

# Structural, electrical and magnetic properties of $\text{RE}_{1/3}\text{Sr}_{2/3}\text{FeO}_3$ compounds (RE= La, Pr, Nd, Eu and Gd).

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**Abstract.** We report results of structural, magnetic and electrical measurements performed on the perovskite  $\text{RE}_{1/3}\text{Sr}_{2/3}\text{FeO}_3$  compounds (RE= rare earth). Samples with light RE (La, Pr or Nd) show a metal-insulator-like transition coupled to an antiferromagnetic ordering upon cooling. This transition is believed to be brought about by a charge ordering of  $\text{Fe}^{3+}$  and  $\text{Fe}^{5+}$  ions in the low temperature phase accompanied by the concomitant structural transition. The replacing of light RE by heavy ones (Gd or Eu) gives rise to high-resistivity compounds with no metal-insulator transition. However, the magnetic transition remains at low temperatures. A previous Mössbauer study reports similar behaviour for RE=Eu compound. This suggests that variations in Mössbauer spectra may be of a magnetic origin in light RE compounds and not coming from a full charge disproportionation of  $\text{Fe}^{4+}$  as deduced previously.

## 1. Introduction.

One of the most intriguing topics in the solid state physics is the electronic localization in highly correlated oxides. Among these compounds, various ferrites with a  $\text{RE}_{1/3}\text{Sr}_{2/3}\text{FeO}_3$  composition (RE=rare earth) undergo a metal-insulator transition at  $T_{\text{MI}}$ .  $T_{\text{MI}}$  depends on the RE size. Compounds with RE heavier than Nd show semiconducting behavior in the whole temperature range. For lighter RE,  $T_{\text{MI}}(\text{La}) > T_{\text{MI}}(\text{Pr}) > T_{\text{MI}}(\text{Nd})$  and a simultaneous antiferromagnetic ordering of the Fe moments is observed at this temperature [1].

First Mössbauer spectra of  $\text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_3$  showed a single signal at room temperature and two sets of six lorentzians curves below  $T_{\text{MI}}$  [2]. This feature was ascribed to a charge disproportionation from  $3\text{Fe}^{3.66+}$  into  $2\text{Fe}^{3+} + 1\text{Fe}^{5+}$ . Subsequent neutron and electron diffraction experiments were interpreted in terms of a charge ordering along the [111] direction of the pseudo-cubic perovskite structure [3,4]. The ordering was ascribed to a sequence of  $\text{Fe}^{3+}\text{Fe}^{3+}\text{Fe}^{5+}\text{Fe}^{3+}\text{Fe}^{3+}\text{Fe}^{5+}$ . The metal-insulator transition was then attributed to this charge ordering since it removes electron jumps between equivalent iron sites. However, x-ray absorption spectra did not agree with the presence of  $\text{Fe}^{5+}$  in La-based compound below  $T_{\text{MI}}$  [5], and recent resonant x-ray scattering experiments have revealed that charge

disproportionation is not significant in  $\text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_3$  [6]. Therefore, the exact nature of the electron localization in these compounds is now an open question.

Few studies have been devoted to the properties of the ferrites with heavy RE, maybe due to the absence of metal-insulator transition. Nevertheless, Mössbauer spectra, similar to the  $\text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_3$  ones, have recently been reported for  $\text{Eu}_{1/3}\text{Sr}_{2/3}\text{FeO}_3$  [7], a compound without metal-insulator transition regarding the phase diagram of ref. 1. This result motivated us to compare the structural, electrical and magnetic properties of a wide set of  $\text{RE}_{1/3}\text{Sr}_{2/3}\text{FeO}_3$  compounds in order to shed light on the changes reported for the Mössbauer spectra of these ferrites.

## 2. Experimental section.

The samples were prepared by conventional solid state methods. Details of the synthetic route and chemical analysis were described previously [8]. In all cases, a final heat treatment under high oxygen pressure is the most important to improve the oxygen stoichiometry. The samples were sintered at 900°C with  $p_{\text{O}_2}=200$  bar during 1d with a last annealing at 450°C at the same pressure during 8 h. The samples were characterized by x-ray powder diffraction using a Rigaku RINT 2000 diffractometer and  $\text{Cu K}_\alpha$  radiation.

Magnetic measurements were carried out using a commercial Quantum Design SQUID magnetometer. Resistivity measurements were carried out using the standard six-probe ac method in the temperature range between 4 and 300 K.

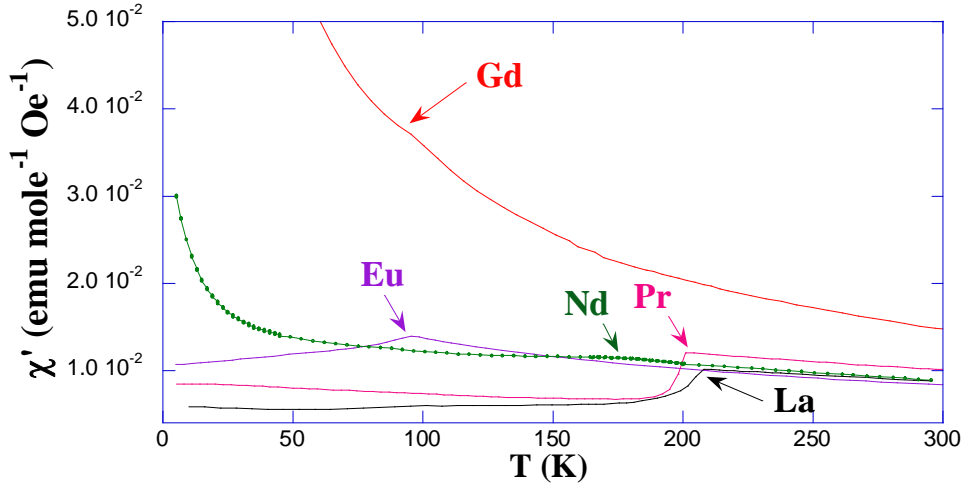
## 3. Results, discussion and conclusions.

$\text{RE}_{1/3}\text{Sr}_{2/3}\text{FeO}_3$  samples were shown to be of single phase by x-ray diffraction. They exhibit different types of distorted perovskites structure as indicated in table 1. The RE=La compound is rhombohedral ( $R-3c$ ) whereas the rest of the studied samples are orthorhombic ( $Ibmm$ ). Overall, the distortion from the ideal cubic structure is small. The unit cell volume decreases as R size decreases in agreement with the lanthanide contraction. The cell shrinking arises not from a decrease of the Fe-O bond length but from a bending of the Fe-O-Fe bond angle away from 180°.

**Table 1.** Lattice parameters, unit cell volume per formula unit (Z) and average Fe-O-Fe bond angles for  $\text{RE}_{1/3}\text{Sr}_{2/3}\text{FeO}_3$  samples. Z=6 (or 4) for rhombohedral (orthorhombic) cell. R is given in each column. Digits in parentheses refer to standard deviations.

	La	Pr	Nd	Eu	Gd
<b>a</b> (Å)	5.4780(8)	5.4857(1)	5.4827(1)	5.4575(3)	5.4556(1)
<b>b</b> (Å)	-	5.4578(1)	5.4497(1)	5.4494(3)	5.4433(1)
<b>c</b> (Å)	13.416(4)	7.7158(2)	7.7027(2)	7.7095(5)	7.6954(3)
<b>Vol/Z</b> (Å <sup>3</sup> )	58.11(1)	57.56(1)	57.53(1)	57.33(1)	57.24(1)
<b>&lt;Fe-O-Fe&gt; (Deg)</b>	175.3(2)	173.8(1)	169.7(1)	169.1(2)	168.3(1)

Figure 1 shows the temperature dependence of the ac magnetic susceptibility ( $\chi$ ) for all compounds. The measurements were taken with an alternating field of 4 Oe and a frequency of 10 Hz. The magnetic susceptibility shows an abrupt decay at the magnetic ordering temperature ( $T_N$ ) for RE=La and Pr. The curves for Nd and Eu-based samples exhibit a peak at  $T_N$ . The antiferromagnetic transition is hardly seen for the Gd compound due to the high paramagnetic contribution from  $\text{Gd}^{3+}$  ions ( $p_{\text{eff}}=7.94\mu_B$ ). A change in the slope of the susceptibility curve is ascribed to  $T_N$ , in agreement with previous reports [1,8]. Fig. 1 clearly shows that  $T_N$  decreases as the R-size diminishes. This is likely related to the increase of the unit cell distortion and consequent decrease of the Fe-O-Fe superexchange interaction which is directly proportional to the Fe-O-Fe bond angle.



**Figure 1.** The in-phase component of the ac magnetic susceptibility vs. temperature for  $\text{RE}_{1/3}\text{Sr}_{2/3}\text{FeO}_3$  compounds. RE is given for each curve and the arrows mark the  $T_N$ .

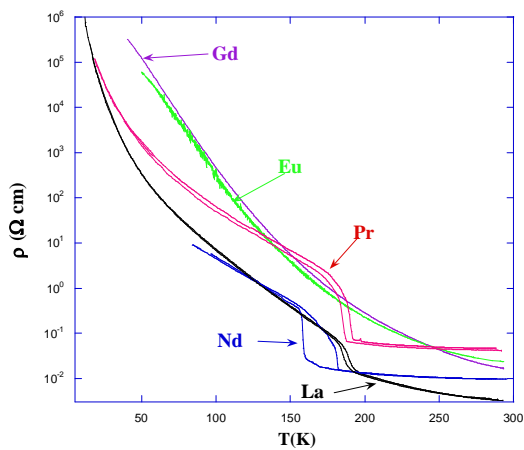
Above  $T_N$ , the temperature dependence of  $1/\chi$  is linear indicating that all samples follow a Curie-Weiss law in the paramagnetic region. Table 2 summarizes the fitted parameters for RE=Nd, Eu and Gd. We have omitted the study of La and Pr- based samples because the temperature range between  $T_N$  and room temperature is too small to obtain reliable data. The listed samples show negative Weiss constant in agreement with the presence of antiferromagnetic correlations. The calculated effective paramagnetic moments agree reasonably well with the ones expected from the contribution of  $1/3 \text{RE}^{3+}$ ,  $1/3 \text{Fe}^{3+}$  and  $2/3 \text{Fe}^{4+}$ . It is worth mentioning that although the theoretical moment for  $\text{Eu}^{3+}$  is 0, the experimentally found moment is usually  $3.5 \mu_B$  as we have observed in our Eu compound.

**Table 2.** Magnetic parameters obtained by fitting  $\chi = C (T-\theta)^{-1}$  to the experimental data in the range indicated.  $\rho_{\text{eff}}$  and  $\rho_{\text{th}}$  stands for calculated and expected (RE+Fe) effective paramagnetic moments.

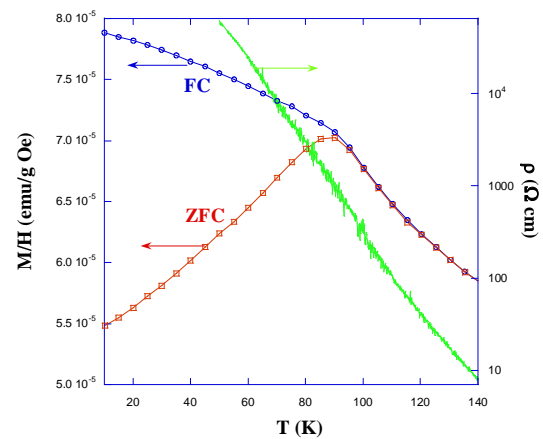
Sample	C ( $\text{emu K}^{-1} \text{mole}^{-1}$ )	$\theta$ (K)	$\rho_{\text{eff}}$ ( $\mu_B \text{f.u}^{-1}$ )	$\rho_{\text{th}}$ ( $\mu_B \text{f.u}^{-1}$ )	Range of fit (K)
Nd	4.35	-218	5.89	5.65	200-300
Eu	4.50	-240	6.0	5.63	170-300
Gd	5.35	-61	6.55	7.0	160-300

Figure 2 shows the temperature dependence of the resistivity for the compounds studied. For RE=La, Pr and Nd, the resistivity shows a clear jump at  $T_{\text{MI}}$ .  $T_{\text{MI}}$  agrees with  $T_N$  suggesting a coupling between both transitions for these compounds. Above  $T_{\text{MI}}$ , the conductivity slightly increases with increasing temperature showing semiconducting-like rather than simply metallic behaviour. Therefore, there is not an actual metal-insulator transition but a sudden change in the activation energy ( $E_A$ ). For instance, the  $E_A$  changes for the RE=La compound from 0.06 eV (above  $T_{\text{MI}}$  with a range of fit of 300-210 K) to 0.115 eV (below  $T_{\text{MI}}$  for 175 - 135 K range). For light RE (La, Pr and Nd) and above  $T_{\text{MI}}$ ,  $E_A$  ranges between 60 and 14 meV. These values are of the same order of magnitude than the thermal  $k_B T$  energy so a contribution from local defects cannot be discarded. The transition exhibits clear thermal hysteresis as occurs in a first order transition. Both Eu and Gd-based compounds exhibit semiconducting behaviour in the whole temperature range. The activation energy at high temperature (140-280 K) is 0.14 and 0.16 eV for Eu and Gd samples, respectively. These values are of the same order of magnitude as the ones found for RE=La, Pr or Nd below  $T_{\text{MI}}$ .

Now we focus on the properties of the RE=Eu compound. Figure 3 compares the magnetization and resistivity measurements for this sample. The magnetization at 2 kOe displays a magnetic irreversibility between zero field cooled (ZFC) and field cooled (FC) conditions. This property is usually ascribed to spin-glass-like behavior. However, similar type of magnetic irreversibility has been found in Nd-compounds which show long range magnetic ordering in neutron diffraction experiments [9]. This effect was explained by the competition of ferro- and anti-ferromagnetic interactions in the ordering of Fe moments. The presence of both interactions may facilitate the canting of the antiferromagnetic structure in the FC conditions.



**Figure 2.** Resistivity vs. temperature for  $\text{RE}_{1/3}\text{Sr}_{2/3}\text{FeO}_3$  compounds. R is given for each curve.



**Figure 3.** Magnetization (ZFC and FC conditions) at 2 kOe and resistivity for  $\text{Eu}_{1/3}\text{Sr}_{2/3}\text{FeO}_3$ .

Finally, we note that there is no anomaly at  $T_N$  in the resistivity curve for  $\text{Eu}_{1/3}\text{Sr}_{2/3}\text{FeO}_3$ . However, the Mössbauer spectroscopy has revealed strong changes between the spectra obtained at room temperature and below  $T_N$  [7]. These variations are similar to the ones reported for La or Nd-based compounds [2,9] so they could have a common origin. The Eu-compound does not undergo a metal-insulator transition (see Fig. 2 and 3) but only a magnetic transition. Therefore, the Mössbauer spectra changes, previously ascribed to the full  $\text{Fe}^{4+}$  disproportionation, can be attributed to the long-range magnetic ordering with two types of magnetic interactions.

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