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Superstructural ordering degree in nanosized strontium ferromolybdate according to ferromagnetic resonance data

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Received July 11, 2022
Revised July 11, 2022
Accepted July 18, 2022

Powders of strontium ferromolybdate ($Sr_2FeMoO_{6-\delta}$) with various degrees of superstructural ordering of iron and molybdenum cations ($P = 67$, 81, 89%) were studied by the ferromagnetic resonance method. These investigations have been carried out taking into account the available information on the structural, magnetic and resistive characteristics of the samples under study. As a result of the analysis of the ferromagnetic resonance spectra, it was concluded that the amplitude of the corresponding signals strongly depends on the magnitude of the superstructural ordering, increasing with its growth. The presence of maxima in the ferromagnetic resonance spectrum in the temperature range 350−370 K, which shift slightly to low temperatures with increasing P, confirms the existence of ferrimagnetic and antiferromagnetic states competing with each other in the region close to the Curie temperature.

Keywords: ferromagnetic resonance, strontium ferromolybdate, superstructural ordering of cations, dynamic light scattering, submicron particles.

DOI: 10.21883/PSS.2022.11.54201.433

1. Introduction

Ferromagnetic resonance (FMR) is an effective tool to study magnetic discontinuities in magnetic materials. The main characteristics of ferromagnetic resonance, such as resonance frequencies, shape and width of electromagnetic wave absorption lines are determined by the collective multi-electron nature of ferromagnetism. We usually deal with nonuniform FMR, when the character of magnetic relaxation and the resonance peak broadening are determined by scattering of spin waves on each other, on conduction electrons, phonons, and on static defects of the crystalline structure.

The study of FMR of complex perovskite-like magnetic metal-oxide compounds is of special interest due to the presence of different magnetic states in them below the Curie point (T_c), as well as quite high cation and anion nonstoichiometry. Some FMR studies were performed on these materials, mainly related to manganites and cobaltites, for example [1–4], where powder and ceramic samples were investigated. We know only one study [5] devoted to FMR of metal-oxide compound, $Sr_2FeMoO_{6-\delta}$ strontium ferromolybdate (SFMO), where magnetocrystalline anisotropy of films was considered under their deformation caused by epitaxial growth on substrates with different lattice constants.

Previously, we have shown that $Sr_2FeMoO_{6-\delta}$ compound, being a half-metal, possesses a number of interesting features [6–9], which are attractive for technological applications of this promising material in spintronics. SFMO at temperatures below the Curie point ($T_c \sim 420-430\,K$) has a structure of the double perovskite and in its ground (single-phase) state it is a ferrimagnetic substance with an almost 100% degree of spin polarization (P). In addition, this compound has high conductivity and magnetoresistance (MR) of tunnel nature, that can be as high as 40% in moderate magnetic fields.

It is important from both the fundamental and applied point of views to have the possibility of direct and easy measurement of P in ferromagnetic substances. The most general definition of the spin polarization degree of conduction band in ferromagnetic substances is [10]:

$$P = \frac{N_{(\uparrow)}(E_F - N_{(\downarrow)}(E_F)}{N_{(\uparrow)}(E_F) + N_{(\downarrow)}(E_F)}, \tag{1}$$

where $N_{(\uparrow,\downarrow)}(E_F)$ — electron state density at the Fermi level with the corresponding spin direction (↑, ↓).

This work presents the results of FMR study of SFMO powders with a different degree of superstructural ordering, which are analyzed taking into account the existing information on the structure, magnetic and resistive characteristics.

2. Experimental procedure

SFMO powders with different degrees of superstructural ordering of Fe/Mo cations were produced using the ceramic technology of solid-phase synthesis with $SrMoO_4$ and $SrFeO_{3-x}$ precursors as initial reagents. The problem of synthesis is associated with multiple stages of phase transformations, low kinetics of phase formation, and low mobility of Fe^{3+} and Mo^{5+} cations [11], however, the use of combined synthesis modes allowed us to synthesize the Sr_2FeMoO_6 single-phase compound. The degree of superstructural ordering of Fe and Mo cations was controlled by

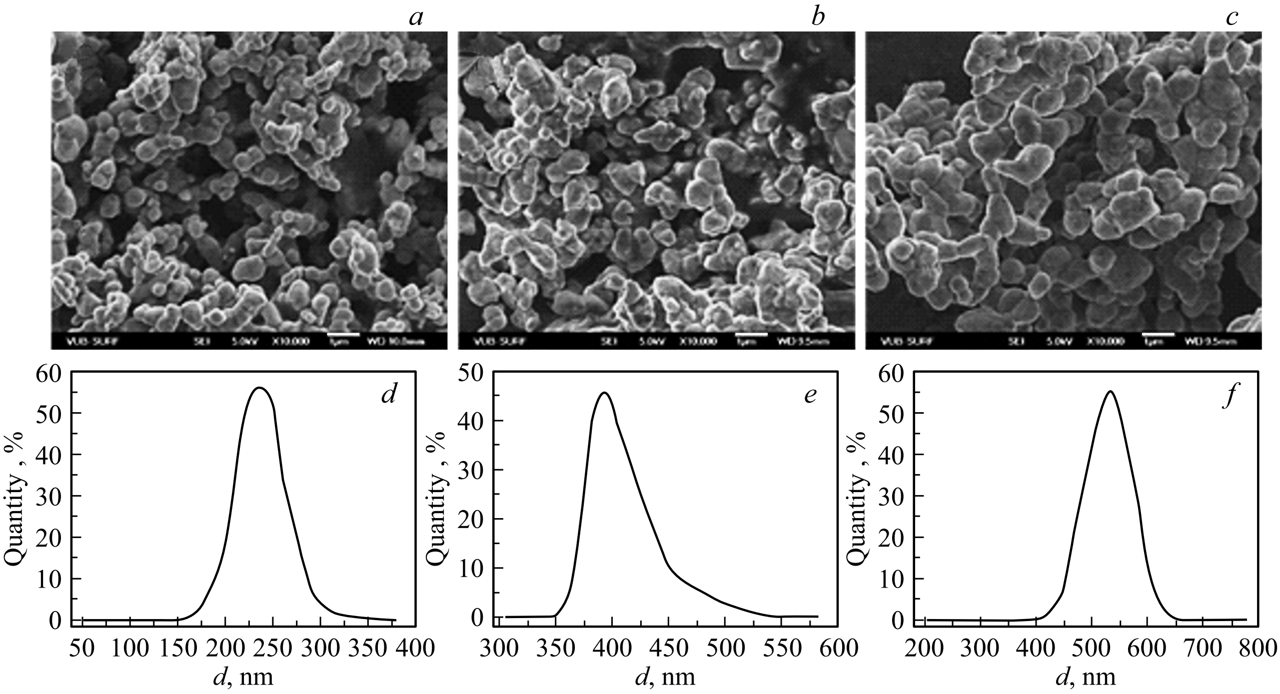

Figure 1. Microstructure (a, b, c) and DLS-analysis (d, e, f) of SFMO-89, SFMO-81 and SFMO-67 samples, respectively.

an additional heat treatment of the samples at a temperature of 1420 K in the flow of 5%H_2/Ar gas mixture for 19 h ($P = 67\%$), 40 h ($P = 81\%$), and 80 h ($P = 89\%$). As a result, 3 series of samples to study the FMR were produced, which were designated as SFMO-67, SFMO-81, and SFMO-89, respectively. To study the FMR on SFMO powders, after the synthesis of compressed samples, they were milled in PM 100 RetschGmbH ball mill in alcohol for 3 h.

Microstructure, morphology, and composition of elements of the grains were investigated by scanning electron microscopy (JEOLJSM-7000F) in combination with energy-dispersive X-ray (EDX) detector. We measured medium sizes of nanoparticles by dynamic light scattering (DLS) method using the Zetasizer Nanoparticles analyzer (Malvern Nano ZS90). FMR measurements were performed using the Bruker Ele Xsys E-500 spectrometer at a microwave frequency of 9.45 GHz in a temperature range of 120−440 K. Measurements were carried out in a constant magnetic field with induction of up to 1.4 T, normal to the electromagnetic wave. Three types of samples were examined: (SFMO-67, SFMO-81, and SFMO-89) in the form of powder, each with a weight of 5 mg.

Value of P was determined on the basis of X-ray diffraction data obtained from the DRON-3 setup in the CuKα-radiation at a room temperature with a recording rate of 60°/h, using PowderCell, FullProf software and the Rietveld method. Formula for the calculation is as follows

$$P = (2 \cdot \mathrm{SOF} - 1) \cdot 100\%,$$

where SOF is seat occupancy factor.

3. Results and discussion

Fig. 1 shows the data of electron microscopy and DLS-analysis. As can be seen, an average size of particles was not greater than 220 nm, which is several orders of magnitude less than the skin-layer depth. This allowed us to neglect the skin-effect and ignore the demagnetization factor in the FMR analysis despite high conductivity of the compound. In can be explicitly seen in the figure, that there is a dependence of average grain size and degree of superstructural ordering on the duration of annealing, which indeed should be reflected in the electromagnetic field energy absorption by the ferromagnetic substance.

Fig. 2 shows FMR spectra of SFMO-67 and SFMO-89 samples as field dependencies of the first-order derivative of electromagnetic wave absorption on a magnetic field, $dP/dB(B)$ for a number of temperatures. It appears from the position of maxima and minima of the dP/dB derivative that the resonance peak electromagnetic wave absorption has a shape close to symmetrical one. This indicates that each sample is a single system of granules with unidirectional magnetization along the field. With an increase in temperature in the range of 120−400 K (below the Curie point), the maximum of resonance absorption shifts toward greater values of the magnetic field, from 1.5 to 3.0 kG.

It can be assumed that, regardless of the value of superstructural ordering of cations, co-existence of two types (valencies) of like cations takes place.

In an ideal crystalline structure of $Sr_2FeMoO_{6-\delta}$ without antistructural defects the exchange interaction in the system

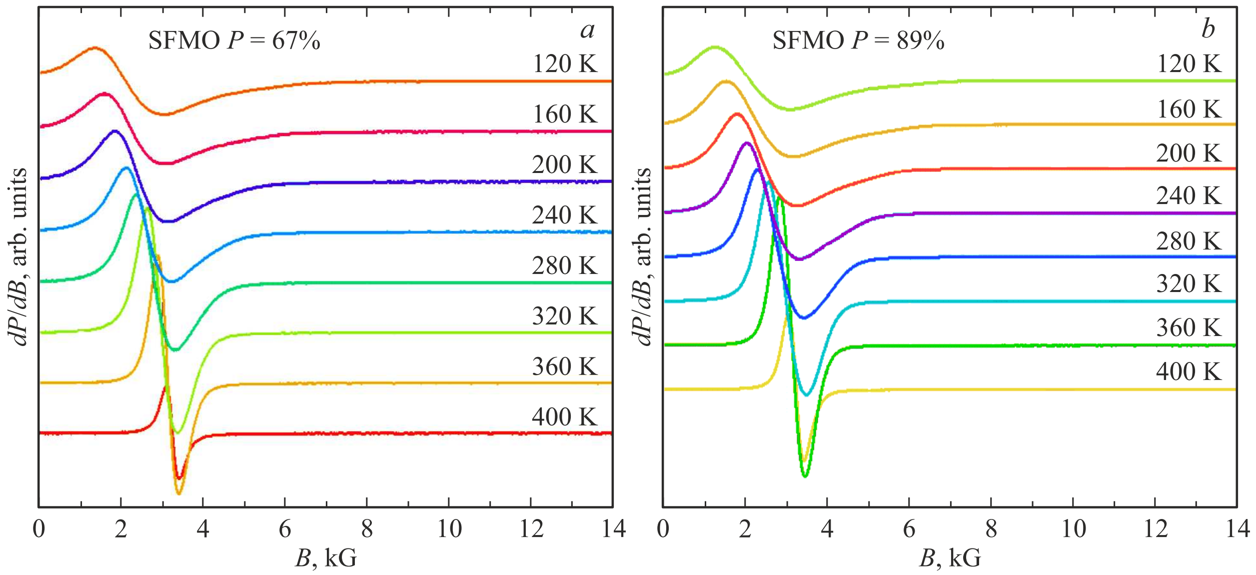

Figure 2. Field dependencies of FMR spectra at different temperatures of SFMO-67 (*a*) and SFMO-89 (*b*) samples.

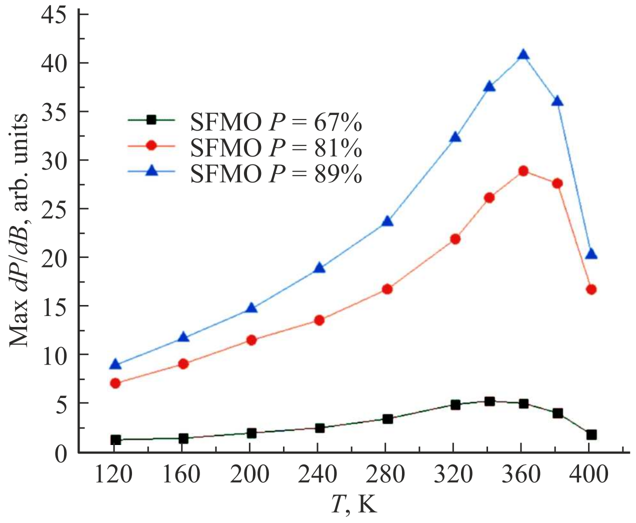

Figure 3. The maximum of dP/dB as a function of temperature for powders with different degree of superstructural ordering of cations.

of aliovalent ions corresponds to the long-chain superstructural ordering of cations — Fe^{3+}-O^{2-}-Mo^{5+} — with high values of saturation magnetization (M_S). A decrease in P results in the redistribution of electron density and transition of some iron and molybdenum cations to lower spin states: $Fe^{3+} \rightarrow Fe^{2+}$ and $Mo^{5+} \rightarrow Mo^{6+}$. At the same time, the decrease in M_S is indicative of the presence of antistructural defects of Fe_{Mo}, Mo_{Fe} type, and theoretical calculations of [12] forecast the possibility of antiferromagnetic ordering in chains of Fe-O-Fe. Also, on the basis of the Mössbauer spectra analysis, the presence of a mixed state of valency of iron cations is detected [7], and with a decrease in P an increase in electron density on atoms of iron takes place to a state close to Fe^{2+}, that promotes formation of antiferromagnetic clusters blocking the magnetic ordering of a long-range order.

Fig. 3 shows FMR data represented as temperature dependencies of dP/dB maximum for powders with different degree of superstructural ordering of cations. It is evident that signal amplitude depends to a significant extent on P increasing with its growth, i.e,. the amplitude of resonance signal grows with an increase in ordering in the cation sublattice. Here the most interesting is the presence of maxima in the temperature range of 350–370 K, that confirm the existence of ferromagnetic and antiferromagnetic states, competing each other in a range close to the Curie point.

Acknowledgments

The authors would like to thank prof. N.A. Sobolev for the provided possibility of samples study by the method of ferromagnetic resonance at the Department of Physics of the Aveiro University (Portugal), as well as senior fellow M.V. Yarmolich (SSPA Scientific-Practical Materials Research Centre of NAS of Belarus) for the help in the synthesis of SFMO powders.

Funding

The study was performed within State Research Programs of the Republic of Belarus glqq Materials science, new materials and technology“, Subprogram 1.1.1 „Condensed state physics and development of new functional materials and production technologies“ („Physics and Technology of Materials“).

Conflict of interest

The authors declare that they have no conflict of interest.

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