



Magnetic properties of $\text{Sr}_2\text{Fe}_{1-x}\text{Ni}_x\text{MoO}_6$ perovskites

E. Burzo¹ and G. Souca^{1,*}

¹ Faculty of Physics, Babes-Bolyai University, 400084 Cluj-Npoca, Romania

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ABSTRACT

The magnetic properties of $\text{Sr}_2\text{Fe}_{1-x}\text{Ni}_x\text{MoO}_6$ perovskites, with $x \leq 0.2$, in a large temperature range, are reported. The saturation magnetizations decrease, while the Curie temperatures increase, as the nickel content is higher. These trends are correlated with the distribution of magnetic ions in B and B' sites. The reciprocal susceptibilities follow non linear temperature dependences. The magnetic properties are analysed assuming a two sublattices model, in the mean field approximation.

1 Introduction

The crystal structure and magnetic properties of $\text{Sr}_2\text{FeMoO}_6$ double perovskite were reported near 60 years ago [1]. Relatively recent studies, showed that this material is half-metallic, having large low field magnetoresistance [2]. Taking into account their Curie point, $T_c \approx 400$ °C, above room temperature, this perovskite was shown to be suitable for spin electronics applications and magnetoresistance based devices.

The ideal structure of $\text{Sr}_2\text{FeMoO}_6$ perovskite can be viewed as a regular arrangement of corner-sharing FeO_6 and MoO_6 octahedra, alternating along the three directions of the crystal. Although the structure falls within the cubic Fm3m space group, the crystal lattice of $\text{Sr}_2\text{FeMoO}_6$ is distorted. Since of large size of Sr^{2+} ions, occupying the voids in between the octahedra, these undergo cooperative tilting distortions,

towards the most energetically favourable structure, which causes reduction of the cube cell to the tetragonal I4/m lattice.

The Fe and Mo atoms, in the ideal structure of $\text{Sr}_2\text{FeMoO}_6$, occupy the B and B' sites, respectively, favouring a NaCl type ordered structure. In this ideal atomic arrangement, the perovskite is ferrimagnetically ordered. The array of parallel Fe^{3+} magnetic moments are antiparallely coupled with the Mo^{5+} spins; the resulting moment per formula unit is expected to be $4\mu_B$ [3]. The experimentally determined magnetic moments, smaller than the above-mentioned value, are due to: (1) antisite B cation disorder, when some Mo^{5+} cations occupy the position of the Fe^{3+} cations and vice versa; (2) a fraction of iron has Fe^{2+} valence state, with concomitant presence of Mo^{6+} ions; (3) the Mo^{5+} magnetic moment, at $T = 4$ K, is smaller than the expected value of $1 \mu_B$.

Address correspondence to E-mail: gabrielasouca@gmail.com

A collinear magnetic structure, with $M_{\text{Fe}} = 3.9 \pm 0.1 \mu_{\text{B}}$ and $M_{\text{Mo}} = -0.37 \pm 0.6 \mu_{\text{B}}$ was determined for $\text{Sr}_2\text{FeMoO}_6$ by a neutron diffraction measurement, at $T = 15 \text{ K}$ [3], or with $M_{\text{Fe}} = 3.97 \pm 0.1 \mu_{\text{B}}$ and $M_{\text{Mo}} = -0.19 \pm 0.1 \mu_{\text{B}}$ at $T = 2 \text{ K}$ [4]. By X-ray magnetic circular dichroism (XMCD), on a polycrystalline $\text{Sr}_2\text{FeMoO}_6$ perovskite, mean magnetic moments $M_{\text{Fe}} = 2.89 \pm 0.03 \mu_{\text{B}}$ and $M_{\text{Mo}} = 0.32 \pm 0.03 \mu_{\text{B}}$, were also reported [5]. By using X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy (XAS) on highly ordered $\text{Sr}_2\text{FeMoO}_6$ sample, a mixed valence state of iron ions, involving 66% Fe^{2+} — Mo^{6+} and 34% Fe^{3+} — Mo^{5+} states has been shown [6]. Also, the presence of a nonuniform composition inside the grains, as well as the effect of grain boundary on the transport properties of ordered $\text{Sr}_2\text{FeMoO}_6$ perovskite, were analysed [7].

The temperature dependence of the magnetic susceptibility, χ , of $\text{Sr}_2\text{FeMoO}_6$, above the Curie point, revealed the presence of magnetic ordered impurities [8]. The analysis of the data, according to Honda-Arrot plot, evidenced a Curie–Weiss type behaviour, with a Curie constant, smaller than that of Fe^{2+} ions [9]. Since the perovskite is ferrimagnetically ordered, deviations from a linear temperature dependence of χ^{-1} values are expected, although not observed in the above report.

The previous studies performed on $\text{Sr}_2\text{Fe}_{1-x}\text{Ni}_x\text{MoO}_6$ perovskites reported an increase of the Curie temperatures, T_c when increasing the nickel content [10, 11]. Different trend for magnetizations, M_s , determined at $T = 300 \text{ K}$, were evidenced, either decreasing [10] or increasing [11], as the iron is gradually substituted by nickel. In the above reports, the M_s values were obtained at different reduced temperatures, T/T_c , located between 0.74 ($x = 0$) and 0.69 ($x = 0.2$) and therefore cannot describe correctly their composition dependence at low temperatures, due to different thermal effects. The sintering method influence also the magnetic properties. The increase of magnetizations in $\text{Sr}_2\text{Fe}_{1-x}\text{Ni}_x\text{MoO}_6$, as iron was substituted by nickel, was correlated with the increase of atomic ordering [11], despite that nickel in B site has a smaller magnetic moment than those of ferrous or ferric ions.

In this report, starting from experimental results, the magnetic properties of $\text{Sr}_2\text{Fe}_{1-x}\text{Ni}_x\text{MoO}_6$ were analysed assuming a two sublattices mean field model, corresponding to B and B' sites magnetizations. The locations of constituent's ions, their valence

states as well as the exchange interactions inside and between magnetic sublattices were discussed in correlation with the sample's compositions.

2 Experimental

The $\text{Sr}_2\text{Fe}_{1-x}\text{Ni}_x\text{MoO}_6$ perovskites, with $x \leq 0.2$, were prepared by solid state reaction, as already described [12]. Stoichiometric amounts of high purity SrCO_3 , Fe_2O_3 , MoO_3 and NiO powders were mixed and calcinated in argon atmosphere, at $T = 900 \text{ }^\circ\text{C}$. The calcinated powders were pelletized and sintered at $T = 1300 \text{ }^\circ\text{C}$, during 8 h in a mixture of $\text{Ar}/3\%\text{H}_2$ atmosphere.

The phase purity, crystal structure and lattice parameters were determined by XRD, in Bragg–Brentano geometry, by using a Seifert-type equipment and CuK_α radiation ($\lambda = 1.54059 \text{ \AA}$). The spectra were analysed by Rietveld method.

The antisite contents were estimated from the intensities of (101), (200) and (112) lines of XRD spectra, $I(101)/[I(200) + I(112)]$ as already suggested [13] or starting from saturation magnetizations. The $\text{Sr}_2\text{FeMoO}_6$ sample has been already studied by XPS and XAS and was assumed to have a composition close to the nominal one [6]. Only the composition of the sample with $x = 0.2$ has been investigated. There are small differences between the grain's compositions, the normalized ones to Sr_2 content for two grains being $\text{Sr}_2\text{Fe}_{0.77-0.81}\text{Ni}_{0.19-0.22}\text{O}_{5.85-5.9}$. Analysing the magnetic properties, we assumed that $\text{Sr}_2\text{Fe}_{1-x}\text{Ni}_x\text{MoO}_6$ perovskites, have compositions close to the nominal ones. As will be shown latter, the errors introduced, as in case of sample with $x = 0.2$, are of the order of $\approx 3\%$.

Magnetic measurements were made at $T = 4.2 \text{ K}$, in field up to 70 kOe, by extraction method with a Maglab 2000 type equipment from Oxford Instruments, working in the temperature range $4 \text{ K} \leq T \leq 400 \text{ K}$. The Curie temperatures were determined analysing the temperature dependencies of magnetizations in low fields. At $T \geq T_c$, the magnetic susceptibilities were determined also by using a Faraday-type balance up to $T = 800 \text{ K}$. The magnetic susceptibilities were determined according to Honda-Arrot plot, from their field dependences, $\chi_0 = \chi + c M'_s H^{-1}$, by extrapolating the measured values at $H^{-1} \rightarrow 0$ [14]. By c is denoted a presumed

magnetic ordered impurity content having M'_s magnetization. In this way any possible alteration of the magnetic susceptibility, due to presence of small quantity of magnetic ordered phase, is avoided.

3 Experimental results

The XRD patterns of $\text{Sr}_2\text{Fe}_{1-x}\text{Ni}_x\text{MoO}_6$ perovskites, at ambient temperature, indicated the presence of a single-phase double perovskite in the composition range $x \leq 0.2$. These crystallize in the tetragonal type structure, space group $I4/mmm$; only traces of impurities were identified. Both the a and c lattice parameters decrease when increasing the nickel content—Fig. 1. The tetragonal distortion parameters increase from 2.73×10^{-3} ($x = 0$) to 2.90×10^{-3} ($x = 0.2$), being only little smaller than those previously determined on the same system [11].

The presence of (101) spots, which reflect the ordering of Fe/Mo ions in B/B' sites, have been evidenced in all samples. The antisite defects, AS, i.e. occupations of Fe(Mo) ions in the Mo(Fe) sites, were determined from the relative intensity of the ratio $I_{101}/(I_{122} + I_{200})$ [13]. The AS content increases from $\approx 4\%$ ($x = 0$) up to 11% ($x = 0.2$). These values are little smaller than that already reported on the same system, [11] being associated with higher sintering temperature and time, than used in previous reports. The AS defects were estimated also from the composition dependence of magnetization, expected as Ni^{2+} ions are located in B sites and that

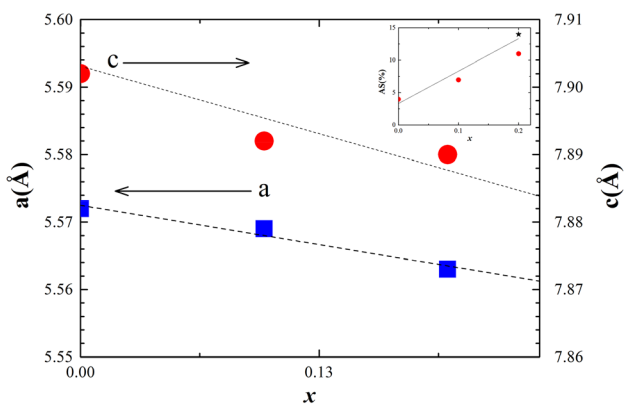


Fig. 1 Composition dependences of the lattice parameters. The antisite content is shown in inset. The AS fraction of 14%, for sample having $x > 0.2$, determined by magnetic measurements is also given (filled star)

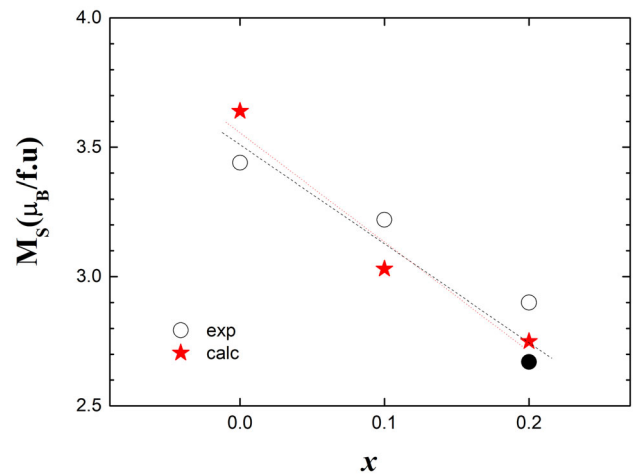


Fig. 2 Composition dependences of the saturation magnetizations, experimentally determined at $T = 4$ K and calculated assuming the AS content determined from XRD (filled star) and magnetic data (filled circle)

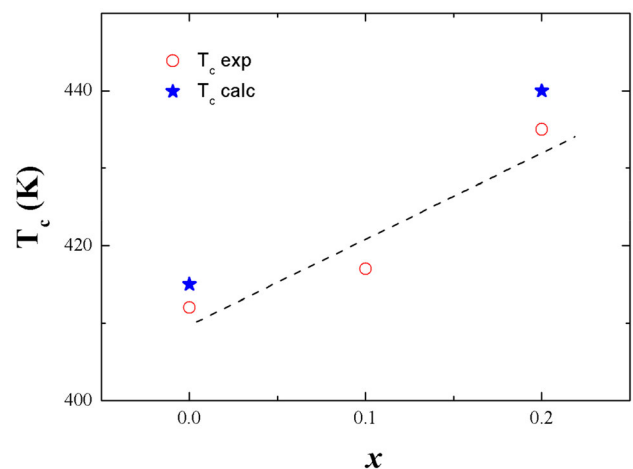


Fig. 3 The composition dependence of the Curie temperatures experimentally determined and the calculated values

experimentally determined. These are little higher than those obtained by XRD—Fig. 1 inset.

The saturation magnetizations, determined at $T = 4.2$ K, decrease when increasing nickel content, while the Curie temperatures, T_c , follow an opposite trend—Figs. 2 and 3. Such a behaviour is rather interesting; commonly an increase of magnetizations taking place parallel with those of T_c values.

The $\text{Sr}_2\text{Fe}_{1-x}\text{Ni}_x\text{MoO}_6$ double perovskites are ferromagnetically ordered, the magnetic moments of the ions located in B sites, being antiparallely oriented to those situated at B' sites. Such a magnetic structure can be analysed assuming a two sublattices model, in the mean field approximation [15]. Additional

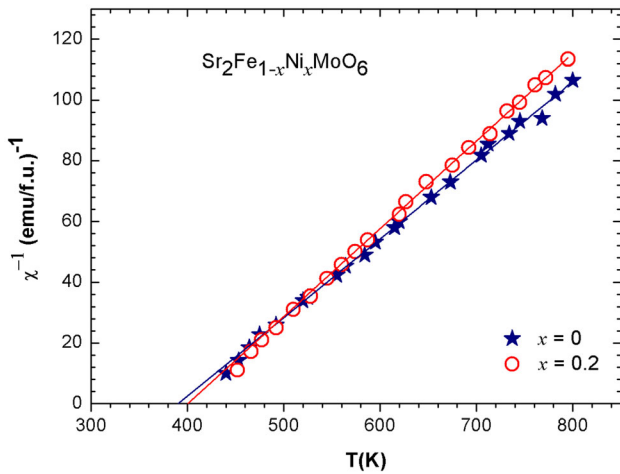


Fig. 4 Thermal variations of reciprocal susceptibilities for Sr₂Fe_{1-x}Ni_xMoO₆ perovskites with x = 0 and 0.2

information on such a system can be obtained from their magnetic behaviour at $T > T_c$ —Fig. 4.

The thermal variations of the magnetic susceptibilities follow non-linear dependences, characteristic for a ferrimagnetic system, as described by Néel relation [15]:

$$\frac{1}{\chi} = \frac{1}{\chi_0} + \frac{T}{C} - \frac{\sigma}{T - \theta} \tag{1}$$

By C is denoted the Curie constant and χ_0^{-1} , σ and θ parameters are related to the exchange interactions between and inside the magnetic sublattices as well as the contributions to the Curie constant of the two sublattices. The parameters involved in relation (1), obtained by fitting χ^{-1} versus T data with relation (1), are listed in Table 1.

The contributions to the Curie constants of the ions situated in B and B' sites, C_B and $C_{B'}$ were evaluated starting from the additional law of magnetic susceptibilities [15] as well as the experimentally determined saturation magnetizations. An ionic model was assumed, where the effective moments of constituent elements are given by their free ion values [9].

According to additional law of magnetic susceptibilities, Curie constants, respectively [15, 16] we have:

$$C = uC_{Fe^{3+}} + (1 - u)C_{Fe^{2+}} + xC_{Ni^{2+}} + vC_{Mo^{5+}} \tag{2}$$

Taking into account also the charge neutrality rule, the content and valences of constituting elements were determined assuming nominal compositions of perovskites. The Fe³⁺ fractions $u = 0.39$ ($x = 0$) and $u = 0.41$ ($x = 0.2$) were obtained. When the mean composition of sample with $x = 0.2$, as determined by SEM, is used, the determined Fe³⁺ content was 0.425 very close to above mentioned values. The content of ferric ions reported on the same Sr₂FeMoO₆ sample, by XPS and XAS, implies 66% Fe²⁺—Mo⁶⁺ and 34% Fe³⁺—Mo⁵⁺ states [6], little different from our estimation using magnetic measurements.

The composition dependences of the experimentally determined magnetizations are best described assuming: (1) the Mo⁵⁺ magnetic moment, at $T = 4$ K, is $\approx 0.4 \mu_B$ /atom, as suggested by neutron diffraction [3, 4] and XMCD [5] studies on Sr₂FeMoO₆ and those of Fe³⁺, Fe²⁺ and Ni²⁺ of $5 \mu_B$, $4 \mu_B$ and $2 \mu_B$, respectively; (2) the Ni²⁺ ions replace ferrous ions in B site; (3) in the B' sites are located, in addition to molybdenum ions, ferric ions, according to antisites content. The magnetizations thus obtained, as shown in Fig. 3, describe rather well the experimental results, the differences being of the order of 3–4%

Starting from above distributions of ions in B and B' sites, the contributions to the Curie constants of the B (C_B) and B' ($C_{B'}$) sublattices were determined, $C = C_B + C_{B'}$. The ratio $C_B/C_{B'}$ is rather high, stressing the dominant contribution of B sublattice to the magnetic susceptibility. Consequently, there are relatively small deviations from a linear χ^{-1} versus T dependence, outside the temperature range $T_c < T < T_c + 180$ K. Thus, in some reports, the magnetic susceptibility of Sr₂FeMoO₆ was assumed to follow a Curie–Weiss type behaviour [8].

The parameters J_{ij} ($i, j = B, B'$) describing the mean exchange interactions inside and between magnetic sublattices, were determined from paramagnetic data, according to Néel's model [15, 16]—Table 2. The exchange interactions parameters $J_{BB'}$ between the two sublattices are negative as expected for a

Table 1 Data obtained by paramagnetic measurements

Composition	C (emuK/f.u.)	χ_0^{-1} (emu/f.u.) ⁻¹	σ (Kemu/f.u.)	θ (K)
Sr ₂ FeMoO ₆	3.96	− 94.8	326	382
Sr ₂ Fe _{0.8} Ni _{0.2} MoO ₆	3.56	− 167.6	398	403

$$1 \text{ emu/f.u.} = 4\pi 10^{-6} \cdot \text{m}^3/\text{f.u}$$

Table 2 The exchange interactions parameters

Composition	$J_{BB'}$	α_{BB}	$\alpha_{B'B'}$
$\text{Sr}_2\text{FeMoO}_6$	– 17	5.8	38
$\text{Sr}_2\text{Fe}_{0.8}\text{Ni}_{0.2}\text{MoO}_6$	– 24	5.7	27

$$J_{BB} = \alpha_{BB}/|J_{BB'}|, J_{B'B'} = \alpha_{B'B'}/|J_{BB'}|$$

ferrimagnetic system. These values, in absolute magnitude, increase as the iron is substituted by nickel. The $J_{B'B'}$ values do not change, while a small increase of J_{BB} is shown for sample with $x = 0.2$, as compared to that determined for the end series perovskite.

4 Conclusions

The $\text{Sr}_2\text{Fe}_{1-x}\text{Ni}_x\text{MoO}_6$ ordered solutions, crystallize in a tetragonal structure, in the composition range $x \leq 0.2$. These perovskites are ferrimagnetically ordered. The Curie temperatures increase while the saturation magnetizations decrease, when increasing nickel content. An opposite trend for the composition dependence of the magnetization, at $T = 300$ K, was shown in disordered $\text{Sr}_2\text{Fe}_{1-x}\text{Ni}_x\text{MoO}_6$ [11]. This behaviour was attributed to the increase of the atomic ordering, followed by those of the magnetizations, although the nickel located in B site has a smaller magnetic moment than the substituted ferrous ions.

The increase of the Curie temperatures when increasing nickel content can be correlated with the exchange interactions between B and B' sublattices, as the number of the antisite content increases, B' magnetization, respectively. Similar behaviour was already reported in $\text{Sr}_2\text{FeMoO}_6$ perovskite and correlated with changes in the fraction of antisites [17]. A theoretical model, also attributed to antisite defects, a role in stabilizing the magnetic ordered phase in perovskite [18].

The Curie temperatures, calculated with the exchange interactions parameters, determined mainly from paramagnetic data, according to mean field model [15], describe well the experimentally determined values—Fig. 3. This fact stresses the reliability of the data obtained both below and above Curie temperatures, in describing the magnetic

properties of perovskites as already showed in case of $\text{Ca}_2\text{Fe}_{1-x}\text{Ni}_x\text{MoO}_6$ perovskites [19].

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