Research articles

The influence of cation ordering and oxygen nonstoichiometry on magnetic properties of Sr₂FeMoO₆₋ₓ around Curie temperature

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ABSTRACT

Sr₂FeMoO₆₋ₓ polycrystalline samples with different oxygen content (6−x) and various degrees of superstructural ordering of Fe/Mo cations (P) were obtained by the solid-phase method from the SrFeO₂.₅₂ and SrMoO₄ precursors. From the investigation on the influence of oxygen non-stoichiometry and the P parameter on the magnetic properties of Sr₂FeMoO₆₋ₓ, it was found that with an increase in P and a decrease in the (6−x) value from 5.99 to 5.94, an increase in the magnetization values is observed in the temperature range 77–600 K. For all the Sr₂FeMoO₆₋ₓ samples there is a tendency that P value rises with increasing x, where, accordingly, the volume fraction of regions in which there are no anti-structural defects increases as well. This is also indicated by Mössbauer spectroscopy data, confirming an increase in the area of the S₁ sextet corresponding to Fe ions in highly ordered regions and a decrease in the area of the S₂ sextet associated with disordered regions. Using the temperature scanning method, the temperatures of the onset and completion of the transition from the paramagnetic to the ferrimagnetic state and, correspondingly, the blurring width of the transition have been estimated. It turned out that with decreasing P, the blurring of the transition increases, which is associated with an increase in the concentration of anti-structural defects.

1. Introduction

The strontium ferromolybdate Sr₂FeMoO₆₋ₓ with a double perovskite structure is one of prospective materials for applications in the microelectronic industry such as magnetic random access memory (MRAM), magnetic reading heads for hard disk drives, and fuel cell electrodes [1–3]. For these applications, structurally perfect Sr₂FeMoO₆₋ₓ samples with high Curie temperatures, saturation magnetization, large degree of the Fe/Mo cations superstructural ordering as well as the high spin polarization of the delocalized electrons are required [4–7].

Thus, a technology for fabricating high-grade structurally perfect Sr₂FeMoO₆₋ₓ samples with reproducible magnetic and electrical transport properties is of utmost importance. One of the most important conditions of the existence of the maximal spin-polarization degree in the strontium ferromolybdate is the superstructural ordering of Fe and Mo cations, located at the centers of the octahedra, while there are oxygen anions O(1) and O(2) at the vertices [8]. In an actual crystal structure, due to the presence of various point defects, especially the anti-structural ones ([Mo]Fe and [Fe]Mo), as well as the anionic vacancies V₀, the crystal structure becomes distorted. It leads to the redistribution of the electronic density and a formation of iron cations, Fe²⁺, 3d⁶(S = 2) and molybdenum cations, Mo⁶⁺, 4d⁴(S = 0). Magnetic cations Mo⁶⁺(4d⁴) do not take part in the exchange interactions, and only negative exchange interactions are possible between the Fe²⁺ (3d⁶) or Fe³⁺ (3d⁵) ions, which leads to a formation of the antiferromagnetic ordering of their magnetic moments.

Physical-chemical properties of the Sr₂FeMoO₆₋ₓ, considerably depend on the oxygen stoichiometry, which influence the degree of superstructural ordering of the iron and molybdenum cations, orbital, charge and spin degrees of freedom and correspondingly on the electronic exchange between Fe³⁺ and Mo⁵⁺ [9–11]. The presence of oxygen ion or their vacancies on the Sr₂FeMoO₆₋ₓ grains surface promotes a modification of the charge electronic density on the grain...
superstructural ordering in the Sr$_2$FeMoO$_6$ 350 K and pressed into pellets. In the process of the SrFeO$_3$ bromill in alcohol during 3 h. The obtained mixtures were dried at metric mixture of the initial reagents have been carried out in the vi-
MoO$_3$, Fe$_2$O$_3$ and SrCO$_3$. Milling and compounding of the stoichio-
cursors were prepared by the conventional ceramic technique from
the presence of the (1 0 1) re
SrFeO$_{2.52}$. hydrogen
phase technique from the SrFeO$_{2.52}$ and SrMoO$_4$ precursors. The pre-
structural ordering of the Sr$_2$FeMoO$_6$ 350 K during 20 h to the SrO simple oxide and Fe
20 h to the SrO simple oxide together with the Fe and
the synthesis for the SrMoO$_4$ compound was realized at 1420 K in the 5% H$_2$/Ar gas mixture
flow of the 5% H$_2$/Ar gas mixture at 1420 K
Fe/Mo cations.

Our investigation reveals the regularities in the atoms placement on a
scale compared with the interatomic one, which is interrelated with the
oxygen vacancies concentration and the superstructural ordering of the
Fe/Mo cations.

2. Material and methods

Sr$_2$FeMoO$_{6-x}$ polycrystalline samples were synthesized by the solid-
phase technique from the SrFeO$_{2.52}$ and SrMoO$_4$ precursors. The pre-
cursors were prepared by the conventional ceramic technique from
MoO$_3$, Fe$_2$O$_3$ and SrCO$_3$. Milling and compounding of the stoicho-
metric mixture of the initial reagents have been carried out in the vi-
bronnill in alcohol during 3 h. The obtained mixtures were dried at
350 K and pressed into pellets. In the process of the SrFeO$_{3-x}$ and
SrMoO$_4$ precursors synthesis, the preliminary annealing was carried out on
air at 970 K and 1070 K during 20 and 40 h, respectively. For the
increase of the batch homogeneity, a secondary milling has been applied.
The final synthesis for the SrFeO$_{3-x}$ compound was realized at
1470 K during 20 h in the argon flow, and the synthesis for the SrMoO$_4$
compound was realized at 1470 K during 40 h at $p$(O$_2$) = 0.21 $\times$ 10$^5$ Pa with a subsequent tempering at the room temperature.
The oxygen content in the SrFeO$_{3-x}$ compound was determined by the
weighing before and after its complete recovery in the hydrogen flow at
1373 K during 20 h to the SrO simple oxide and Fe metal. It was determined that the strontium ferrite has a composition SrFeO$_{2.52}$.

A synthesis of the strontium ferromolybdate was carried out in
pellets with diameter of 10 mm and thickness of 4-5 mm, pressed from
the initial reagents SrFeO$_{2.52}$ and SrMoO$_4$ in the stoichiometric ratio. Pellets were annealed in a flow of the 5% H$_2$/Ar gas mixture at 1420 K
during 5 h with a subsequent tempering at room temperature. The oxygen content in the Sr$_2$FeMoO$_{6-x}$ compound was determined by the
weighing before and after the complete recovery in the hydrogen flow
at 1373 K during 20 h to the SrO simple oxide together with the Fe and
Mo metals.

Samples with a various oxygen content and a different super-
structural ordering of Fe/Mo cations were obtained by means of the
annealing of Sr$_2$FeMoO$_{6-x}$ at 1420 K in the 5% H$_2$/Ar gas mixture flow
during 20 h - A-1 (Sr$_2$FeMoO$_{6.97}$, $P = 76\%$), during 50 h - A-2
(Sr$_2$FeMoO$_{6.94}$, $P = 86\%$), and 90 h - A-3 (Sr$_2$FeMoO$_{6.94}$, $P = 93\%$). A presence of the (1 0 1) reflex indicates the formation of Fe/Mo cations
superstructural ordering in the Sr$_2$FeMoO$_{6-x}$ unit cell (Fig. 1).

Phase composition and the crystal lattice parameters were determined using the ICSD-PDF2 (Release 2000) database and PowderCell, FullProf software by the Rietveld technique on the base of the XRD data. The XRD patterns were taken at room temperature with the rate 60°/h in the angular range 10–90° on the DRON-3 setup in the CuK$_\alpha$ emission. The degree of iron and molybdenum cations super-
structural ordering ($P$) has been calculated by the formula
$P = (250F–1)\times100\%$, where SOF is the factor of the population of
positions calculated on the base of the XRD data.

Mössbauer spectra were measured by means of the MS11104Em
spectrometer. $^{57}$Co in the Rh matrix has been used as a source of the γ-
quanta. The Mössbauer spectra were measured in the constant acceler-
ations mode in the moving source geometry; the rate value was measured by the law of triangle. For the cooling process the samples were placed in the CCS-850 (Janisinc) helium cryostat cavity. Heating of the samples has been carried out in the furnace with the air atmosphere. The model identification of spectra was carried out by means of the SpectrRelax program [15]. Isomer shifts were calculated relative to the metallic α-Fe.

The Curie temperature has been determined in the process of in-
estigations of the Sr$_2$FeMoO$_{6-x}$ samples magnetization temperature
dependences by the ponderomotive method in the temperature range
77–600 K in the external magnetic field 0.86 T by means of the “Liquid
Helium Free High Field Measurement System” setup by the Cryogenic
Ltd., containing the closed cycle refrigerator.

3. Results and discussion

The effect of oxygen nonstoichiometry and the Fe/Mo cations su-
perstructural ordering degree on the magnetic properties has been ex-
plored. Firstly, with the increase of $P$ from 76 (A-1) to 93% (A-3), the
oxygen index (6-x) decreases from 5.99 to 5.94, where the magnetiza-
tion $M(T)$ measured in the magnetic field 0.86 T is observed to in-
crease in the temperature range 77–600 K. At $T = 32.36$ K, $M(A-1)$ = 26.41,
$M(A-2)$ = 32.36 and $M(A-3)$ = 42.66 A m$^2$ kg$^{-1}$.

The transition from the paramagnetic to the ferrimagnetic state in
these samples is diffused. Measurements of the temperature depen-
dences of the magnetization has made it possible to determine the
starting temperature of this transition ($T_C$) at the cooling process, which
corresponds to the crossing of tangent lines plotted to the $M(T)$ curves.
Determined $T_C$ values are found to increase from 422, 428, to 437 K for
the samples with $P = 76$, 86 and 93%, respectively (Fig. 2).

This is explainable based on the fact that the FeMo$_6$ and MoFe$_6$
anti-structural defects concentration $n = (100–P)/2 = 3.5\%$, which is
considered to be nearly absent in the case of $P = 93\%$ and
(6-x) = 5.94. According to the neutron diffractometry data, the
ordered double perovskite lattice is observed with alternating FeO$_6$ and
MoO$_6$ octahedrons along all the three crystallographic axis [16].
A decrease of the $P$ value with the increase of the (6-x) value leads to the appearance of FeMo$_6$ and MoFe$_6$ anti-structural defects, where the Fe
cations occupy the Mo sites and vice versa. Besides, the anti-structural
defects result in a decrease of the $T_C$ values as well as magnetization in
the overall temperature range. Monotonic decrease of $T_C$ with the
lowering of $P$ value might be also correlated with an increase of the
The Mössbauer spectroscopy data indicate the influence of the oxygen vacancies and the \( P \) value on the change of the free charge carrier concentration on the Fermi level. The spectra measured at 14 K, are the superposition of the four Zeeman sextets (Fig. 3). The S1, S2 and S3 sextets are related to the perovskite phase.

The S1 sextet isomer shift value (\( \delta_1 \approx 0.71 \text{ mm/s} \)), which is larger than the isomer shift values observed for Fe\(^{3+} \) cations in perovskites at low temperatures (Table 2). As a rule, \( \delta \) values at low temperatures for Fe\(^{3+} \) in perovskites are in the range 0.49–0.55 mm/s [16–20]. With that, the \( \delta_1 \) value of the S1 sextet is considerably lower than the values for Fe\(^{3+} \) in the oxygen octahedrons (\( \approx 1.2–1.8 \text{ mm/s} \)) [18].

Therefore, the \( \delta_1 \) value corresponds to the mixed valent state Fe\(^{2+}/^{3+} \). According to the perovskite band structure, electrons of the Fe\(^{3+} \)\( t_2g \)\( 3d \)\( \uparrow \) cations with spins \( \uparrow \) are placed in the valence band lower than the Fermi level on the\( (t_{2g}) \)\( t_d \)\( g \)\( 3d \)\( \downarrow \) orbitals of the Fe\(^{3+} \)\( t_d \)\( t_2g \)\( 3d \)\( \uparrow \) cations with spins \( \downarrow \) are placed in the conduction band on the\( (t_{2g}) \)\( t_d \)\( g \)\( 3d \)\( \downarrow \) orbitals (Fig. 4). According to the electronic structure calculations [7], an overlap of the\( (t_{2g}) \)\( t_d \)\( g \)\( 3d \)\( \uparrow \) electronic orbitals of the Mo\( d \)-level and the\( (t_{2g}) \)\( t_d \)\( g \)\( 3d \)\( \uparrow \) electronic orbitals of the Fe\(^{3+} \)\( t_d \)\( t_2g \)\( 3d \)\( \downarrow \) level takes place in the Sr\(_2\)FeMoO\(_6\)-\( x \) compound. The overlap leads to the Mo\( d \)\( l \) electron shift to the position of iron, whereupon the Fe\(^{3+} \)\( \downarrow \) valent state is lowered to the values Fe\(^{2+}/^{3+} \) \([21–23]\).

Value of the \( \delta_2 \) of S2 sextet is even larger than the values for Fe\(^{3+} \), and it is lower than \( \delta_1 \). A difference of the \( \delta_1 \) and \( \delta_2 \) values is possibly caused by a distinction in the cation environment of the Fe ions. Obviously, a larger value of \( \delta_1 \) is caused by the fact that predominantly Mo cations are the nearest neighbors of the corresponding Fe ions, while the Fe ions, corresponding to the S2 sextet with \( \delta_2 \) are surrounded by a smaller quantity of the Mo cations. Therefore, the S1 sextet probably corresponds to the Fe\(^{2+}/^{3+} \)\( t_d \)\( t_2g \)\( 3d \)\( \uparrow \) ions in highly-ordered areas and the S2 sextet corresponds to the Fe\(^{2+}/^{3+} \)\( t_d \)\( t_2g \)\( 3d \)\( \downarrow \) ions in disordered areas. Moreover, an overlap of the Mo\(_{28}\) band and the low-spin Fe\(_{28}\) band, leads to the decrease of the complete magnetic moments of the Fe ions from 5 \mu_B to 4.4 \mu_B [7]. Consequently, the value of the hyperfine magnetic field \( H \) intensity for the Fe ions in the highly-ordered areas should be lower than the corresponding values, usually observed for the high-spin Fe\(^{3+} \) ions in the oxygen octahedrons at low temperatures (500 kOe and higher) [18–20]. The S1 and S2 sextets of the Mössbauer spectra of the Sr\(_2\)FeMoO\(_{6−x}\) samples possess \( H_1 \approx 477 \text{ kOe} \) and \( H_2 = 500 \text{ kOe} \) at 14 K (Table 2). The outlined values confirm the assumption that the appearance of the S1 and S2 sextets are caused by Fe ions in the ordered and disordered areas, respectively.

Since the Sr\(_2\)FeMoO\(_{6−x}\) samples differ by the ordering degree of the B-sublattice cations, as far as the ordering degree is lowered, the decrease of the S1 sextet area is observed, with a simultaneous increase of the S2 sextet area. The area value \( A \) of the Mössbauer spectra components is proportional to the Fe ions concentration in the corresponding phases. Changes of the spectra areas with the lowering of the ordering degree are in good agreement with the XRD investigations data (Fig. 1). With that, the absolute values of ordered and disordered phases concentrations obtained by means of the Mössbauer spectroscopy data, are lower than the values obtained from the analysis of the XRD patterns. This is possibly concerned with the fact that the disordered phase is formed in the areas divided by the ordered phase. As a result, part of iron ions of the ordered phase, placed on the boundaries with a disordered phase, forms a signal corresponding to the disordered phase.

The \( \delta_3 \) value of the S3 sextet corresponds to Fe\(^{3+} \) ions with the electrical resistivity due to a drop down of the density of states at the Fermi level (Table 1).

![Fig. 2. Temperature dependences of the A-1, A-2 and A-3 samples magnetization, measured at the magnetic field of 0.86 T. Insert: temperature dependences of the electrical resistivity of the samples.](image)

![Fig. 3. Mössbauer spectra of the Sr\(_2\)FeMoO\(_{6−x}\) samples measured at 14 K (the blue sextet is Fe\(^{3+} \) in the ordered clusters; the green sextet is Fe\(^{3+} \) in the disordered clusters; the purple sextet is Fe\(^{3+} \) in the defect clusters; the red doublet is the metallic Fe; the orange doublet is the impurity phase). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)](image)

### Table 1

Fe/Mo cations superstructural ordering degree (\( P \)), oxygen nonstoichiometry (\( 6−x \)), resistivity at 300 K (\( \rho_{300K} \)), Curie temperature (\( T_c \)), and the magnetization at 300 K at \( B = 0.86 \text{ T} \) for the A-1, A-2 and A-3 samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( P ) ± 1, %</th>
<th>( 6−x ) ± 0.01</th>
<th>( \rho_{300K} ) ± 0.01, Ohm cm</th>
<th>( T_c ) ± 1, K</th>
<th>( M_{300K} ) ± 0.01, A m(^2) kg(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-1</td>
<td>76</td>
<td>5.97</td>
<td>16.89</td>
<td>422</td>
<td>13.73</td>
</tr>
<tr>
<td>A-2</td>
<td>86</td>
<td>5.94</td>
<td>9.4</td>
<td>428</td>
<td>17.36</td>
</tr>
<tr>
<td>A-3</td>
<td>93</td>
<td>5.94</td>
<td>6.73</td>
<td>437</td>
<td>22.91</td>
</tr>
</tbody>
</table>

The absence of the anti-structural defects. A position of the Fermi level is indicated by the dashed line. (a) Iron energy levels; (b) molybdenum energy levels.

spin through a ligand, this exchange is the ferromagnetic one without the overlap of the occupied and the empty electronic orbital of metal...

dependence in the investigated samples. The values of isomer shift and hyperfine magnetic field ($H$) of the S4 sextet are close to the values observed for the Fe$^{3+}$ ions, placed in clusters in the state being close to the metallic one [17,18]. Results of the small-angle neutron scattering investigations also indicate the presence of magnetically-inhomogeneous state in the samples with magnetic regions having different magnetic nature [25]. The paramagnetic doublet, which is presumably caused by the presence of the superparamagnetic state in the part of Sr$_2$FeMoO$_6$ grains, is observed for the A-1 sample.

Therefore, it flows from the above stated information, that a tendency in the A-1, 2, 3 samples is observed, when with the increase of oxygen nonstoichiometry and Fe/Mo cations superstructural ordering, the volumetric fraction of the defectless areas (areas with the ordered placement of iron and molybdenum cations) is rising. This circumstance indicates that the spin-polarized charge carriers on the Fermi level play an important role in the exchange interactions, which agrees with conclusions from previous reports [26,27]. Let us consider possible types of exchange interactions for the description of the obtained results.

According to the Goodenough–Kanamori–Anderson rule [28], at the overlap of the occupied and the empty electronic orbital of metal through a ligand, this exchange is the ferromagnetic one without the spin-flip at the overlap angle in the metal-ligand-metal chain, equal to $\sim 80^\circ$. On this concern, one could suppose that exchange interactions between cations with different valencies in the Sr$_2$FeMoO$_6$ compound through the oxygen anion (Fe$^{3+}$ – O$^{2-}$ – Mo$^{5+}$) are realized through the double exchange Zener mechanism. In this case, 100% degree of the spin polarization of electrons being in the conduction band is preserved. At that, the double exchange process takes place between the Fe$^{4d^9(t_{2g})}$ and Mo$^{4d^3(t_{2g})}$ orbitals, as the iron electronic levels are empty, and one electron is placed on the molybdenum level. This electron can hop between the orbitals (Fig. 5).

One could suppose that the exchange interaction between the magnetic cations of iron and molybdenum takes place through the excited O$^{2-}$ anions, in the same way as in manganites. Upon the overlap of the wave functions of the nonmagnetic anions 2p orbitals and the iron magnetic cations 4d orbitals, a finite probability of the transition of 2p electron to the 4d electronic orbital exists. The O$^{2-}$ oxygen anion passes to the excited state and it becomes the magnetic one with spin $S = \frac{1}{2}$. As a result of the exchange interactions of the magnetic anion with the molybdenum cation, the electron is hopping from the 4d electronic orbital of molybdenum to the 2p orbital of anion (Fig. 5).

Therefore, it is supposed on the base of the above argument, that the exchange interaction between iron and molybdenum cations observed in the double perovskite might take place in frames of the Zener mechanism, as in the case of manganites [29–31]. Nevertheless, it should be mentioned that according to the neutron diffraction data, the Mo 4d$^1$ cations possess a very small magnetic moment about $\mu$(Mo) $\sim 0.0(1)$–0.42(6) $\mu_B$ [32,33], which indicates a delocalized character of electrons with spins $\downarrow$, placed on the Mo ($t_{2g}$) electronic orbitals. Moreover, as we have shown above, the distance between the Fe cations in the Sr$_2$FeMoO$_6$ crystal structure is $\sim 7.9$ Å, whereas the distance between Mn cations in manganites is $\sim 3.5$ Å. At the same time, this factor did not preclude the double perovskite from having the higher $T_C$ values, than those for the manganites, implying the presence

Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>Component</th>
<th>$\delta \pm 0.01$, mm/s</th>
<th>$\delta^*$, mm/s</th>
<th>$\epsilon/\Delta \pm 0.01$, mm/s</th>
<th>$H \pm 1$, kOe</th>
<th>$A \pm 1$, %</th>
<th>$G \pm 0.01$, mm/s</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-3</td>
<td>S1</td>
<td>0.71</td>
<td>0.47–0.55 [18]</td>
<td>0.00</td>
<td>477</td>
<td>52</td>
<td>0.30</td>
<td>1.415</td>
</tr>
<tr>
<td></td>
<td>S2</td>
<td>0.65</td>
<td>0.54 [19]</td>
<td>0.04</td>
<td>502</td>
<td>36</td>
<td>0.60</td>
<td>1.333</td>
</tr>
<tr>
<td></td>
<td>S3</td>
<td>0.33</td>
<td>0.51 [20]</td>
<td>$-0.16$</td>
<td>524</td>
<td>10</td>
<td>0.52</td>
<td>1.375</td>
</tr>
<tr>
<td></td>
<td>S4</td>
<td>0.12</td>
<td>0.03</td>
<td></td>
<td>315</td>
<td>2</td>
<td>0.29</td>
<td>1.46</td>
</tr>
<tr>
<td>A-2</td>
<td>S1</td>
<td>0.71</td>
<td>0.00</td>
<td></td>
<td>476</td>
<td>55</td>
<td>0.31</td>
<td>1.333</td>
</tr>
<tr>
<td></td>
<td>S2</td>
<td>0.63</td>
<td>0.04</td>
<td></td>
<td>498</td>
<td>36</td>
<td>0.65</td>
<td>1.375</td>
</tr>
<tr>
<td></td>
<td>S3</td>
<td>0.26</td>
<td>$-0.18$</td>
<td></td>
<td>527</td>
<td>7</td>
<td>0.42</td>
<td>1.375</td>
</tr>
<tr>
<td></td>
<td>S4</td>
<td>0.12</td>
<td>$-0.02$</td>
<td></td>
<td>342</td>
<td>2</td>
<td>0.29</td>
<td>1.46</td>
</tr>
<tr>
<td>A-1</td>
<td>S1</td>
<td>0.71</td>
<td>0.00</td>
<td></td>
<td>475</td>
<td>37</td>
<td>0.34</td>
<td>1.375</td>
</tr>
<tr>
<td></td>
<td>S2</td>
<td>0.67</td>
<td>0.05</td>
<td></td>
<td>500</td>
<td>28</td>
<td>0.61</td>
<td>1.375</td>
</tr>
<tr>
<td></td>
<td>S3</td>
<td>0.33</td>
<td>$-0.11$</td>
<td></td>
<td>514</td>
<td>13</td>
<td>0.53</td>
<td>1.375</td>
</tr>
<tr>
<td></td>
<td>S4</td>
<td>0.13</td>
<td>$-0.01$</td>
<td></td>
<td>334</td>
<td>9</td>
<td>0.29</td>
<td>1.46</td>
</tr>
</tbody>
</table>

where $\delta$ is the isomer shift; $\delta^*$ is isomer shift value taken from the literature; $\epsilon$ is the quadrupole shift; $\Delta$ is the quadrupole splitting; $H$ is the hyperfine magnetic field on the $^{57}$Fe nuclei; $A$ is the area of the spectrum components; $G$ is the width of the lines; $\chi^2$ is the Pearson criterion.

Fig. 4. Schematic image of the electrons distribution on the energy levels of iron (Fe$^{3+}$ 3$d^5$) and molybdenum (Mo$^{5+}$ 4$d^1$) in the Sr$_2$FeMoO$_6$ compound at the absence of the anti-structural defects. A position of the Fermi level is indicated by the dashed line. (a) Iron energy levels; (b) molybdenum energy levels.
of at least one more exchange interaction mechanism in the Sr$_2$FeMoO$_6$-$_x$ compound. Therefore, it is not quite correct to assume that the exchange interactions mechanism is realized only according to the Fe$^{3+}$–O–Mo$^{5+}$ scheme. Moreover, a number of authors indicate the possibility of a realization of various exchange interaction mechanisms in the strontium ferromolybdate. In this way, it is pointed out in the paper [29], that the superexchange interaction between the ordered magnetic moments can realize the ferromagnetic magnetization of the samples. Tovar et al. [34] have admitted that the exchange interaction is realized through the free spin-polarized electrons, according to the Ruderman – Kittel – Kasuya – Yosida (RKKY) theory [29,31]. We are intent to support this assumption, as well, since according to the RKKY theory an increase of the free charge carriers leads to the rise of the density of states on the Fermi level, and, correspondingly, to the increase of the exchange interactions density and the rise of the Curie temperature at the increase of $P$, as we have observed in the present study. The Mössbauer spectroscopy data indicates an influence of the concentration of the spin-polarized charge carriers on the Fermi level on the magnetic properties of the compound.

It has been found in the process of a consideration of the Mössbauer spectra, measured in the paramagnetic phase at temperature 473 K, i.e. higher than the Curie temperature, that the Mössbauer spectrum of the A-1, A-2 and A-3 samples is successfully approximated as a superposition of three components (one $S_1$ singlet, two D1 and D2 doublets) (Fig. 6). Moreover, the $S_4$ sextet lines are observed for the A-1 sample. This sextet was observed at low temperature (14 K), which corresponds to the iron clusters with the state close to the metallic one. The absence of $S_4$ sextet lines on the spectra of other samples indicate the rise of magnetic inhomogeneity with an increase of the degree of the Fe/Mo cations superstructural ordering and the oxygen nonstoichiometry.

A singlet component on the Mössbauer spectra of the Sr$_2$FeMoO$_6$-$_x$ compound at 473 K corresponds to the Fe$^{3+}$ ions in the areas ordered by the Fe/Mo cations, and the D1 doublet relates to the paramagnetic state of Fe ions in disordered areas (Table 3). Consequently, both ferrimagnetism and paramagnetism can coexist in the samples at a temperature close to $T_C$. Similar spectra, consisting of a singlet and a doublet, are observed for the PbFe$_{1/2}$Sb$_{1/2}$O$_3$ samples and solid solution on their base, having the cation ordering [35,37]. The D3 doublet with the minimal isomer shift corresponds to the Fe$^{3+}$ with coordination number in the range 4–5 (Table 3). With a decrease of the ordering degree, the structural inhomogeneity rises in the samples, which leads to the increase of the width of the Mössbauer spectra component lines. For the same reason, the quadrupole splitting of the D2 and D3 doublets increases. The line broadening in the spectra of A-1 sample leads to a weak resolution of the quadrupole splitting lines depending on the local symmetry of electrical charge, and a zero quadrupole splitting takes place of the D3 doublet. This indicates the presence of various defects, whose concentration is larger than in the A-2 and A-3 samples, and promoting the increase of magnetic inhomogeneity in the A-1 sample.

For the investigation of the influence of the Fe/Mo cations superstructural ordering and oxygen nonstoichiometry on the magnetic transition temperature ($T_C$), temperature scanning technique has been implemented. Its essence is in a determination of the intensity of the Mössbauer spectra at the gradual decrease of temperature, where not the entire spectrum is measured, but fragments of spectrum are measured in the maximum of the resonance absorption for the paramagnetic phase ($v = 0–1.2$ mm/s) and in the absence of the resonance absorption ($v = 12$ mm/s). Difference of impulses in the indicated fragments corresponds to the maximum of the Mössbauer spectra lines intensity. At the magnetic phase transition the Mössbauer spectrum experience the Zeeman splitting, accompanied by a considerable decrease of the intensity of the lines, corresponding to the spectrum in the paramagnetic phase. Therefore, one can determine the magnetic phase transition temperature by the declination of the temperature dependence of the Mössbauer spectra lines intensity. This method was used for the investigations of the behavior of magnetic phase transitions temperatures in AFe$_{1/2}$B$_{1/2}$O$_3$ compounds (A = Ba, Ca, Pb, B-Nb,Ta, Sb), as well as in the solid solutions on their base [35–38]. The obtained results are in a good agreement with the data from the magnetic susceptibility measurements [39,40].

The the temperature scanning technique has been applied for a
The most intensive decline of the intensity of the Mössbauer spectra paramagnetic lines of the Sr$_2$FeMoO$_6$ samples, normalized on their values at 473 K are presented in Fig. 7.

As it has been mentioned before, a transition from the paramagnetic to the ferrimagnetic state is blurred. The point of the start ($T_{\text{start}}$) of the intensive decline of the $I_m(T)$ seems to be almost the same ($\approx$ 423 K) for all the samples. This value is close to those determined by the indirect cation-anion-cation exchange interaction, but the interaction through the conduction electron conduction degree, the number of Fe$^{3+}$ cations concentration and the increase of the number of iron cations concentration [41]. At the increase of B-sublattice cations ordering degree, the number of Fe-O-Fe chains decreases, which leads to the lowering of the $T_C$ value [37]. Probably, magnetic ordering in the studied samples is determined not only by the indirect cation-anion-cation exchange interaction, but the interaction through the conduction electrons, as well.

According to the Mössbauer spectroscopy investigations results, a fraction of the S1 sextet is increasing at the decrease of the anti-structural defects concentration with the increase of the oxygen vacancies in the A-1, A-2 and A-3 samples. This leads to a decrease of the $I_m(T)$ dependence, is $\approx$ 88, $\approx$ 78 and $\approx$ 66 K for the A-1, A-2 and A-3 samples, respectively. It is observed that the transition blurring increases with a decrease of $P$, at least fractionary, which could be caused by the increase of the anti-structural defects concentration.

It is well known, that the spin-polarization dynamics and the magnetic phase transition from the ferrimagnetic state to the paramagnetic one depends on the strength of the exchange interactions, as the $T_C$ value in the AB'B'O$_3$ compounds depends on the Fe-O-Fe chains concentration [41]. At the increase of B-sublattice cations ordering degree, the number of Fe-O-Fe chains decreases, which leads to the lowering of the $T_C$ value [37]. Probably, magnetic ordering in the studied samples is determined not only by the indirect cation-anion-cation exchange interaction, but the interaction through the conduction electrons, as well.

The most intensive decline of the $I_m(T)$ dependence makes it also possible to estimate the temperature of completion of the transition from the paramagnetic to the ferrimagnetic state, estimated by the $I_m(T)$ dependence, is $\approx$ 88, $\approx$ 78 and $\approx$ 66 K for the A-1, A-2 and A-3 samples, respectively. It is observed that the transition blurring increases with a decrease of $P$, at least fractionary, which could be caused by the increase of the anti-structural defects concentration.


definition of the temperature range of the magnetic phase transition. Temperature dependences of the intensity of paramagnetic lines ($I_m$) of the Mössbauer spectra, normalized on their values at 473 K are presented in Fig. 7.

$$\delta$$ is the isomer shift; $\epsilon$ is the quadrupole shift; $\Delta$ is the quadrupole splitting; $H$ is the hyperfine magnetic field on the $^{57}$Fe nuclei; $A$ is the area of the spectrum components; $G$ is the width of the lines; $\chi^2$ is the Pearson criterion.

![Fig. 7. Dependences of the intensity of the Mössbauer spectra paramagnetic lines of the Sr$_2$FeMoO$_6$ samples, normalized on their values at 473 K.](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Component</th>
<th>$\delta \pm 0.01$, mm/s</th>
<th>$\epsilon/\Delta \pm 0.01$, mm/s</th>
<th>$H \pm 1$, kOe</th>
<th>$A \pm 1$, %</th>
<th>$G \pm 0.01$, mm/s</th>
<th>$\chi^2$</th>
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<td>0.49</td>
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<td>0.41</td>
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<td>58</td>
<td>0.29</td>
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<tr>
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<td>0.03</td>
<td>312</td>
<td>8</td>
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</table>

Table 3
The Mössbauer spectra parameters of the Sr$_2$FeMoO$_{6-x}$ samples, measured at 473 K.

An increase of the Fe$^{2+}$(3$d^6$) and Mo$^{6+}$(4$d^0$) cations number...
promotes a partitioning of the long-chain ordering of the Fe\(^{3+}\)-O\(^{2-}\)-Mo\(^{5+}\) type and a decrease of the density of the free spin-polarized charge carriers on the Fermi level, and correspondingly, a decrease of the density of the exchange interactions and the Curie temperature, as we have observed earlier. Previous works [42–44] indicate a dependence of the Curie temperature on the bulk density of the exchange coupling, as well. Being based on the fact that the Mo\(^{6+}\) (4\(d^0\)) diamagnetic cation does not take part in the exchange coupling, and only negative exchange couplings are possible between the Fe\(^{3+}\) (3\(d^0\)) ions having smaller magnetic moment than the Fe\(^{3+}\) (3\(d^0\)) ions, it is considered that the Fe\(^{3+}\) (3\(d^0\)) ions are forming the antiferromagnetic ordering of magnetic moments. A similar situation with the negative exchange integral J < 0 has been observed in the double perovskites (Sr\(_2\)BMoO\(_6\), where B = Ni, Co) with the substitution of iron and the presence of Mo\(^{5+}\) (4\(d^0\)) in the molybdenum sublattice [43,45].

4. Conclusions

The single-phase Sr\(_2\)FeMoO\(_{6-x}\) polycrystalline samples with different oxygen content (6 – x) and various degrees of superstructural ordering of Fe/Mo cations (P) were obtained by the solid-phase method from the SrFeO\(_{2.52}\) and SrMoO\(_4\) precursors.

It has been determined as a result of the investigations of the influence of oxygen nonstoichiometry and the Fe/Mo cations superstructural ordering on magnetic properties of the Sr\(_2\)FeMoO\(_{6-x}\) compound, that with the rise of P and decrease of the oxygen index from 6 – x = 5.99 to 5.94, the magnetization values M(T) increase in the temperature range 77–600 K.

It has been shown, that a monotonic decrease of T\(_C\) with a lowering of the P value is correlated also with an increase of the resistivity of the investigated samples, and correspondingly, with the drop of the concentration of the free charge carriers on the Fermi level. Our observation indicates an important role of the delocalized charge carriers, which agrees with the RKKY theory.

For all samples, it was found that with an increase in oxygen nonstoichiometry, the degree of superstructural ordering of Fe/Mo cations and, accordingly, the volume fraction of defect-free regions increases. The Mössbauer spectroscopy investigations results indicate this as well. These data confirm the increase of the S1 sextet area, corresponding to the Fe\(^{3+}\)/\(^{3+}\)\(^{3+}\) ions in the highly-ordered regions and the decrease of the area of the S2 sextet, related to the disordered regions.

Temperatures of the starting (T\(_{\text{start}}\)) and completion (T\(_{\text{compl}}\)) of the transition from the paramagnetic to the ferrimagnetic state are analyzed together with the width of the transition blurring based on the type of the L\(_m\)(T) dependence. The T\(_{\text{compl}}\) values at cooling are \(\approx 335\), \(\approx 345\), and \(\approx 357\) K, for the A-1, A-2 and A-3 samples, respectively. Values for the width of the blurring region for the transition from the paramagnetic to the ferrimagnetic state is \(\approx 88\), \(\approx 78\) and \(\approx 66\) K for the A-1, A-2 and A-3 samples, respectively. The transition blurring width increases with a decrease of P, at least fractionary, which could be caused by the decrease of the anti-structural defects concentration.

CRediT authorship contribution statement


Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

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