Change of lattice constant due to hybridization effect of a ferromagnetic semiconductor EuO

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Abstract. We have measured the temperature-dependent X-ray diffraction pattern of a single-crystalline EuO (100) thin film to investigate the change of the lattice constant due to the ferromagnetic phase transition. No structural transition was observed and the contracting rate of the lattice constant was dramatically increases below the ferromagnetic phase transition temperature. It indicates that the hybridization intensity between the Eu 4f states and the other O 2p and Eu 5d states increases in the ferromagnetic phase.

1. Introduction
Europium monoxide (EuO), a ferromagnetic semiconductor, with a Curie temperature ($T_C$) of 69 K, has been attracting attention due to its anomalous magneto-optical and transport properties [1-6]. In the case of electron doping with excess Eu or the substitution of Eu$^{2+}$ ions with Gd$^{3+}$ or La$^{3+}$ ions, $T_C$ increases to as high as 150 K and a metal-insulator transition (MIT) appears in which the electrical resistivity drops by more than 12 orders of magnitude with decreasing temperature [3,7,8]. When an external magnetic field is applied, the MIT temperature is shifted to the higher temperature side and the electrical resistivity decreases due to the colossal magnetoresistive (CMR) effect [9]. Since the CMR effect originates from localized Eu$^{2+}$ 4f electrons, the spin polarization of carriers is predicted to be fully 100 % below $T_C$ [10-12]. EuO is therefore one of candidate compounds for next-generation spintronics applications such as charge-spin converters.

To clarify the origin of the ferromagnetic phase transition, changes in the electronic structure of EuO at $T_C$ have been investigated using infrared and angle-resolved photoemission spectroscopy (ARPES) [13-16]. These results indicate that the hybridizations of the Eu 4f – O 2p states and the Eu 4f – 5d states, which correspond to the superexchange and indirect exchange interactions, respectively, play an important role to the ferromagnetic phase transition. In the next step, to clarify the origin of the change of the hybridization intensity, which effect is dominant, the distortion or the contraction is investigated. In this paper, we investigated the temperature-dependent lattice parameter using a temperature-dependent X-ray diffraction (XRD) method of a single-crystalline EuO thin film across
As a result, we found a clear contraction of the lattice constant across $T_C$ without distortion. This result indicates that the hybridization intensity between the Eu 4f and O 2p states increases in the ferromagnetic phase than in the paramagnetic phase.

2. Experimental Procedure

Single-crystalline EuO thin films were grown using a molecular beam epitaxy (MBE) method [16]. The thin films were grown on 0.05 wt% Nb-doped SrTiO$_3$ (001) single-crystalline substrates. To obtain clean surface substrates, the substrates were heated at 600 °C for 1 hour in an ultra high vacuum ($2.0 \times 10^{-7}$ Pa). Barium metal with a purity of 99.9 % was evaporated using an effusion cell under an oxygen pressure of $1.0 \times 10^{-4}$ Pa to create a buffer layer of BaO with a thickness of 2.0 nm before growing EuO films. The Eu metal was evaporated under an oxygen pressure of $8.0 \times 10^{-6}$ Pa on the BaO buffer layer at a substrate temperature of 350 °C to make EuO films. The value of $T_C$ measured with a superconducting quantum interference device was 71 K. The temperature-dependent crystal structure as well as the lattice constant was observed using a $\theta − 2\theta$ XRD with a Cu Kα radiation source, after taking out to the atmosphere. A BaO capping layer with a thickness of 10 nm was evaporated onto the EuO thin film to protect from air.

3. Results and Discussion

Figure 1 shows the temperature-dependent XRD patterns of the fabricated EuO thin film with a thickness of 100 nm in the paramagnetic phase at 300 K and in the ferromagnetic phase at 20 K. Calibrated Si powder (NIST SRM640c) was also measured simultaneously for reference. As shown in Fig. 1, one diffraction peak at 35° can be attributed to EuO (002) and the other peaks can be assigned to originate from the Si powder and SrTiO$_3$ substrate. Since no diffraction peak from Eu$_2$O$_3$ (the peak should appear at about 31.5° if exists [17]) is observed in the XRD patterns, no Eu$_2$O$_3$ phase is contained. At 20 K, all diffraction peaks are consistent with those at 300 K, i.e., the crystal structure in the ferromagnetic phase at 20 K is the same as that in the paramagnetic phase at 300 K. This indicates that no distortion appears at $T_C$.

Figure 1. Temperature-dependent XRD patterns of a EuO thin film with a thickness of 100 nm on a SrTiO$_3$ substrate in the paramagnetic phase at 300 K and in the ferromagnetic phase at 20 K. Since calibrated Si powder was simultaneously measured, the diffraction peaks from the Si powder and SrTiO$_3$ substrate also appears as indicated by open circles [16]. The intensity at 20 K was multiplied by 0.1 for clarify.

Figure 2 (a) shows the detailed temperature-dependent XRD peak of EuO (002). With decreasing temperature, all of EuO (002) peaks gradually shift to the higher 2θ side. As shown in Fig. 2 (b), the
lattice constant along the perpendicular direction of the EuO thin film that can be derived from Fig. 2(a) is contracted with decreasing temperature, which is a trivial phenomenon. However the contracting rate below \( T_C \) suddenly increases from that above \( T_C \). The additional contraction of the lattice constant can be believed to originate from the ferromagnetic phase transition. From the observation of the electronic structure by ARPES measurements, the ferromagnetic phase transition is concluded to originate from by the hybridization between the Eu 4f and O 2p states and also between the Eu 4f and 5d states [15]. Due to the stronger hybridization in the ferromagnetic phase than that in the paramagnetic phase, the reduction of the unit cell volume is expected. This speculation is consistent with our observation of the temperature-dependent lattice constant of EuO, i.e., the additional contraction originates from the stronger hybridization intensity in the ferromagnetic phases than that in the paramagnetic phase. Therefore both the observed temperature dependence of the lattice constant and the previous ARPES data indicate that the hybridization effects of the Eu 4f – O 2p and Eu 4f – 5d states surely play an important role in the ferromagnetic phase transition of EuO.

**Figure 2.** (a) The detailed temperature-dependent XRD patterns of the EuO (002) peak observed in Fig. 1. The temperature-dependent lattice constant of EuO (b) obtained by the XRD patterns in (a). \( T_C = 71 \) K is evaluated from the magnetization measurements. The solid and dashed line is a linear fitting above and below \( T_C \).

4. Conclusion
In conclusion, we measured the temperature dependence of XRD patterns of the fabricated single-crystalline EuO (100) thin film. The contracting rate of the lattice constant was observed to increase below \( T_C \). The observed change of the contracting rate of the lattice constant can be attributed to the hybridization effect related to the origin of the ferromagnetic phase transition.

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