

La-doped EuO: A rare earth ferromagnetic semiconductor with the highest Curie temperature

H. Miyazaki,^{1,2,a)} H. J. Im,³ K. Terashima,^{1,b)} S. Yagi,² M. Kato,² K. Soda,² T. Ito,^{1,4,c)} and S. Kimura^{1,4,d)}

¹UVSOR Facility, Institute for Molecular Science, Okazaki 444-8585, Japan

²Graduate School of Engineering, Nagoya University, Nagoya 464-8603, Japan

³Department of Advanced Physics, Hirosaki University, Hirosaki 036-8560, Japan

⁴School of Physical Sciences, The Graduate University for Advanced Studies (SOKENDAI), Okazaki 444-8585, Japan

(Received 10 March 2010; accepted 7 April 2010; published online 9 June 2010)

We report the fabrication of single-crystalline La-doped EuO thin films with a Curie temperature (T_C) of about 200 K, the highest among rare-earth compounds without transition metals. From first-principle band calculation and x-ray diffraction measurement, the observed increase in T_C cannot be explained only by the increase in hybridization intensity due to lattice contraction and the increase in up-spin electrons of the Eu 5d state caused by the electron doping. Hybridization between the Eu 4f and donor states and/or Ruderman–Kittel–Kasuya–Yoshida interaction mediated by the doped La 5d state is a possible origin of the increase in T_C . © 2010 American Institute of Physics. [doi:10.1063/1.3416911]

The advent of next-generation spintronics has led to renewed interest in rare-earth oxide ferromagnetic semiconductors such as europium monoxide (EuO), whose magnetism arises from partially filled and highly localized 4f states. EuO, which has a rocksalt crystal structure, is regarded as a typical Heisenberg ferromagnetic semiconductor with a Curie temperature (T_C) of about 70 K and a band gap of 1.12 eV at room temperature.^{1–3} In the case of electron doping by the Eu excess or the substitution of Eu²⁺ ion with Gd³⁺ or La³⁺ ions, T_C increases to 150 K and the electrical resistivity then drops 12-orders of magnitude below T_C , in other words, a metal-insulator transition (MIT) appears.^{4–20} With applying an external magnetic field, the MIT temperature is decreased substantially, causing a colossal magnetoresistance with a change in the electrical resistivity of up to six orders of magnitude.^{6,9} Since the Eu 4f up- and down-spin states are perfectly occupied and unoccupied, respectively, the carriers are expected to be fully polarized below T_C . Due to its remarkable properties, EuO attracts much attention for next-generation spintronics applications such as spin valves and spin switches.^{19,21,22} For the use of EuO in spintronics applications, however, it is desirable to increase T_C to above room temperature.

We have succeeded in fabricating single-crystalline thin films of pristine EuO and clarified their electronic structure by angle-resolved photoemission and infrared spectroscopy.^{23–26} The origin of the ferromagnetic phase transition in pristine EuO is the hybridization between Eu 4f and other states, such as the O 2p (super-exchange interaction) and Eu 5d states (indirect-exchange interaction). This result indicates that the increase in hybridization intensity between Eu 4f and other states is important to increase T_C .

There are two methods to enhance the hybridization intensity exist: one is the contraction of the lattice constant and the other is the increase in the number of up-spin electrons. Since the unoccupied Eu 5d band is also polarized, electron doping of the Eu 5d band is an effective means of increasing T_C . The substitution of some of the Eu²⁺ ions with La³⁺ ions, whose ionic radius is smaller than that of Eu²⁺ ions, is effective for both lattice contraction and charge doping.

In this letter, we report the fabrication of single-crystalline La-doped EuO thin films. The T_C of the thin films was surprisingly found to be about 200 K, which is the highest Curie temperature of rare-earth compounds other than those containing transition metals. From first principle electronic structure calculation with the lattice constant obtained by x-ray diffraction (XRD), it was found that the mechanism of the high T_C cannot be explained by band calculation using the combination of the lattice constant contraction and the shift of the Fermi level due to the charge doping. This indicates that another effect exist that cannot be explained by band calculation.

Single-crystalline La-doped EuO thin films were grown by using the molecular beam epitaxy (MBE) method. The thin films were grown onto 0.05 wt % Nb-doped SrTiO₃ (001) single-crystalline substrates. To obtain high-quality EuO thin films, a buffer layer of BaO was evaporated before preparing the EuO film.^{27,28} Eu and La metals were evaporated at temperatures of 525 and 1260 °C, respectively, under an oxygen pressure of 8.0×10^{-6} Pa at a substrate temperature of 400 °C. The composition of the fabricated La-doped EuO was confirmed to be La_{0.1}Eu_{0.9}O by analysis using energy-dispersive x-ray (EDX) spectroscopy (SEA2010, SII Co.). The crystal structure was checked by low energy electron diffraction (LEED) after deposition and confirmed to have the fcc 1 × 1 (001) pattern, the same as pristine EuO. The crystal structure and magnetization were observed by x-ray diffractometer (RINT-Ultima III, Rigaku Co.) with a Cu K_α radiation source and by superconducting quantum interference device magnetometer (MPMS-7,

^{a)}Electronic mail: hmiyazak@ims.ac.jp.

^{b)}Present address: Department of Physics, Ritsumeikan University, Kusatsu, Shiga 525-8577, Japan.

^{c)}Present address: Graduate School of Engineering, Nagoya University, Nagoya 464-8603, Japan.

^{d)}Electronic mail: kimura@ims.ac.jp.

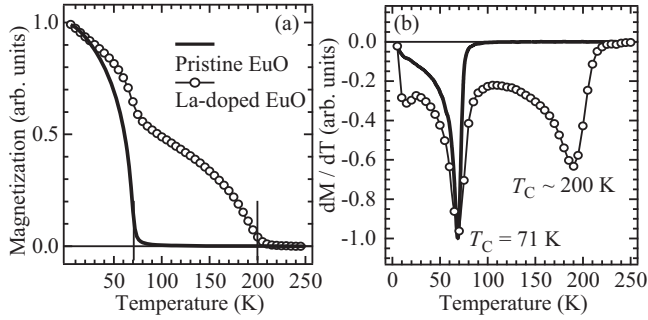


FIG. 1. Temperature dependence of the magnetization (a) and its first derivative as a function of temperature (b) for fabricated La-doped EuO and pristine EuO thin films with a thickness of 100 nm on SrTiO_3 substrate. The magnetization and its derivative are normalized at their maximum and minimum, respectively.

Quantum Design Co.), respectively, under an atmosphere. For these measurements, a BaO capping layer with a thickness of 10 nm was evaporated onto the EuO thin film for protection.

Figure 1 shows the temperature-dependent magnetization of pristine and La-doped EuO thin films with a magnetic field of 1000 Oe applied along the EuO [010] direction along the substrate plane. In the pristine EuO, the onset of the magnetization appears at around 70 K (T_C) due to ferromagnetic ordering. In the La-doped EuO, on the other hand, there are two onsets at around 70 and 200 K. To clarify the origin of the onset, the first-derivative of the magnetization in Fig. 1(a) is shown in Fig. 1(b). The first-derivative of the pristine EuO has one peak that corresponds to the ferromagnetic transition. On the other hand, another peak appears at around 200 K in the La-doped EuO in addition to the identical peak of pristine EuO. The two onsets of the magnetization (two peaks of the first-derivative) indicate that two phases with different T_C values coexist in the La-doped EuO; one is the same as that of the pristine EuO and the other an additional T_C of 200 K due to the La doping. In previous studies on electron-doping EuO, the highest T_C was about 160 K, except for transition-metal-doped rare-earth compounds (for example, Fe-doped EuO).²⁹ Therefore, this is the highest T_C achieved for electron-doped EuO without transition metals.

To clarify the origin of the high- T_C phase of the La-doped EuO thin film, the lattice constant was determined by

XRD, as shown in Fig. 2(a). The pattern contains not only from the SrTiO_3 (001) substrate and the fabricated EuO thin film, but also a small La_2O_3 peak originating from surface contamination due to the evaporation of La-metal. However, since the diffraction peak of EuO (001) and clear LEED spots appear, it is confirmed that the La-doped EuO was epitaxially grown along [001] direction onto the SrTiO_3 substrate.

Figure 2(b) shows the EuO (002) peaks of pristine and La-doped EuO. The pristine EuO has a single peak at 35.2° ,²⁵ whereas the La-doped EuO has an additional peak at the higher angle side of the main peak, which implies the shorter lattice constant. This suggests that fabricated La-doped EuO contains two phases: one from the pristine EuO, and the other from the actual La-doped EuO. In the above discussion of the magnetization, two phases were also suggested to exist in fabricated La-doped EuO. Therefore, the shorter lattice constant can be considered to originate from actual La-doped EuO.

To confirm the consistency between the magnetization and the additional XRD peak due to La doping, the volume fraction of the La-doped EuO was evaluated. From the Gaussian fitting of the (002) XRD peak as shown in Fig. 2(b), the volume fraction of the pristine and La-doped EuO phases is $0.39:0.61 \pm 0.01$. On the other hand, from the fitting of the summation of two Brillouin functions of the magnetization assuming two T_C values, the volume fraction of the pristine and La-doped EuO phases is determined to be $0.38:0.62 \pm 0.03$. These results are in good agreement with each other. Therefore the additional XRD peak of the La-doped EuO phase originates from the genuine peak of the actual La-doped EuO phase and hence the lattice contraction is one possible for the increase in the T_C .

Next, the origin of the high T_C in the La-doped EuO is discussed. Local spin density approximation plus Coulomb repulsion U (LSDA+ U) band calculation was performed using the WIEN2K code.³⁰ In the band calculation, the electron correlation energy U was fixed at 7.0 eV, which can explain an angle-resolved photoemission spectrum.^{23,26} The theoretical T_C can be evaluated from the total energies of three variant spin configurations, such as one ferromagnetic ordering (FM) and two antiferromagnetic ordering (AFM-I and AFM-II),³¹ as shown in Figs. 3(a)–3(c), using the following equations:

$$E_{\text{FM}} = E_0 + S(S+1)(-12J_1 - 6J_2),$$

$$E_{\text{AFM-I}} = E_0 + S(S+1)(4J_1 - 6J_2),$$

$$E_{\text{AFM-II}} = E_0 + S(S+1)(6J_2),$$

$$k_B T_C = 4S(S+1)(2J_1 + J_2),$$

where J_1 and J_2 are the first- and second-nearest-neighbor exchange constants, and S is the spin quantum number of Eu^{2+} 4f electrons ($S=7/2$). In the calculation, we used the experimental lattice constants of 0.5152 nm and 0.5116 ± 0.0014 nm for pristine and La-doped EuO, respectively, evaluated from the XRD pattern in Fig. 2. From the calculation, T_C of pristine EuO is evaluated as 92 K, which is consistent with the experimentally obtained T_C (70 K) taking into account the overestimation of T_C by the band calculation. On the other hand, in La-doped EuO, T_C can be evalu-

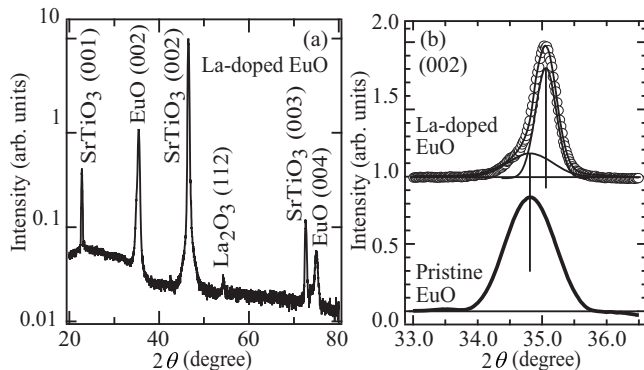


FIG. 2. (a) XRD pattern of La-doped EuO thin film with a thickness of 100 nm on SrTiO_3 substrate. (b) XRD patterns around the EuO (002) peak of La-doped EuO (open circles) and pristine EuO (thick line) thin films. The thin lines show the decomposition of the La-doped EuO (002) pattern into two Gaussian components.

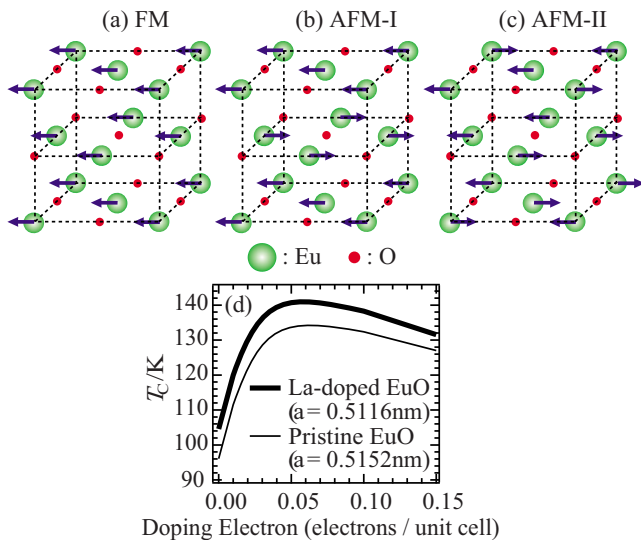


FIG. 3. (Color online) Three spin configurations of one ferromagnetic (FM) (a) and two antiferromagnetic (AFM-I and AFM-II) [(b) and (c)] structures. (d) Calculated T_C as a function of the doped electron number using the lattice constants of pristine EuO (thin line) and La-doped EuO (thick line).

ated as 101 K. Therefore T_C increases by 9 K as a result of the lattice contraction.

La doping also pushes up the Fermi level due to the increase in the electron number. To calculate the electron doping effect, we assume a rigid band model where the Fermi level is shifted to the high-energy side without a change in the electronic structure. Figure 3(d) shows the calculated T_C as a function of the doped electron number using the experimentally obtained lattice parameters of the pristine and La-doped EuO. As seen in Fig. 3(d), the maximum T_C increases by about 40 K due to the La doping. This is not consistent with the experimentally obtained T_C of 200 K. These results indicate that an unknown effect other than that shown by band calculation possibly plays an important role in this case. One possible reason for the high T_C is hybridization between the Eu 4f and donor states due to the La doping or/and oxygen defect proposed by Arnold and Kroha.³² Another possibility is that the Eu 4f states interact with each other mediated by La 5d conduction electrons, namely, the Ruderman-Kittel-Kasuya-Yoshida (RKKY) interaction, because the density of La ions is very high in the actual La-doped EuO phase. To understand the origin of the high T_C of La-doped EuO, further experimental and theoretical studies are needed including determination of whether the donor states and La 5d conduction band exist or not.

To summarize, we have succeeded in fabricating single-crystalline La-doped EuO thin films on SrTiO₃ substrates using the MBE method. The surface structure of the fabricated La-doped EuO thin film was fcc 1×1 (001), which is the same as that of the pristine EuO, but the lattice constant is decreased by 0.7% from 0.5152 to 0.5116 ± 0.0014 nm. The Curie temperature of the La-doped EuO was about 200 K, which is the highest T_C achieved for electron-doped EuO without transition metals. The origin of the high T_C can be qualitatively explained by first-principle band calculation but the actual increase in T_C cannot be precisely explained. To explain the T_C quantitatively, other effects such as the hybridization between Eu 4f and doped donor states and/or

the RKKY interaction mediated by the doped La 5d state must be taken into account.

We would like to thank Professor T. Takeuchi for his experimental support of EDX measurement and technical staff members of the Institute for Molecular Science and of the UVSOR Facility for their devoted support. This work was partly supported by a Grant-in-Aid for Young Scientists (Start-up) (Grant No. 21840057) from MEXT of Japan.

- ¹B. Matthias, R. Bozorth, and J. V. Vleck, *Phys. Rev. Lett.* **7**, 160 (1961).
- ²N. Tsuda, K. Nasu, A. Fujimori, and K. Siratori, *Electronic Conduction in Oxides*, Springer Series in Solid-State Sciences (Springer, New York, 2000).
- ³A. Mauger and C. Godart, *Phys. Rep.* **141**, 51 (1986).
- ⁴M. W. Shafer and T. R. McGuire, *J. Appl. Phys.* **39**, 588 (1968).
- ⁵K. Y. Ahn and T. R. McGuire, *J. Appl. Phys.* **39**, 5061 (1968).
- ⁶M. R. Oliver, J. O. Dimmock, A. L. McWhorter, and T. B. Reed, *Phys. Rev. B* **5**, 1078 (1972).
- ⁷A. A. Samokhvalov, B. A. Gizhevskii, M. I. Simonova, and N. I. Solin, *Sov. Phys. Solid State* **14**, 230 (1972).
- ⁸M. W. Shafer, J. B. Dimmock, and T. Penny, *J. Phys. Chem. Solids* **33**, 2251 (1972).
- ⁹Y. Shapira, S. Foner, and T. Reed, *Phys. Rev. B* **8**, 2299 (1973).
- ¹⁰A. A. Samokhvalov, T. I. Arbutova, M. I. Simonova, and L. D. Fal'kovskaya, *Sov. Phys. Solid State* **15**, 2459 (1974).
- ¹¹J. Schoenes and P. Wachter, *Phys. Rev. B* **9**, 3097 (1974).
- ¹²A. Mauger, C. Godart, M. Escorne, J. C. Achard, and J. P. Desfours, *J. Phys. (Paris)* **39**, 1125 (1978).
- ¹³F. Meier, P. Zurcher, and E. Kaldis, *Phys. Rev. B* **19**, 4570 (1979).
- ¹⁴C. Godart, A. Mauger, J. P. Desfours, and J. C. Achard, *J. Phys. Colloq.* **41**, C5-205 (1980).
- ¹⁵A. Mauger, M. Escorne, C. Godart, J. P. Desfours, and J. C. Achard, *J. Phys. Colloq.* **41**, C5-263 (1980).
- ¹⁶H. Rho, C. S. Snow, S. L. Cooper, Z. Fisk, A. Comment, and J. Ph Ansermet, *Phys. Rev. Lett.* **88**, 127401 (2002).
- ¹⁷T. Matsumoto, K. Yamaguchi, K. Yamada, and K. Kawaguchi, *J. Phys.: Condens. Matter* **16**, 6017 (2004).
- ¹⁸H. Ott, S. J. Heise, R. Sutarto, Z. Hu, C. F. Chang, H. H. Hsieh, H. J. Lin, C. T. Chen, and L. H. Tjeng, *Phys. Rev. B* **73**, 094407 (2006).
- ¹⁹A. Schmehl, V. Vaithyanathan, A. Herrnberger, S. Thiel, C. Richter, M. Liberati, T. Heeg, M. Rotherath, L. F. Kourkoutis, S. Muhlbaier, P. Boni, D. A. Muller, Y. Barash, J. Schubert, Y. Idzerda, J. Mannhart, and D. G. Schlom, *Nature Mater.* **6**, 882 (2007).
- ²⁰R. Sutarto, S. G. Altendorf, B. Coloru, M. M. Sala, T. Haupricht, C. F. Chang, Z. Hu, C. Schussler-Langeheine, N. Hollmann, H. Kierspel, J. A. Mydosh, H. H. Hsieh, H. J. Lin, C. T. Chen, and L. H. Tjeng, *Phys. Rev. B* **80**, 085308 (2009).
- ²¹P. G. Steeneken, L. H. Tjeng, I. Elfimov, G. A. Sawatzky, G. Ghiringhelli, N. B. Brookes, and D. J. Huang, *Phys. Rev. Lett.* **88**, 047201 (2002).
- ²²T. S. Santos, J. S. Moodera, K. V. Raman, E. Negusse, J. Holroyd, J. Dvorak, M. Liberati, Y. U. Idzerda, and E. Arenholz, *Phys. Rev. Lett.* **101**, 147201 (2008).
- ²³H. Miyazaki, T. Ito, S. Ota, H. J. Im, S. Yagi, M. Kato, K. Soda, and S. Kimura, *Physica B* **403**, 917 (2008).
- ²⁴S. Kimura, T. Ito, H. Miyazaki, T. Mizuno, T. Iizuka, and T. Takahashi, *Phys. Rev. B* **78**, 052409 (2008).
- ²⁵H. Miyazaki, T. Ito, H. J. Im, K. Terashima, S. Yagi, M. Kato, K. Soda, and S. Kimura, *Jpn. J. Appl. Phys., Part 2* **48**, 055504 (2009).
- ²⁶H. Miyazaki, T. Ito, H. J. Im, S. Yagi, M. Kato, K. Soda, and S. Kimura, *Phys. Rev. Lett.* **102**, 227203 (2009).
- ²⁷N. Iwata, G. Pindoria, T. Morishita, and K. Kohn, *J. Phys. Soc. Jpn.* **69**, 230 (2000).
- ²⁸N. Iwata, T. Morishita, and K. Kohn, *J. Phys. Soc. Jpn.* **69**, 1745 (2000).
- ²⁹T. R. McGuire, G. F. Petrich, B. L. Olson, V. L. Moruzzi, and K. Y. Ahn, *J. Appl. Phys.* **42**, 1775 (1971).
- ³⁰P. Blaha, K. Schwarz, P. L. Sorantin, and S. B. Trickey, *Comput. Phys. Commun.* **59**, 399 (1990).
- ³¹J. S. Smart, *Effective Field Theories of Magnetism* (W. B. Saunders Company, Philadelphia, 1966).
- ³²M. Arnold and J. Kroha, *Phys. Rev. Lett.* **100**, 046404 (2008).