Pressure Effect in Multiferroic Phase Transition of Perovskite Ferrite Crystals NdFeO$_3$ and ErFeO$_3$

G H Hu$^a$, I Umehara$^a$, X Shuang$^a$, S Yuan$^b$ and S X Cao$^b$

$^a$Department of Physics, Faculty of Engineering, Yokohama National University, Yokohama, Japan

$^b$Department of Physics, Shanghai University, Shanghai, China

E-mail: izuru@ynu.ac.jp

Abstract. High quality single crystals of NdFeO$_3$ and ErFeO$_3$ were grown by the floating zone method. The pressure effect of their magnetic properties has been measured in the temperature range of 10–300K and under pressure up to 1.27GPa by the SQUID magnetometer with the micro high pressure cell which is designed in our laboratory. We show that the variation of magnetic properties including the Spin Reorientation (SR) transitions of the $R$FeO$_3$ ($R$: Nd and Er) under pressure. In both materials, SR transition temperatures increase with increasing applied pressures. The values of $\Delta T_{SR}/\Delta P$ are 39.1 K/GPa and 6.8 K/GPa, respectively.

1. Introduction
The $R$FeO$_3$ ($R$ is rare earth elements) with a structure of CaTiO$_3$ perovskite type in which Fe occupies the Ti position and $R$ occupies the Ca position is considered to be one of the ideal candidate of ferroelectric or multiferroic materials.

The magnetic properties of $R$FeO$_3$ are interesting since the magnetic interactions of the two different types of magnetic ions: Fe$^{3+}$ and $R^{3+}$. The competition of their interactions leads to interesting phenomena in these materials [1]. One of outstanding phenomena in rare earth orthoferrite is a spin reorientation transition of the ordered Fe$^{3+}$ magnetic moments at low temperature which originates from the competition of the Fe-Fe and R-Fe interactions. In this transition, the direction of the easy axis of magnetization changes from one crystal axis to another induced by variation of temperature or applied field [2]. The spin reorientation transitions occur between 100 K and 170 K in NdFeO$_3$ and between 88 K and 97 K in ErFeO$_3$ [3].

It has been reported that the magnetic interactions of rare earth orthoferrites are mainly due to the superexchange via Fe-O-Fe bonds [4]. While the average Fe-O-Fe angle decreases continuously from 153.3° in PrFeO$_3$ to 140.7° in LuFeO$_3$, the Néel temperature decreases from 740 K down to 623 K. It is noted that the Fe–O–Fe angle increases with increasing temperature in NdFeO$_3$ [1].

The structural and magnetic properties of $R$FeO$_3$ have been widely studied in the last decade. In this paper, we present new results of magnetization measurements under pressure in order to clarify the spin reorientation transition process.

2. Experimental detail
Rare-earth orthoferrite single crystal $R$FeO$_3$ ($R$=Nd, Er) has been successfully grown by the floating-zone technique using a four-mirror-image furnace with flowing air in Shanghai University [5].
Structural characteristics of $R$FeO$_3$ single crystal were studied using a metallurgical microscope and by scanning electron microscopy (SEM) with energy-dispersive X-ray spectroscopy (EDX). The perfect assignment for X-ray diffraction patterns of the grown crystals indicates their excellent quality, clarifying the absence of sub-grain.

Crystal axis of them was determined using X-ray Laue method. The magnetic properties under pressure has been carried out by commercial SQUID magnetometer (Quantum Design, MPMS) with the micro pressure cell which is designed by our laboratory in the temperature range from 10 K to 300 K and under pressure up to 1.2 GPa [6]. The direction of magnetic field is along $c$-axis for both compounds. Mixture of fluorinert 70 and 77 was used as pressure medium and the pressures at low temperature were determined from the values of superconducting transition temperatures of Sn.

3. Results and discussion

![Figure 1](image1.png)

**Figure 1.** Temperature dependence of magnetization for NdFeO$_3$ under different applied pressure, $H=100$ Oe.

![Figure 2](image2.png)

**Figure 2.** Temperature dependence of magnetization for ErFeO$_3$ under different applied pressure, $H=100$ Oe.
Figure 1 and 2 show the temperature dependence of magnetization (M-T) for NdFeO$_3$ and ErFeO$_3$ single crystals under different applied pressures in magnetic field of 100 Oe along the c-axis with zero field cooling to 10 K and then measured magnetism while heating the samples to room temperature, respectively.

Figure 3 and 4 show the spin-reorientation temperature dependence of applied pressure for NdFeO$_3$ in 100 Oe magnetic field.

Figure 3. Spin-reorientation temperature dependence of applied pressure for NdFeO$_3$ in 100 Oe magnetic field.

Figure 4. Spin-reorientation temperature dependence of applied pressure for ErFeO$_3$ in 100 Oe magnetic field.

In many of the orthoferrites, the easy axis direction of magnetization is known to change from one crystallographic axis to another as the temperature is raised. These transitions are called spin-reorientation transitions. Here $T_{SR}$ is defined as temperature when it reaches a new orientation. The pressure dependencies of $T_{SR}$ are shown in figure 3 and 4 for NdFeO$_3$ and ErFeO$_3$, respectively.

Figure 3 and 4 show the spin-reorientation temperature dependence of applied pressure for NdFeO$_3$ and ErFeO$_3$ in 100 Oe magnetic field. As show in above two figures, there is a jump of $T_{SR}$ at about 1 GPa for both samples. Since our sample was pressurized at room temperature and measured from 10K to 300 K, and fluorinert was used as pressure medium, and the space in micro pressure cell is too small to sample, the quality of pressurized state was not good while the pressure higher than about 1 GPa. So we chose the lower pressure data to characterize the spin-reorientation temperature dependence of applied pressure. As shown in the figures, the spin reorientation transition temperatures increase with increasing applied pressures in both materials. NdFeO$_3$ compound is more sensitive to pressure than ErFeO$_3$ compound, and the values of $\Delta T_{SR}/\Delta P$ in NdFeO$_3$ and ErFeO$_3$ are estimated as 39.1 K/GPa and 6.8 K/GPa, respectively.

Temperature dependence of the unit cell volumes of NdFeO$_3$ and ErFeO$_3$ have been measured by W Sławiński et al. from Rietveld refinement of neutron diffraction patterns data [1] and A Bombik et al. from X-ray measurements data [7], respectively. As shown in the papers mentioned above, the temperature dependence of lattice parameter of b-axis in NdFeO$_3$ reaches a minimum near 160 K and it begins to increase when the temperature becomes lower. Therefore, we compared the sensitivity of lattice condensation against temperature for two compounds in the temperature range of 160~300 K.
The lattice volumes and change ratio of NdFeO$_3$ and ErFeO$_3$ are shown in table 1. The data come from figure 3 in reference [1] and figure 4 in reference [7]. From the above data, we can consider that the structure of NdFeO$_3$ is easier to change than that of ErFeO$_3$ against temperature changes. This is in good agreement with our experiment results, because the lattice is generally shortened under pressure.

In addition, according to previous data on the orthoferrites [8, 9], the structural arrangement of the FeO$_6$ octahedra network is also important to understand the magnetic properties of rare earth orthoferrites because the magnetic interactions are mainly due to the superexchange via Fe-O-Fe bonds [4]. Therefore, the change of Fe-O-Fe angle may also play an important role in SR transition under pressure. However, we do not have enough information about that until now. Thus we are planning to study it in future.

### Table 1. The lattice volumes and change ratio of NdFeO$_3$ and ErFeO$_3$.

|          | NdFeO$_3$     | ErFeO$_3$     |
|----------|---------------|---------------|
| $V_{300K}$ (Å$^3$) | 236.50 [1]  | 223.50 [7]   |
| $V_{160K}$ (Å$^3$) | 235.75 [1]  | 222.85 [7]   |
| $R$      | 0.0032        | 0.0029        |

\[ R = \frac{V_{300K}-V_{160K}}{V_{300K}} \] (1)

In addition, according to previous data on the orthoferrites [8, 9], the structural arrangement of the FeO$_6$ octahedra network is also important to understand the magnetic properties of rare earth orthoferrites because the magnetic interactions are mainly due to the superexchange via Fe-O-Fe bonds [4]. Therefore, the change of Fe-O-Fe angle may also play an important role in SR transition under pressure. However, we do not have enough information about that until now. Thus we are planning to study it in future.

### 4. Conclusions

The following results have been obtained: (1) Rare-earth orthoferrite single crystal $R$FeO$_3$ ($R$=Nd, Er) were successfully grown by the floating-zone technique. (2) The temperature dependence of magnetization for NdFeO$_3$ and ErFeO$_3$ single crystal under different applied pressure was measured and the values of $\Delta T_{SR}/\Delta P$ in NdFeO$_3$ and ErFeO$_3$ are estimated as 39.1 K/GPa and 6.8 K/GPa, respectively. (3) The change of $T_{SR}$ under pressure in $R$FeO$_3$ is understood as an effect of lattice condensation.

### References

[1] Sławiński W, Przeniosło R, Sosnowska I and Suard E 2005 J. Phys.: Condens. Matter 17 4605-4614
[2] Yamaguchi T 1974 J. Phys. Chem. Solids 35 479
[3] Sosnowska I, Steichele E and Hewat A 1986 Physica B 136 394
[4] Landolt-Börnstein 1994 Numerical Data and Functional Relationships in Science and Technology Group III vol 27f3 ed H P J Wijn (Berlin: Springer)
[5] Yuan S J, Wang Y B, Shao M J, Chang F F, Kang B J, Isikawa Y and Cao S X 2011 Journal of Applied Physics 109 07E141
[6] Umehara I, Tomioka F, Tsuboi A, Ono T, Hedo M and Uwatoko Y 2004 J. Magn. Magn. Mater 272-276 2301-2302
[7] Bombik A, Böhm H, Kusz J, Pacyna A W and Wanklyn B M 2005 Solid State Communications 134 277–281
[8] Marezio M, Remeika J P and Dernier P D 1970 Acta Crystallogr. B 26 2004
[9] White R L 1969 J. Appl. Phys. 40 1061