EXTRINSIC MAGNETORESISTANCE
OF $Sr_{1.8}Ca_{0.2}Fe_{1-x}Gd_xMoO_6$ DOUBLE PEROVSKITES[⋆]

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Double perovskites of the type $Sr_{1.8}Ca_{0.2}Fe_{1-x}Gd_xMoO_6$ were synthesized by an improved ceramic technology, in air at 1200°C. The samples contain practically only one crystalline phase; the real structure varies from I4/m to P2₁/n with the change of the Ca concentration. The differences in Curie temperature and the transport charge behavior are due to variations of the conduction bandwidth resulting from the differences of the Fe-O-Mo bond topology, which are caused by the distinct size of the A^{2+} cations. Our aim is to investigate the behavior of charges transport in the $Sr_{1.8}Ca_{0.2}Fe_{1-x}Gd_xMoO_6$ system in function of temperature and the Fe/Gd concentrations ratio.

INTRODUCTION

A_2FeMoO_6 (A = Sr, Ba, Ca) are half-metallic ferromagnets well above room temperature. Its behavior arises from the fact that the carriers are spin-polarized at Fermi level. The Fe 3d electrons are localized, whereas the minority-spin Mo 4d electrons are delocalized and form the conduction band. An important contribution to the magnetoresistance is a consequence of the charge transport dependence on the scattering at magnetic domain and/or grains boundaries layers (tunneling magnetoresistance (TMR)). The polarization of localized electrons is enhanced by the external magnetic field, implicitly by the defaults of the boundaries layers. The resistivity of some double perovskites can be monitored, by using a relatively small external magnetic field, near room temperature. It makes these materials very attractive for applications in magnetoelectronics.

The ideal structure of $A_2BB'O_6$ double perovskites is cubic, F m –3 m (SG 225), with Fe on B and Mo on B′ places. In this structure Fe and Mo are perfectly ordered on B and, respectively, B′ positions, by forming two interpenetrating cubic sublattices. However, in the real double perovskite the

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order of Fe and Mo cations is not perfect and influences the Curie temperature. On other hand, because the magnetoresistance decreases near Curie temperature, the main goal of numerous studies has been the enhancement of the Curie temperature [1÷3]. The substitution of Ca with Sr induces only a small increase of the Curie temperature, despite the large difference between the ionic radii of Ca and Sr. Our goal is to obtain a new type of double perovskites, with a modified conduction band topology by a partial substitution of Fe with Gd.

EXPERIMENTAL

The $Sr_{1.8}Ca_{0.2}Fe_{1-x}Gd_xMoO_6$ double perovskites were obtained by standard ceramic technology, the final sintering taking places at 1200°C, in air. We used a reducing agent to improve the phase composition of the samples. On this way we have obtained the almost pure double perovskites. Because the resistivity of the samples strongly depends on the sintering/annealing conditions, we have treated/annealed the samples at temperatures smaller as 450 K. We investigated the sintered samples by X–ray (CoKα filtered radiation) at room temperature. The patterns were corrected for $Kα_{12}$ doublet and the instrumental broadening. The electrical measurements were performed between 300 and 450 K, by means of four probe method, at the 0 and 2T intensity magnetic field. The magnetic measurements were performed between 77 and 450 K, at 1 T, using a Foner type magnetometer.

RESULTS AND DISCUSSIONS

At temperatures higher as 460 K, the parent compound of this row, Sr_2FeMoO_6, (SFMO) ideally crystallizes in F m –3 m space group, while at lower temperatures SFMO crystallizes in I4/m space group [1]. The partial substitution of Sr with Ca leads to a change of the crystalline structure, from I4/m to $P2_1/n$ space group [1]. Chains of alternate MoO_6 and FeO_6 octahedra, more or less distorted, form the double perovskites structure, in agreement with the unit cell (s. Fig. 1). The typical diffractogram of sintered sample is presented in Fig. 2, where the pattern was indexed as being due to a $P2_1/n$ unit cell.

However, as resulted from the Rietveld tests, the difference between the atoms positions in the unit cells belonging to I4/m and $P2_1/n$ is small. From the Rietveld tests result also that a small concentration of I4/m phase (about 5–7%) could coexist together with $P2_1/n$ majority phase at room temperature.

The lattice constants, Fe-O, Mo-O distances and Fe-O-Mo angles, calculated in agreement with the atoms positions in the unit cell due to Ritter *et al.* [1] and

Fig. 1 – The $P2_1/n$ unit cell of $(Sr, Ca)_2FeMoO_6$ double perovskite.
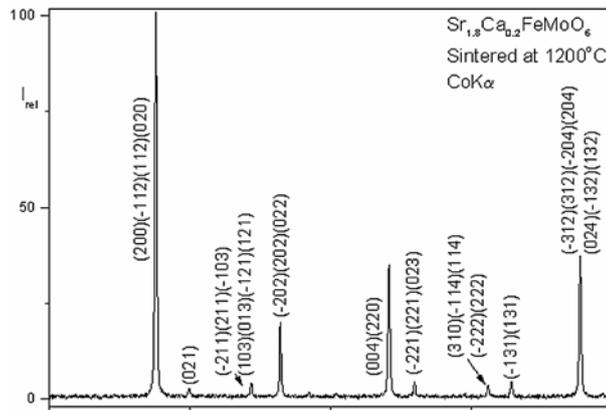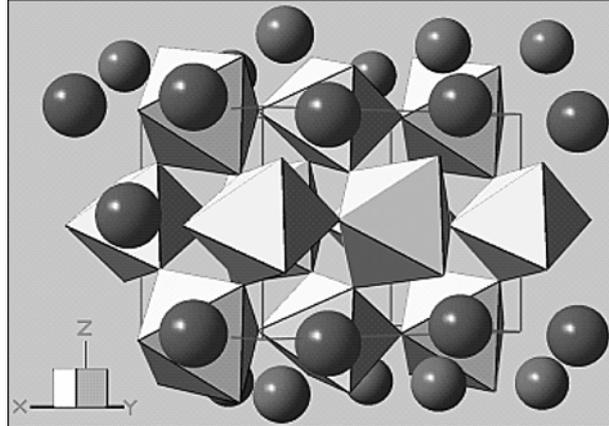

Fig. – 2 The diffractogram of sintered $Sr_{1.8}Ca_{0.2}FeMoO_6$.

obtained from the XRD data of our samples are presented in Table 1 and, respectively, Table 2. The increase of the lattice constants and of the unit cell volume takes place probably due to the increase of the low valence cations concentration. $Sr_{2-x}Ca_xFeMoO_6$ double perovskites change their phase composition with the variation of the temperature and the Ca concentration. The FullProf tests shown that in a large range of compositions/temperatures there is a mixture between the low temperature phase ($P2_1/n$) and high temperature phase (I4/m). The end temperature of the crystallographic transition between I4/m and $P2_1/n$ phase increases with the Ca concentration in the $Sr_{2-x}Ca_xFeMoO_6$ system [1].

Despite smaller Fe-O-Mo angles and larger cation-anion distances, the Curie temperature is larger for $Sr_{1.8}Ca_{0.2}FeMoO_6$ as for Sr_2FeMoO_6 [1], that it supposes a higher magnetoresistance near room temperature for double perovskites substituted with Ca. On other hand, the substitution of Fe^{3+} ($r_{Fe^{3+}} = 0.645$ Å) with Gd^{3+} ($r_{Gd^{3+}} = 0.938$ Å) should lead to a large distortion of the lattice, local modifications of the B-O and B′-O distances and B-O-B′ angles.

Table 1

The space groups (SG), lattice constants (a, b, c, β), Fe-O and Mo-O distances ($d_{\text{Fe-O}}$, $d_{\text{Mo-O}}$) and Fe-O-Mo angles for Sr_2FeMoO_6 and $Sr_{1.8}Ca_{0.2}FeMoO_6$ double perovskites[*]

Chemical composition	SG	a [Å]	b [Å]	c [Å]	β [°]	$d_{\text{Fe-O}}$	$d_{\text{Mo-O}}$	Fe-O-Mo [°]
Sr_2FeMoO_6	I4/m	5.554_9	5.554_9	7.903_4	90.0	1.970	1.981	180.00
						1.975	1.970	169.49
$Sr_{1.8}Ca_{0.2}FeMoO_6$	P2$_1$/n	5.563_9	5.551_1	7.848_4	90.01	2.011	1.936	167.64

[*] in agreement with the data from [1].

Table 2

The lattice constants (a, b, c, β), Fe-O and Mo-O distances ($d_{\text{Fe-O}}$, $d_{\text{Mo-O}}$) and Fe-O-Mo angles ($\langle$Fe-O-Mo$\rangle$) of $Sr_{1.8}Ca_{0.2}Fe_{1-x}Gd_xMoO_6$ double perovskites at room temperature

x	SG	a [Å]	b [Å]	c [Å]	β [°]	$\langle d_{\text{Fe-O}}\rangle$	$\langle d_{\text{Mo-O}}\rangle$	$\langle$Fe-O-Mo$\rangle$ [°]
0.0	P2$_1$/n	5.558_9	5.553_1	7.858_4	90.01	2.124	1.893	156.139
0.1	P2$_1$/n	5.560_3	5.557_1	7.859_4	90.01	2.130	1.899	155.071
0.2	P2$_1$/n	5.563_1	5.560_2	7.862_5	90.01	2.113	1.902	156.767

The average distances (Fe, Mo) – O have a maximum with the increase of the Gd concentration in the samples (s. Table 2) and are larger as the corresponding values of $Sr_{1.8}Ca_{0.2}FeMoO_6$, founded by Ritter *et al.* [1]. On other hand, the interatomic Fe–O distance is intermediate between Fe^{3+} (high spin state) – O and Fe^{2+} (high spin state) –O (~2 14 Å) distances in agreement with the XANES result [4]. It means that the Fe cations on the B site are in an intermediate valence state, between 3+ and 2+.

The superexchenge interaction between Fe and Mo (or Fe) cations decreases with the increase of the Fe (Mo)–O distances, that leads to the observed values of Curie temperature (Table 3). On other hand, the Curie temperature decreases with the decrease of the Fe–O–Mo angles, in agreement with the literature [1–3] and present data.

Table 3

The magnetic properties (σ_0 -specific magnetization, p – molecular magnetization (at 77 K), T_C – Curie temperature), average size of the crystalline blocks (D) and microstrains (ε) of $Sr_{1.8}Ca_{0.2}Fe_{1-x}Gd_xMoO_6$ double perovskites

x	σ_0 [uem/g][*]	p (μ_B/f.u.)[*]	T_C [K]	V_{cell} [Å^3]	D [Å]	ε
0.0	33.55	2.48	369.5	242.582	1053	0.00075_7
0.1	27.03	2.05	329.3	242.849	738	0.00265_3
0.2	22.53	1.75	345.6	243.202	859	0.00116_5

[*] extrapolated at 0 K

The maximum of the specific magnetization of the $Sr_{1.8}Ca_{0.2}Fe_{1-x}Gd_xMoO_6$ double perovskites decreases monotonously with the increase of the Gd concentration in the samples, while the Curie temperature presents a minimum for $x = 0.1$ (Table 3). Between observed and calculated specific (molecular) magnetization there is a large difference, which can be attributed to: 1) the existence of antiphase domains boundaries; 2) the iron cations on antisite positions (a Fe cation is surrounded by six Fe cations); 3) the iron cation is surrounded by four Mo cations and two Fe cations [2]. The iron cations from the antiphase domains boundaries behave paramagnetic, while the magnetic moments of iron cations from the antisite positions are antiferromagnetic aligned. We suppose that the transfer possibility of the iron cations from B to B′ sites is enhanced by the disorder induced in the actual $Sr_{1.8}Ca_{0.2}Fe_{1-x}Gd_xMoO_6$ double perovskites by the sintering process.

The disorder, produced by the presence of the Ca on A places and Gd on B places, decreases the volume corresponding ferromagnetic aligned iron cations, and increases the volume occupied by the antiphase domains boundaries and the concentration of antisite positions. On other hand, the change in the phase composition with the temperatures or/and Gd concentration (increase of I4/m structure phase concentration with the increase of the temperature) leads to a decrease of the difference between the volumes of FeO_6 and MoO_6 octahedra; implicitly to a change of the charge transfer characteristics. The substitution of Fe with Gd leads to the breaking of the Fe-O-Mo-O-… chain and the forming of some antiferromagnetic and/or paramagnetic zone, because the magnetic moment of Gd does not contribute to the magnetic moment of the perovskite lattice, implicitly to the double exchange interaction.

The substitution of Fe with Gd determines the appearance of a large local distortion of the B places lattice. A nonuniform distribution of the Gd^{3+} cations in the crystallite, with a larger concentration at the boundary layers, is possible. Because the Gd^{3+} cations accommodate better with the distorted boundary layers, take place: 1) an increase of the thickness of the boundary layers; 2) an increase of the specific magnetization of the crystalline core and of the Curie temperature; 3) a decrease of the double exchange interactions, implicitly, of the Curie temperature and specific magnetization corresponding to the boundary layers volume.

In agreement with the Rubi et al the observed Curie temperature depends on the antisite places concentration [3]. Taking account the minimum of the Curie temperature variation with the Gd concentration, we consider that the antisite places concentration will present a minimum of concentration around $x = 0.1$. The effect of the Gd concentration increase prevails, as comparing with the effect of antisite places concentration, on the decrease of the specific magnetization. Because the volume of the boundary layer is much smaller as the

volume corresponding to the crystalline core, the specific magnetization is not depending on the magnetization processes, which take place in the boundary layers. On the other hand, the decrease of the Fe-O-Mo bond angle, leads to a decrease of ferromagnetic coupling and a corresponding decrease of the Curie temperature (Table 2).

The increase of the temperature should lead to the increase of the I4/m phase and a modification of the concentration of the lattice defaults, implicitly of the variation of the resistivity with the temperature. In agreement with [1] the increase of I4/m phase concentration should lead to a decrease of the difference between the volumes of FeO_6 and MoO_6 octahedra and, implicitly, to the modification of the charge transfer between B and B' places, implicitly the resistivity of the samples. Kobayashi et al have explained the transport properties of Sr_2FeMoO_6 double perovskite by the polarization of electronic spin at Fermi level [5]. The observed resistivity values of the $Sr_{1.8}Ca_{0.2}Fe_{1-x}Gd_xMoO_6$ double perovskites at room temperatures are two orders higher as those obtained by Kobayashi et al [5]. The substitution of Fe with other metallic trivalent cations as Mn or Al leads to different effects in the phase composition, despite the approach between the Fe^{3+}, Mn^{3+} and Al^{3+} radii. The substitution of Fe with Mn seems to produce an electronic phase segregation and appearance of Sr_2MnMoO_6 AFM phase, which coexists with a $Sr_2(Fe,Mn)MoO_6$ FM phase, while no difference exists between the crystallographic structures of these two phases [6].

On other hand, the substitution of Fe with Al broke the Fe-O-Mo-O-Mo-. chains, which become more sensitive to the low field variation, and suppress the antiferromagnetic exchange [7]. However, these substitutions did not lead to so much increase of the resitivity. The actual values of the resistivity can be explained by: 1) an oxidation of the boundary layers of the crystallites and 2) the contribution of Gd cations on the lattice distortions.
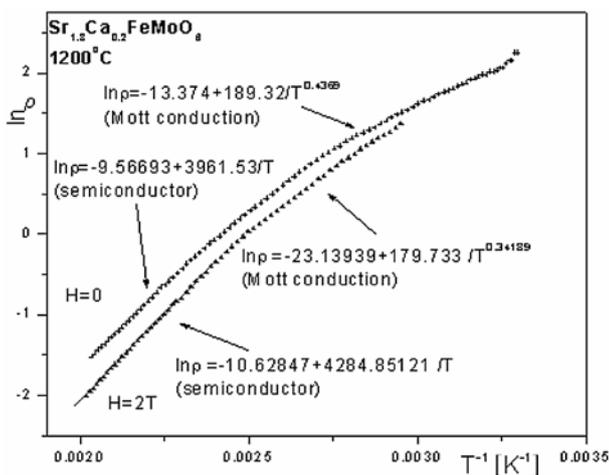

Fig. 3 – Variation of resistivity with the temperature and intensity of the magnetic field for $Sr_{1.8}Ca_{0.2}FeMoO_6$.

The variation of the resistivity with the temperature demonstrated that the all the samples have a negative magnetoresistivity between 300 and 450 K (Fig. 4). Near the room temperature predominates the VHR (variable hopping range) mechanism, while at higher temperature predominates the semiconductor mechanism. The results concerning the VHR mechanism, including the density of state at Fermi level, will be published elsewhere. The activation energy for the semiconductor mechanism is practically the same, independent on the Gd concentration in the samples ($E_S \approx 0.346$ eV). The largest values of the resistivity and of the magnetoresistance are associated with the largest values of the microstrain and the smallest values of average size of the crystalline blocks (Figs. 3 and 4 and Table 2).

Fig. 4 – Magnetoresistivity of the $Sr_{1.8}Ca_{0.2}Fe_{1-x}Gd_xMoO_6$ double perovskites.
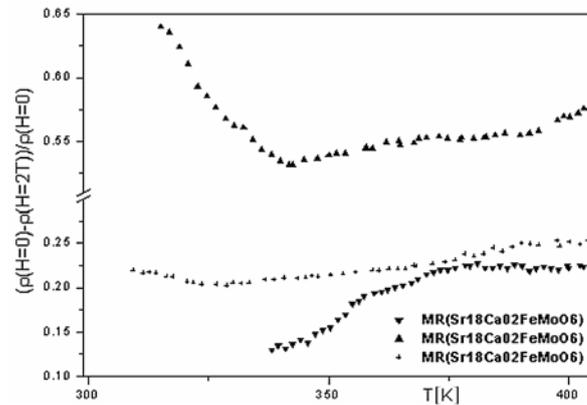
CONCLUSIONS

The substitution of Fe with Gd allowed us to obtain the double perovskites with large magnetoresistivity around room temperature.

The lattice constants are larger as thus corresponding the $Sr_{1.8}Ca_{0.2}Fe_{1-x}Gd_xMoO_6$ double perovskites from literature, because the used reduction procedure implies the appearance of a large concentration of the cations with low valence state. The $Sr_{1.8}Ca_{0.2}Fe_{1-x}Gd_xMoO_6$ double perovskites crystallize in $P2_1/n$ space group (SG 14) at room temperature. The observed values of the resistivity are higher as those typical values of the metallic state. This behavior is associated with the presence of the carriers scattering at boundaries grains. The change of ration between the concentration of monoclinic and, respectively, tetragonal phases with temperature leads to a change of the microstrains and average dimension of the crystallites. It is associated with a change of the defects concentration not only in the boundaries grains, but also in the grains "core".

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