ of EuO can be increased by charge carrier doping. Although the change of $T_C$ is ultimately resulting from a change of $n$, the comparison of experiment and theory has been based on the measurements of the dependence of the $T_C$ on the doping concentration $x$, assuming that every dopant donates one electron to the EuO conduction band [12,24,25]. To assess the validity of this assumption and to investigate if increasing the carrier density in EuO inevitably leads to a maximum of $T_C$, we have systematically measured the carrier densities and Curie temperatures of Gd-doped EuO films over a wide range of doping concentrations. These measurements reveal that only a small fraction of the introduced dopants donate electrons to the conduction band. With increasing $n$, no maximum of $T_C$ is found; $T_C$ shows a maximum only if plotted as a function of the dopant concentration $x$. These findings open the question of whether the observed maxima of the $T_C(x)$ for various dopants are truly the intrinsic limit for the doping-induced $T_C$ increase of EuO.

The $Eu_{1-x}Gd_xO$ films with doping concentrations in the range of $0 \leq x \leq 0.195$ were grown using reactive oxide molecular-beam epitaxy. Gadolinium was chosen as its effects on $T_C$ of EuO have been widely investigated and therefore offers the broadest database of all possible dopants. Europium and gadolinium were coevaporated from effusion cells in oxygen partial background pressures of $1 \times 10^{-9}$ Torr. The substrate temperature ($T_{\mathrm{growth}} = 350\,^{\circ}\mathrm{C}$) and the oxygen pressure were chosen for adsorption-controlled growth [26] to minimize the density of oxygen vacancies, which would otherwise act as uncontrolled dopants. The incident Eu and Gd fluxes were calibrated using a quartz crystal microbalance and adjusted to result in the desired Gd/Eu ratio (Eu-flux $= 10^{14}$ atoms/cm$^2$ s). All films were grown to thicknesses $d$ of $\sim$35 nm on (110)-orientated $YAlO_3$ single crystalline substrates [26]. $YAlO_3$ was chosen because of its outstanding insulating properties (band gap = 7.5 eV [27]) which prevent shunting of the highly resistive films at low doping concentrations $x$. Twelve samples were grown in three batches. The thicknesses of the samples were determined by Rutherford backscattering spectrometry. These thicknesses were assumed to be the same for all films of a batch. The Gd content $x$ for the four samples with the highest doping concentrations was determined by prompt-gamma activation analysis and by the Eu and Gd $M_{4,5}$ edges using x-ray absorption spectroscopy (XAS) [22]. With these values, the average ratio between calibrated Gd flux and measured Gd content was calculated and hence $x$ of the remaining samples determined.

After growth the films were capped *in situ* with $\sim$20 nm of amorphous silicon to prevent oxidation in air. The crystalline quality of all films was examined by four-circle x-ray diffraction. $\theta - 2\theta$ scans demonstrated single-phase films within the resolution limit of XRD. Rocking curves of the 002-peaks indicate that the main fractions of the films are coherently strained by the substrates with a clear onset of relaxation [28]. The in- and out-of-plane magnetic properties of all samples were characterized by superconducting quantum interference device magnetometry [28]. Temperature dependent measurements of the magnetization (zero-field cooled) were used to determine the Curie temperatures of the films. The measured characteristics [Fig. 1(a)] are in agreement with the behavior reported in the literature [6,19,20,22]. Field-dependent magnetization measurements performed at 5 K were used to determine the in-plane and out-of-plane saturation magnetizations ($M_{\mathrm{sat}}$) and fields ($H_{\mathrm{sat}}$). Typical values for $\mu_0 H_{\mathrm{sat}}$ range from 0.12 to 0.19 T for in-plane and 2.6 to 3.2 T for out-of-plane measurements [28].

To measure transport properties, bridges were patterned into the $Eu_{1-x}Gd_xO$ films using photolithography in combination with *in situ* ion-etching and sputter deposition [29]. Low resistance contacts were provided by Mg pads. On the patterned bridges, the temperature dependence of the resistivities [$\rho(T)$] were measured in a four point geometry.

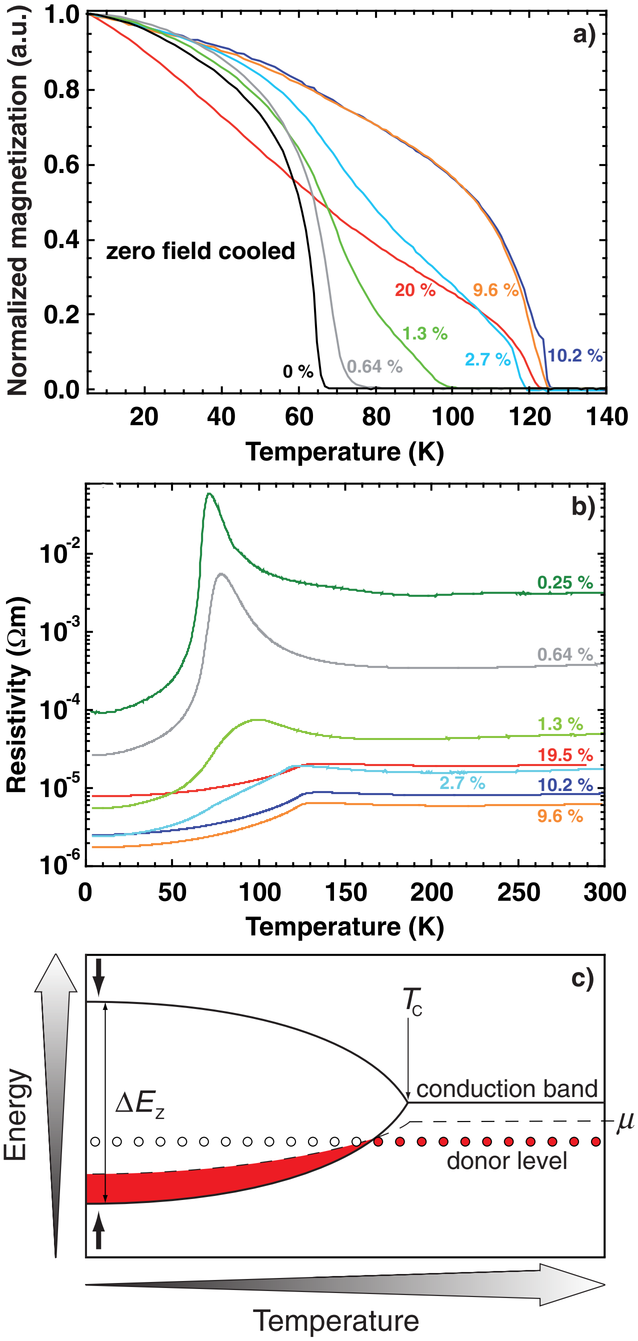

FIG. 1 (color online). (a) temperature dependence of the magnetization of $Eu_{1-x}Gd_xO$ samples measured in zero magnetic field; (b) resistivities of $Eu_{1-x}Gd_xO$ films as a function of temperature; (c) simplified band diagram of Gd-doped EuO. Below $T_C$ the large splitting of the conduction band leads to draining of the dopant electrons into the lower conduction band. For $T \ll T_C$ the carrier density is almost exclusively determined by the active dopants.

Figure 1(b) displays the temperature dependence of the resistivities of $Eu_{1-x}Gd_xO$ films with $x$ in the range of 0.0025 to 0.195. The $\rho(T)$ curves show the typical behavior for doped EuO (see, e.g., [20,30]). For all temperatures, the resistivities strongly depend on the doping concentration $x$, with a minimum at $x = 0.096$ [Fig. 1(b)].

Out-of-plane magnetic fields $H$ were applied to measure the Hall resistance $R_H$ of the bridges at $T = 4.2$ K [28]. From these measurements the mobile carrier densities $n$ of the films were calculated. At these low temperatures, contributions of the anomalous Hall effect are negligible [5], and for fields above $H_{\mathrm{sat}}$, the Hall resistance depends linearly on the applied magnetic field:

$$R_H(H) = -\frac{1}{end}\mu_0(H + M_{\mathrm{sat}}). \tag{1}$$

Here $e$ designates the elementary charge and $\mu_0$ the vacuum permeability. For the determination of $n$ the slopes of $R_H(H)$ were fitted for fields $4\ \mathrm{T} \le |\mu_0 H| \le 8$ T, well above the measured out-of-plane saturation fields. The measurements were performed on two different bridges on every sample. At $T = 4.2\ \mathrm{K} \ll T_C$, the Zeeman splitting of $\Delta E_Z = 0.6$ eV of the conduction band [31] causes the lower conduction band to intersect with the donor level, which energetically is located closely below the conduction band [Fig. 1(c), [18] ]. This induces a charge transfer from the donor levels into the conduction band. At 4.2 K, thermal excitations of electrons from the valence band into the conduction band can be neglected and the measured carrier density originates almost exclusively from electrons donated by the dopants.

The dependence of $T_C$ and $n$ on the doping concentration $x$ are shown in Fig. 2. The data provide evidence that $T_C$ and $n$ are closely correlated. Both increase with $x$ and reach a maximum in the range of $x = 0.10$. The maximum values are $T_C = 129$ K for $x = 0.102$ and $n = 9.0 \times 10^{20}\ \mathrm{cm}^{-3}$ for $x = 0.096$. The $T_C(x)$ dependence is in good agreement with the behavior reported in the literature [17,21,22]. The carrier density measurements, however, reveal that the reduction of $T_C$ at high doping levels is accompanied by a reduction of $n$. This behavior is in contrast to the existing assumption that the maximum of the $T_C(x)$ characteristics is caused by $n$ exceeding a critical threshold [12,24,25]. The direct correlation of $T_C$ and $n$ is demonstrated in the $T_C(n)$ plot shown in Fig. 3. $T_C$ increases almost logarithmically with $n$, up to the highest achievable charge carrier densities. A minimum carrier density of $n \sim 1 \times 10^{19}\ \mathrm{cm}^{-3}$ is needed to induce a measurable increase of $T_C$.

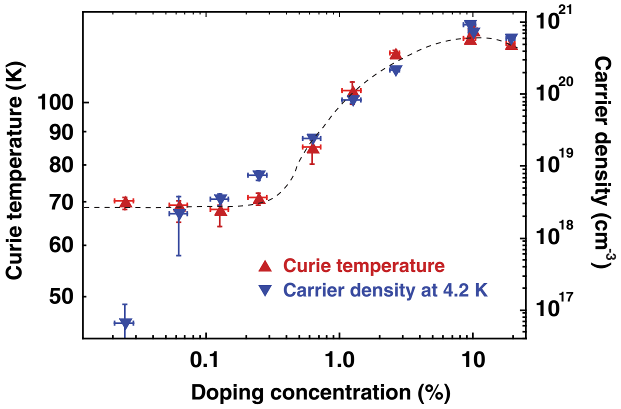

FIG. 2 (color online). Dependence of $T_C$ on $x$ in $\mathrm{Eu}_{1-x}\mathrm{Gd}_x\mathrm{O}$ films measured at 4.2 K. Because of the high sample resistivities at low doping concentrations, charge carrier densities could not be measured for $x < 0.02\%$. The Gd concentrations were determined by XAS. The dotted line is a guide to the eye.

To understand the reduction of $n$ at high doping levels and to assess how many of the dopants donate electrons, we have calculated the expected carrier density $n_{\mathrm{ex}}$ assuming that every Gd atom donates one electron into the conduction band according to $n_{\mathrm{ex}} = x n_{\mathrm{Eu}}$, where $n_{\mathrm{Eu}}$ designates the density of Eu atoms in EuO. The ratio of the measured charge density $n$ and the expected charge carrier density therefore provides the fraction of active dopants $p = n/n_{\mathrm{ex}}$. The dependence of the dopant activation $p$ on $x$ is shown in Fig. 4. All samples show activations below 35%. After an activation plateau of $p \approx 30\%$ for $0.014 \le x \le 0.10$, the sample with the highest doping concentration again shows a strongly reduced activation. For $x = 0.195$, only 10.1% of the dopants donate an electron into the conduction band.

The data indicate that in our samples the reduction of $T_C$ at high doping levels originates from a decrease in dopant activation. This is, in particular, surprising, because the XAS data show no indication of Gd ionization states other than $\mathrm{Gd}^{3+}$ [28]. Therefore almost all dopants must have donated one electron. This result implies the existence of charge compensating effects, which block the majority of the donated electrons from being transferred into the conduction band. Only once has a related effect been reported. The origin of this behavior of a Gd-doped EuO crystal has, however, not been identified [16]. As even at the highest doping level neither the $\theta - 2\theta$ scans nor the rocking curves indicate the presence of second phases or a decline in crystalline quality of the $\mathrm{Eu}_{1-x}\mathrm{Gd}_x\mathrm{O}$ films, the origin of the low dopant activation remains an important question.

The results provide a new perspective to utilize rare earth doping to increase $T_C$ in EuO films. In providing a model for the $T_C(x)$ dependence, Mauger, for example,

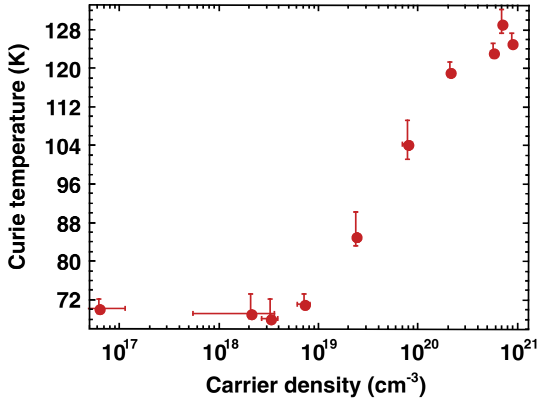

FIG. 3 (color online). Dependence of $T_C$ on $n$ in $\mathrm{Eu}_{1-x}\mathrm{Gd}_x\mathrm{O}$ films. A minimum charge carrier density of $\sim 10^{19}\ \mathrm{cm}^{-3}$ is required to increase $T_C$ above 69 K. For higher concentrations $T_C$ increases approximately logarithmically with $n$.

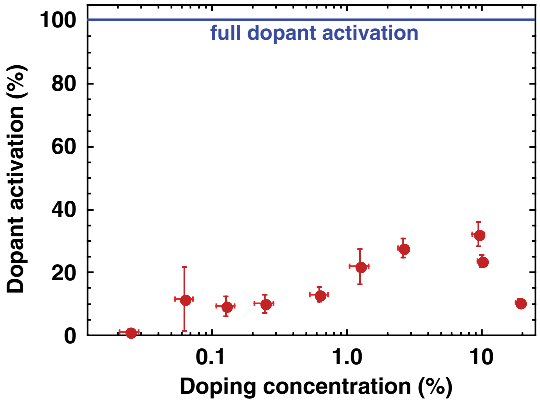

FIG. 4 (color online). Calculated dopant activation $p$ as a function of the doping concentration $x$ in $Eu_{1-x}Gd_xO$.

attributes the existence of the $T_C$ maximum to a spiral instability in the ferromagnetic order along the [111] EuO direction, that is expected to occur for $n > 2 \times 10^{21}$ cm$^{-3}$ [24] ($x > 0.068$ for $p = 1$). In the model developed by Ingle and Elfimov, doping levels $x > 0.08$ ($n > 2.35 \times 10^{21}$ cm$^{-3}$ for $p = 1$) are expected to cause antiferromagnetic order which is postulated to limit $T_C$ to about 150 K [12]. As our samples do not reach such high charge carrier densities but show increasing Curie temperatures with increasing $n$, they open the question if an intrinsic limit of $T_C(n)$ exists. Furthermore our data indicate that $n > 1 \times 10^{19}$ cm$^{-3}$ is needed to increase $T_C$ (Fig. 3). This finding is in qualitative agreement with the model of Mauger, yet the measured carrier density required is about an order of magnitude smaller than predicted [24].

In conclusion, our measurements of epitaxial $Eu_{1-x}Gd_xO$ films show a close correlation between $T_C$ and $n$. Our measurements indicate that the maximum in $T_C$ is accompanied by a maximum in $n$. This would be in contrast to the existing understanding that this maximum is due to the charge carrier density exceeding a critical level. We found that only a small fraction ($< 35\%$) of the introduced dopants acts as donors, whereas the majority of the Gd is rendered inactive. This clearly demonstrates that the widespread assumption of every dopant being a donor is questionable, and that doping experiments to increase the Curie temperature of EuO have to be correlated to the charge carrier density, not only to the doping concentration $x$. The origin of the low dopant activation has yet to be identified. Furthermore, the data demonstrate that a minimum charge carrier density is required to increase $T_C$. Finally we want to point out that our data are in very good quantitative agreement with those of [22] and that the Curie temperatures of both experiments are well below the reported maximum $T_C$ for Gd-doped EuO. As latter experiments were performed on polycrystalline films with unknown oxygen stoichiometry, the influence of oxygen vacancies and defects on the dopant activation is an important question to be addressed with respect to the further increase of the Curie temperature of EuO.

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