Investigation of magnetic phase separation in strontium-substituted gadolinium ferromanganite by Mössbauer spectroscopy and EPR

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Abstract. Multiferroics of rare-earth manganites $RMnO_3$ attract a lot of attention due to the significant correlation of electrical and magnetic parameters. The replacement of rare-earth ions in $RMnO_3$ with atoms of a different radius and / or valence leads to the appearance of new effects, such as colossal magnetoresistance and various thermomagnetic effects. These phenomena are usually associated with magnetic separation in the subsystem of magnetic moments - the formation of microregions of ferromagnetic ordering in an antiferro- or paramagnetic matrix. When studying this phenomenon, it is promising to use the methods of Mössbauer spectroscopy and electron paramagnetic resonance (EPR), which make it possible to register the presence of magnetic impurities in small amounts.

Strontium-substituted gadolinium ferromanganite $Gd_{0.82}Sr_{0.18}Mn_{0.9}Fe_{0.1}O_3$ was prepared by ceramic technology. Its magnetic microstructure was investigated by the method of Mössbauer spectroscopy at temperatures of 100-300 K and EPR at temperatures of 100-340 K.

The data of Mössbauer and EPR measurements indicate the magnetic phase separation in the system of magnetic moments in strontium-substituted gadolinium ferromanganite.

Keywords: ferromanganites, Mössbauer spectroscopy, EPR, magnetic phase separation.

Introduction

$RMnO_3$ compounds are characterized by two types of crystal structures: hexagonal (ilmenite type) and orthorhombic (perovskite-like), depending on the ionic radius of rare earth elements R^{3+} [1]. In this case, the orthorhombic structure with the space group P_{bnm} is characteristic of "light" lanthanides ($R = La – Eu$). These materials, when hole doped with divalent cations with a large ionic radius ((Ca^{2+}, Sr^{2+}, Pb^{2+}) have colossal magnetoresistance (CMR), and some of them are ferroelectrics, and the ferroelectric properties are induced by magnetic ordering ($R = Dy – Gd$) [2]. Another family of compounds with a smaller ionic radius (from *Ho* to *Lu*) form a stable hexagonal structure with the space group $P6_3cm$ at room and lower temperatures and also exhibit CMR and multiferroic properties [3]. The coexistence of ferroelectric order and magnetic ordering in $RMnO_3$ with a hexagonal or orthorhombic structure gives a complex physical picture of interactions between charge, orbital, lattice, and spin degrees of freedom. The magnetically non-single-phase state in solid solutions $R_{1-y}A_yMnO_3$, where *R* — are-earth cation, *A* — divalent cation, arises due to the frustration of magnetic moments caused by the competition of ferromagnetic and antiferromagnetic interactions, close to each other in magnitude. The maximum value of magnetoresistance (negative and `bipolar '[4]) is usually observed at temperatures close to the Néel temperature. Consequently, ferromagnetic clusters can exist in both antiferromagnetic and paramagnetic matrices. Such a magnetic phase separation was found in lanthanum and neodymium ferromanganites [5]. The aim of this work was to study the magnetic microstructure in strontium-substituted gadolinium ferromanganite by the methods of Mössbauer and EPR spectroscopy.

Experimental methods

Strontium-substituted gadolinium ferromanganite $Gd_{0.82}Sr_{0.18}Mn_{0.9}Fe_{0.1}O_3$ was prepared by ceramic technology from a mixture of oxides of gadolinium, manganese, iron, and strontium carbonate. To increase the signal-to-noise ratio in Mössbauer measurements, iron oxide was enriched in the Mössbauer isotope ^{57}Fe (≈ 30%). X-ray structural analysis was performed on an MD-10 mini-diffractometer, and it was found that the sample is single-phase and has orthorhombic crystal symmetry (space group *Pnma*).

The magnetic microstructure was investigated by EPR and Mössbauer spectroscopy. Mössbauer measurements were carried out on a standard WissEL spectrometer (Germany) in a CFICEV flow cryostat (ICE Oxford, UK). Mössbauer spectra were processed using the SpectrRelax program [6]. EPR spectra were obtained on an *EMXplus* EPR spectrometer in the X-band (9.46

GHz). The temperature dependences of the g-factor, resonance field, width and intensity of the EPR line were found at temperatures of 100-340 K.

Results and discussion

In the course of the experiment, the Mössbauer spectra of strontium-substituted gadolinium ferromanganite $Gd_{0.82}Sr_{0.18}Mn_{0.9}Fe_{0.1}O_3$ were obtained at different temperatures (T = 100-300 K) (figure 1). All spectra contain one quadrupole doublet, the isomeric shift of which corresponds to Fe^{3+} (tab. 1), as well as the superposition of two Zeeman sextets, which may indicate the stratification of the magnetic subsystem of the sample, similar to that observed earlier for ferromanganites of other lanthanides [7, 8].

With increasing temperature, the relative area of the doublet does not change (within the processing accuracy). The isomeric shift of the doublet in both sextets decreases with increasing sample temperature, remaining within the limits characteristic of the Fe^{3+} ion [7, 8]. The decrease in the isomeric shift of these components is due to the second order Doppler effect. Fig. 2 shows the temperature dependence of the isomeric shift of the doublet. The solid line shows the curve approximating the experimental data in the approximation of the Debye model, with a characteristic temperature, θ_D = 378±30 K. The effective field H_{eff} of both sextets also decreases with increasing temperature, and for the second sextet it is approximately twice as fast as for the first one (Tab 1). The relative area of the "magnetic" structures behaves differently with increasing temperature: it grows in the first sextet and decreases in the second. It can be assumed that a magnetic phase separation is observed in the studied $Gd_{0.82}Sr_{0.18}Mn_{0.9}Fe_{0.1}O_3$ sample, which leads to the appearance in the spectra of two sextets corresponding to the magnetically ordered phase. Stoichiometric gadolinium manganite $GdMnO_3$ is an A-type antiferromagnet with a low (44K) Neel temperature [9]. Antiferromagnetic ordering is realized in $GdMnO_3$ due to the indirect exchange interaction in the Mn^{3+} sublattice. The replacement of some of the Gd^{3+} ions with Sr^{2+} ions leads to the appearance in the 3*d*-sublattice, along with Mn^{3+} cations, of Mn^{4+}cations, which enter into kinetic feromagnetic exchange with trivalent manganese ions. As a result, regions of ferromagnetic ordering appear in the antiferromagnetic or paramagnetic matrix [5]. A ^{57}Fe Mössbauer probe falling into this region exhibits a magnetic hyperfine structure in the spectra.

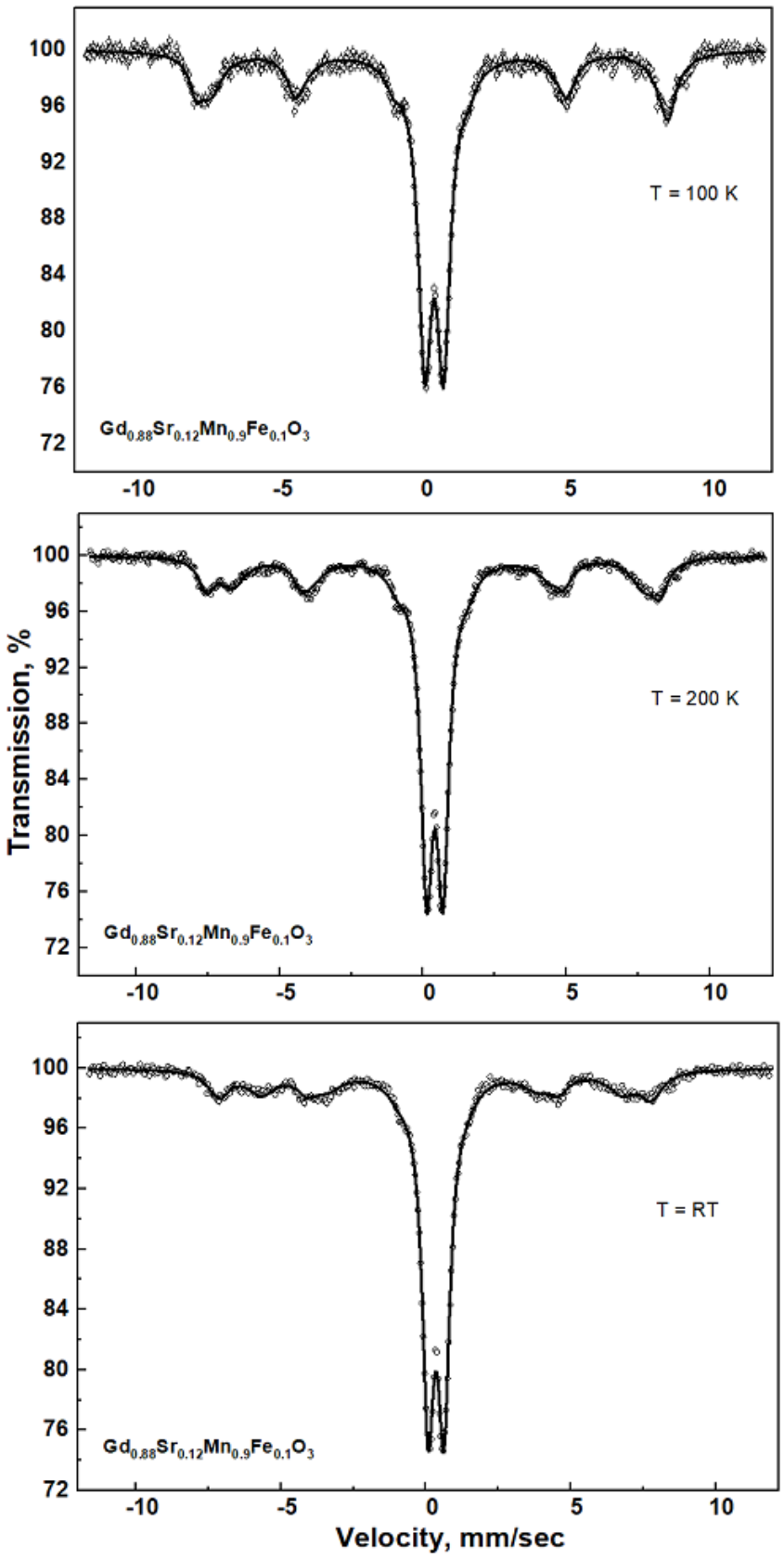

Figure 1. Mössbauer spectra $Gd_{0.82}Sr_{0.18}Mn_{0.9}Fe_{0.1}O_3$ at T = 100-300 K

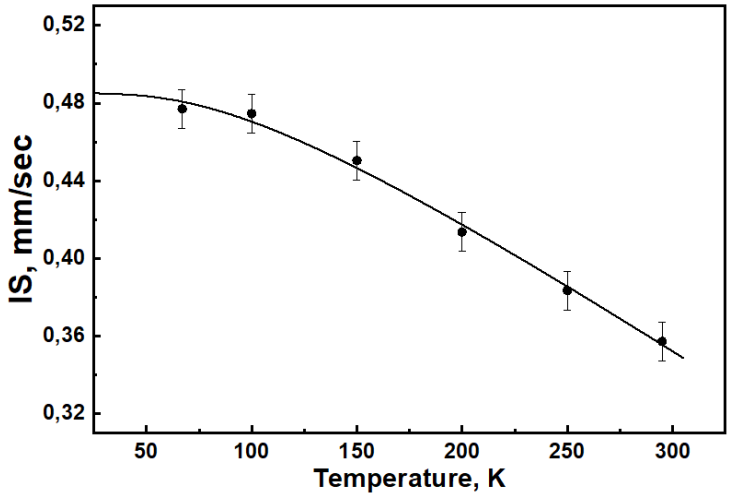

Figure 2. Temperature dependence of the isomeric shift of the doublet

Table 1. Mössbauer parameters for strontium-substituted gadolinium ferromanganite $Gd_{0.82}Sr_{0.18}Mn_{0.9}Fe_{0.1}O_3$ at different temperatures

T, K		IS, mm/s	QS, mm/s	Relative area, %	H_{eff}, kE
100 K	Doublet	0.48 (0,01)*	0.66 (0,01)	62 (1)	
	Sextet 1	0.39	0.12	11	512 (2)
	Sextet 2	0.48	0.16	27	489
200 K	Doublet	0.41	0.57	62	
	Sextet 1	0.35	-0.01	14	490
	Sextet 2	0.41	0.26	24	447
300 K	Doublet	0.36	0.54	63	
	Sextet 1	0.28	0.10	18	463
	Sextet 2	0.37	0.34	19	386

* - the parameter determination error is indicated in brackets.

EPR spectra were studied for the $Gd_{0,82}Sr_{0,18}Mn_{0,9}Fe_{0.1}O_3$ sample at temperatures of 100-340 K (fig. 3). In the entire temperature range, the EPR spectrum line shapes were described by f. 1 [10].

$$P = \left[\frac{\Delta B + \alpha(B - B_0)}{4(B - B_0)^2 + \Delta B^2} + \frac{\Delta B - \alpha(B + B_0)}{4(B + B_0)^2 + \Delta B^2}\right] \quad (1)$$

where$P$ - the power of absorbed microwave radiation, B – the magnetic field, B_0 – the resonant field, ΔB – the absorption line width, α - the asymmetry parameter.

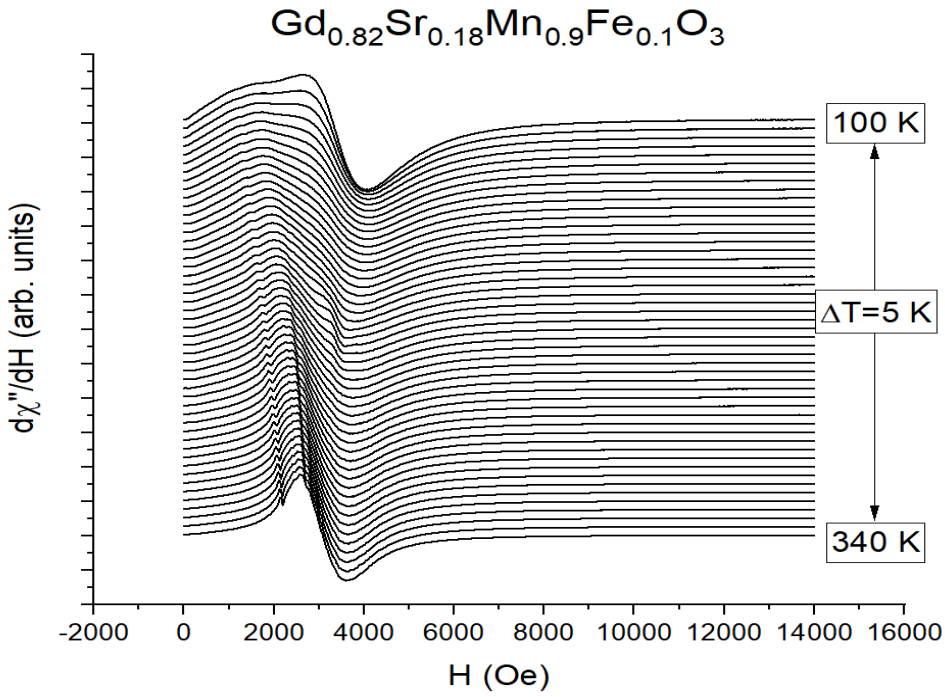

Figure 3. Spectrum view of EPR $Gd_{0.82}Sr_{0.18}Mn_{0.9}Fe_{0.1}O_3$ at T = 100-340 K

From the analysis of the EPR spectra of the ceramic sample $Gd_{0,82}Sr_{0,18}Mn_{0,9}Fe_{0.1}O_3$, the temperature dependences of the absorption line width, resonance field, g-factor, and integrated intensity of the EPR line were obtained, which are shown in fig. 5, 6, 7, 8, respectively. The EPR spectra in $Gd_{0,82}Sr_{0,18}Mn_{0,9}Fe_{0.1}O_3$ ceramics were described using three lines L_1, L_2 and L_3 (fig. 4), which coincides with the result obtained in Mössbauer spectroscopy (doublet and 2 sextets).

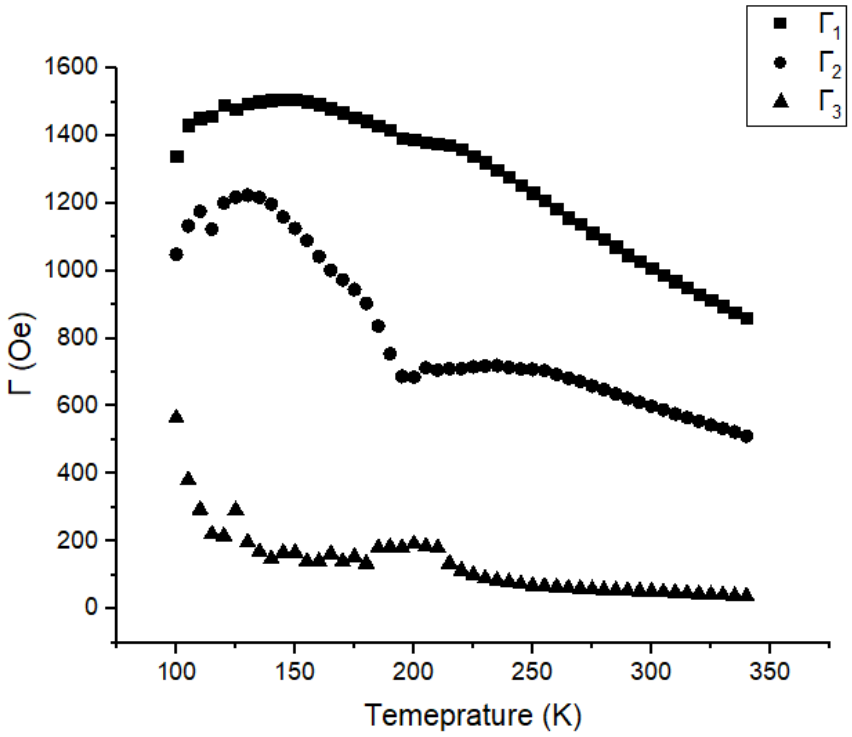

Figure 4. Temperature dependence of the absorption line width at T = 100-350 K

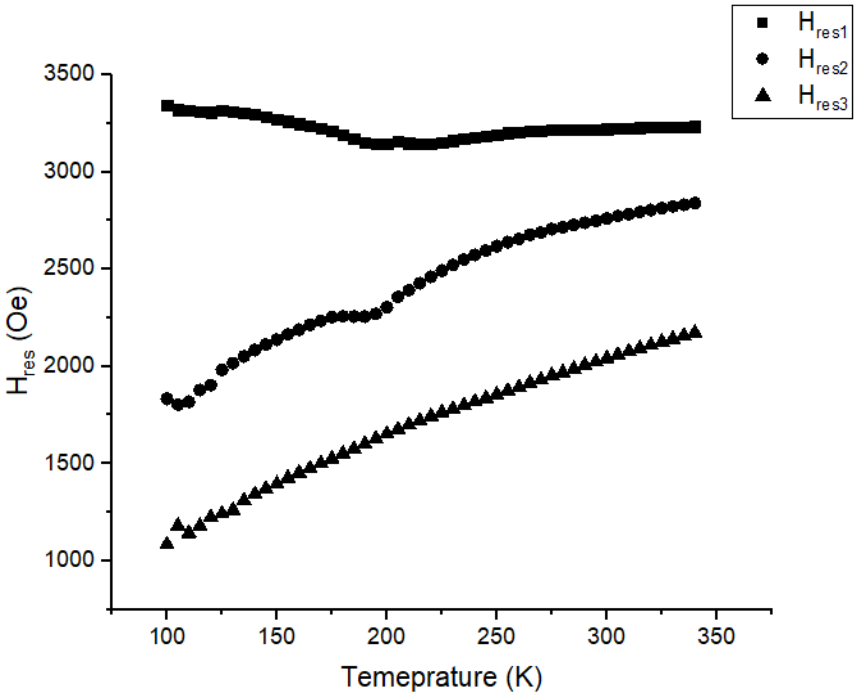

Figure 5. Temperature dependence of the resonance field at T = 100-350 K

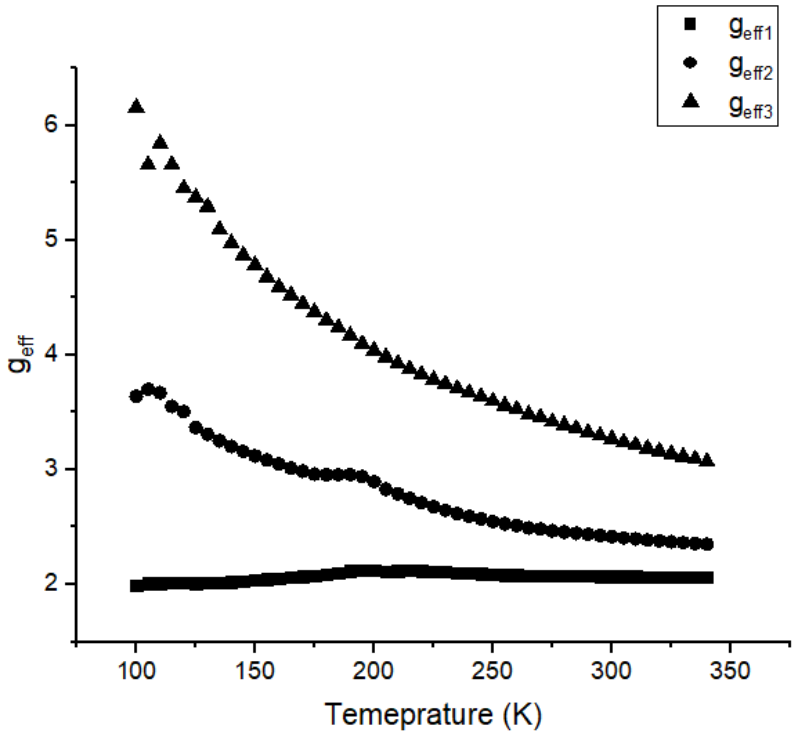

Figure 6. Temperature dependence of the g-factor at T = 100-350 K

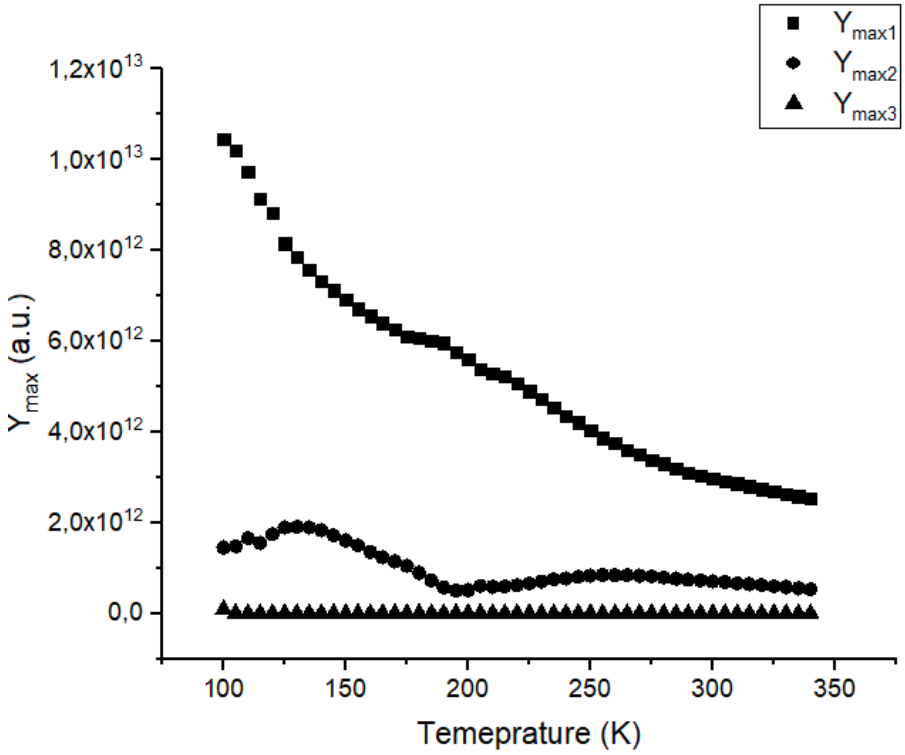

Figure 7. Temperature dependence of the integrated intensity atT = 100-350 K

The effective g-factor for the first line ($g_{eff} \approx 2$) is practically independent of temperature, for

the second line it varies from 3.64 at T = 100 K to 2.35 at 340 K, and for the third, from 6.16 (100 K) to 3.07 (340 K). The spins of iron and manganese ions in gadolinium ferromanganites are related by isotropic exchange interaction, which narrows the EPR line in the paramagnetic phase. It is also known that g_{Mn} and $g_{Fe} \approx 2$. From this, it can be concluded that L_1 with an effective g-factor of ≈ 2 in the EPR spectrum under study is associated with manganese and iron ions in the paramagnetic state. However, we believe that L_2 *and* L_3, belong to ferromagnetic clusters that are observed in a paramagnetic matrix at temperatures exceeding the Néel temperature. The integral intensity and linewidth of the second line signal have a maximum at 130 K, corresponding to the blocking temperature T_{B1} [11]. As the temperature increases, the line width of the ferromagnetic signal (L_2) decreases approximately 2.4 times from 1224 Oe at 130 K to 511 Oe at 340 K, and for the other (L_3) – from 564 Oe at 100 K to 37 Oe at 340 K. The linewidth of the paramagnetic signal (L_1) of the matrix increases from 1339 Oe to 1500 Oe in the range of 100-120 K and practically does not change at temperatures from 120 to 160 K, and with an increase in temperature to 340 K it decreases by about 1.7 times (to 861 E). A similar behavior of the magnetic subsystem was observed in ceramics $Eu_{0.65}Sr_{0.35}Mn_{1-x}Fe_xO_3$ [8].

Conclusions

As a result of the study of the magnetic microstructure of strontium-substituted gadolinium ferromanganite $Gd_{0,82}Sr_{0,18}Mn_{0,9}Fe_{0.1}O_3$ мby the method of Mössbauer spectroscopy, one quadrupole doublet was detected, the isomeric shift of which corresponds to Fe^{3+}, ions, and the superposition of two Zeeman sextets, which speaks of a superposition of two Zeeman subsystems of the magnetism. The EPR spectrum of $Gd_{0,82}Sr_{0,18}Mn_{0,9}Fe_{0.1}O_3$ can be described by three lines, which correlates with the results of nuclear gamma resonance. Two lines refer to ferromagnetic clusters, which are observed in a paramagnetic matrix at temperatures above the Néel temperature, and the third is associated with manganese and iron ions in the paramagnetic state.

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