MAGNETIC PROPERTIES OF THE COBALTITES-GALLATES OF SAMARIUM SmCo_{1-x}Ga_xO_3 IN THE TEMPERATURE RANGE 5-300K

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Abstract

Using a solid-state reaction method the ceramic samples of the cobaltites-gallates of samarium SmCo_{1-x}Ga_xO_3 (0 ≤ x ≤ 0.5) were synthesized. In these samples a magnetic dilution of the Co^{3+} ions by diamagnetic Ga^{3+} ions took place. The parameters of the crystal lattice were determined. Molar magnetic susceptibility (\chi_{mol}) of SmCo_{1-x}Ga_xO_3 was investigated at 5-300K in a magnetic field of 0.8 T. Analysis of the results obtained showed that in the temperature range 10-60K the effective magnetic moment of the Sm^{3+} ions practically didn't depend on the x and its value (0.50 – 0.59\mu_B) was less than the theoretical value (0.84\mu_B) indicating the “partial freezing” of the orbital magnetic moment by the crystal field of the perovskite structure. Temperature-independent contribution (\chi_0) in \chi_{mol} increases at growth of x at 10-60K.

Keywords and phrases: perovskite, cobaltites-gallates of samarium, magnetic susceptibility, effective magnetic moment, Van-Vleck polarization paramagnetism.

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Increase of $\chi_{\text{mol}}$ for SmCo$_{1-x}$Ga$_x$O$_3$ at growth of $x$ presumably is due to the increase of temperature independent Van-Vleck paramagnetism of Sm$^{3+}$ ions rather than transition of the Co$^{3+}$ ions in paramagnetic state.

1. Introduction

Cobaltites of rare-earth elements LnCoO$_3$ (Ln-lanthanum and other rare-earth metals) with the crystal structure of the distorted perovskite have a number of unique magnetic, electrical, electrochemical, catalytic, and sensory properties. These properties are largely determined by the spin state of the cobalt Co$^{3+}$ ions, depending on the temperature, the degree of distortion of the perovskite crystal lattice, and other factors [1, 2].

It is established [3-9] that at temperatures close to the 0K the Co$^{3+}$ ions are presumably in a low-spin (LS) state (electron configuration of the 3$d^6$-electrons is $t_{2g}^6e_{g}^0$, $S = 0$), and cobaltites LnCoO$_3$ are diamagnetic dielectrics. In the lanthanum cobaltite LaCoO$_3$ in the temperature range 35-100K a part of the Co$^{3+}$ ions transforms from the (LS) to the intermediate-spin (IS) ($t_{2g}^5e_{g}^1$, $S = 1$) or high-spin (HS) ($t_{2g}^4e_{g}^2$, $S = 2$) state, and it becomes a paramagnetic semiconductor. At the temperatures above 500K in LaCoO$_3$ an increase in population of energy levels of Co$^{3+}$ ions in the IS- and HS-state is observed, which is accompanied by the occurrence of diffuse phase transition semiconductor-metal, leading to the significant increase of the electrical conductivity. In the cobaltites of other rare-earth elements LnCoO$_3$, where ionic radius of Ln$^{3+}$ is smaller than the ionic radius of La$^{3+}$, the spin transition of Co$^{3+}$ ions occurs at temperatures above 300K [4, 8, 9]. In this connection in [10] investigation of magnetization and magnetic susceptibility of samarium cobaltite SmCoO$_3$ in the range 4.2-300K is carried out taking
into account the fact that the magnetic behaviour of SmCoO$_3$ at these temperatures is determined mainly by the Sm$^{3+}$ ions, because Co$^{3+}$ ions are in the LS-state and they are diamagnetic. Co$^{3+}$ ions in the LnCoO$_3$ crystal lattice are located in the center of an octahedron, whose vertices are occupied by oxygen ions, and crystal field of cubic symmetry “freezes” the orbital magnetic moment of unscreened 3$d$-electrons. For this reason, the effective magnetic moment of the Co$^{3+}$ ions ($\mu_{\text{eff}, \text{Co}^{3+}}$) is basically a spin one [11]. Magnetic properties of rare-earth ions are determined by 4$f$-electrons which are largely screened from the influence of crystal field by 5$s^2$- and 5$p^6$-electrons, and the effective magnetic moment of rare-earth elements ions is determined by the total spin angular moment ($J = L \pm S$). Ions of rare-earth elements in the LnCoO$_3$ crystal lattice are surrounded by 12 oxygen ions, whose symmetry of the arrangement is described by the point group of symmetry $C_s$ (distorted cuboctahedron). As it is shown in [12], the crystal field of such symmetry can lead to the “partial freezing” of the orbital moment of rare-earth ions and, consequently, to decrease of its effective magnetic moment that was observed for the Sm$^{3+}$ ions in the samarium cobaltite SmCoO$_3$ [10]. Magnetic dilution of paramagnetic ions leads to a decrease of their interaction and as a rule to the decrease of influence of crystal field on their magnetic properties.

In [13-15] influence of partial substitution of Co$^{3+}$ ions by diamagnetic Ga$^{3+}$ ions in LaCoO$_3$, NdCoO$_3$ on magnetic susceptibility and Co$^{3+}$ ions spin state in solid solutions LaCo$_{1-x}$Ga$_x$O$_3$, NdCo$_{1-x}$Ga$_x$O$_3$ was studied. It is found that such a substitution of Co$^{3+}$ ions by Ga$^{3+}$ ions leads to the stabilization of Co$^{3+}$ ions in low-spin LS-state.
The aim of this work is to study at 5-300K magnetization, magnetic susceptibility and effective magnetic moment of Sm$^{3+}$, Co$^{3+}$ ions in the solid solutions SmCo$_{1-x}$Ga$_x$O$_3$ ($0 \leq x \leq 0.5$), where the partial substitution of the Co$^{3+}$ ions by diamagnetic Ga$^{3+}$ ions in SmCoO$_3$ takes place.

### 2. Experimental

Cobaltites-gallates SmCo$_{1-x}$Ga$_x$O$_3$ ($x = 0; 0.1; 0.2; 0.3; 0.4; 0.5$) were prepared by a solid-state reaction method from the samarium (Sm$_2$O$_3$), cobalt (Co$_3$O$_4$), gallium oxides (Ga$_2$O$_3$) in air at 1523K for 5 hours. All oxides had «chemically pure» grade. Samarium oxide was preheated in air at 1273K for 2h.

X-ray diffraction patterns were obtained by using a D8 ADVANCED diffractometer with CuK$_\alpha$-radiation. Crystal lattice parameters of the samarium cobaltites-gallates were determined by the X-ray Table Processor as well as Rietveld method using ICDD JCPDS data.

Molar magnetization ($\sigma_{\text{mol}}$) at 5-300K in magnetic field up to 14 T as well as molar magnetic susceptibility ($\chi_{\text{mol}}$) at 5-300K in magnetic field 0.8 T were measured for the SmCo$_{1-x}$Ga$_x$O$_3$ using vibration method by means of a universal high-field measuring system (Cryogenic Ltd., London, 4IS). The signal from the empty sample holder was subtracted from the signal for the filled sample holder. Magnetic measurements were made in the Scientific-Practical Materials Research Center of NAS of Belarus.

### 3. Results and Discussion

Analysis of X-ray diffraction patterns of SmCo$_{1-x}$Ga$_x$O$_3$ samples showed (see Figure 1) that at $0 \leq x \leq 0.5$ a continuous series of SmCo$_{1-x}$Ga$_x$O$_3$ solid solutions with a structure of orthorhombically distorted perovskite was formed. Crystal lattice parameters $a$, $b$, $c$ of
these samples obtained by RTP linearly increased from 5.2847Å, 5.3499Å, 7.4971Å for SmCoO₃ to 5.3385Å, 5.4340Å, 7.5895Å for sample with \( x = 0.5 \), respectively (see Figure 2). Note that for SmCoO₃ Rietveld method gives: \( a = 5.2832\text{Å}, b = 5.3445\text{Å}, c = 7.4959\text{Å} \) whereas the data of [2] are: \( a = 5.289\text{Å}, b = 5.354\text{Å}, c = 7.541\text{Å} \).

The samples \( \text{SmCo}_{1-x}\text{Ga}_x\text{O}_3 \) with \( 0.2 \leq x \leq 0.5 \), in addition to the basic phase of solid solutions with orthorhombically distorted perovskite structure, also contained a small amount of the \( \text{Sm}_4\text{Ga}_2\text{O}_9 \) phase (Figure 1, curves 3-6). It should be noted that because of the low volatility of the samarium, cobalt oxides the total content of the magnetic \( \text{Sm}^{3+}, \text{Co}^{3+} \) ions in the \( \text{SmCo}_{1-x}\text{Ga}_x\text{O}_3 \) samples remained unchanged and therefore the presence of a small amount of the \( \text{Sm}_4\text{Ga}_2\text{O}_9 \) phase should not substantially affect the value of the magnetic susceptibility of these samples.

Figure 1. X-ray diffraction patterns of \( \text{SmCo}_{1-x}\text{Ga}_x\text{O}_3 \) samples at different degree of substitution (\( x \)): 0 (1), 0.1 (2), 0.2 (3), 0.3 (4), 0.4 (5), 0.5 (6) (* – phase \( \text{Sm}_4\text{Ga}_2\text{O}_9 \)).
Figure 2. Parameters of crystal lattice \((a, b, c)\) of solid solutions \(\text{SmCo}_{1-x}\text{Ga}_x\text{O}_3\).

To confirm this assumption we have synthesized samarium gallate \(\text{Sm}_4\text{Ga}_2\text{O}_9\) by the above method. \(\text{Sm}_4\text{Ga}_2\text{O}_9\) had monoclinic structure and its crystal lattice parameters were: \(a = 7.6461\text{Å}, b = 10.8514\text{Å}, c = 11.5635\text{Å}, \beta = 109.018^\circ, V = 907.064\text{Å}^3\). Magnetic susceptibility of this phases have been investigated at 5-300K (see Figure 3). On the basis of these data, effective magnetic moment of samarium ions \(\mu_{\text{eff,Sm}^{3+}}\) has been evaluated and it was equal to 0.41\(\mu_B\) for the 10-70K temperature interval.
Figure 3. Temperature dependence of molar magnetic susceptibility ($\chi_{\text{mol}}$) (a) and inverse value ($\chi_{\text{mol}}^{-1}$) (b) for Sm$_4$Ga$_2$O$_9$.

Dependence of the molar magnetization ($\sigma_{\text{mol}}$) of the SmCo$_{1-x}$Ga$_x$O$_3$ samples on the magnetic field ($H$) at 300K are linear up to $H = 10$ T (Figure 4(a)). At 5K $\sigma_{\text{mol}}$ linear dependence on $H$ realizes up to $H \approx 1$ T, while
for $H > 1\ \text{T}$ slowing down in the growth of the magnetization (tendency to the saturation) with increasing field $H$ is observed (Figure 4(b)).

Figure 4. Dependence of the molar magnetization ($\sigma_{\text{mol}}$) on the magnetic field ($H$) at 300K (a) and 5K (b) for SmCo$_{1-x}$Ga$_x$O$_3$ samples at different degree of substitution $x$. 
Temperature dependences of molar magnetic susceptibility ($\chi_{\text{mol}}$) determined in the temperature range 5-300K in a magnetic field 0.8 T for SmCo$_{1-x}$Ga$_x$O$_3$ ($0 \leq x \leq 0.5$) are shown in Figure 5(a). It is seen that increase of the degree of substitution of paramagnetic Co$^{3+}$ ions by diamagnetic Ga$^{3+}$ ions for SmCo$_{1-x}$Ga$_x$O$_3$ does not lead at a certain temperature to the invariability (constancy) or decrease of the molar magnetic susceptibility ($\chi_{\text{mol}}$), as it should be observed at invariability of magnetic state of Sm$^{3+}$, Co$^{3+}$ ions. On the contrary it leads to the increase of the molar magnetic susceptibility ($\chi_{\text{mol}}$) and magnetization ($\sigma_{\text{mol}}$). Consequently, the magnetic state of Sm$^{3+}$, Co$^{3+}$ ions for SmCo$_{1-x}$Ga$_x$O$_3$ differs from their state in SmCoO$_3$.

According to the literature data [8, 10] Co$^{3+}$ ions in SmCoO$_3$ below 300K are in the LS-state, i.e., they are diamagnetic and the magnetic properties of SmCoO$_3$ at low temperatures are caused mainly by Sm$^{3+}$ ions. Temperature dependence of the reciprocal molar magnetic susceptibility ($1/\chi_{\text{mol}}$) for SmCo$_{1-x}$Ga$_x$O$_3$ within whole temperature interval 5-300K is strongly nonlinear (Figure 5(b)) and thus cannot be described by the Curie-Weiss law.
Figure 5. Temperature dependence of molar magnetic susceptibility ($\chi_{\text{mol}}$) (a) and reciprocal molar magnetic susceptibility ($1/\chi_{\text{mol}}$) (b) for SmCo$_{1-x}$Ga$_x$O$_3$. 
In this connection processing of the temperature dependences of the magnetic susceptibility for solid solutions SmCo$_{1-x}$Ga$_x$O$_3$ is carried out (as in [10] for SmCoO$_3$) by construction dependences of $\chi_{\text{mol}}T$ product on the temperature [16] for the narrow temperature ranges. For all SmCo$_{1-x}$Ga$_x$O$_3$ samples $\chi_{\text{mol}}T$ is a linear function of temperature (Figure 6(b)) in the interval 10-60K, while at higher temperatures there is another linear plot with different slope to the temperature axis (Figure 6(a)). Note that this classical model does not take into account splitting of the ground state of Sm$^{3+}$ ions which was used in [10] for SmCoO$_3$. Furthermore, one cannot agree with the authors of [10] that for SmCoO$_3$ Curie-Weiss law is not valid at 4.2-300K. Analysis of the corresponding figure from their paper allows us to make a conclusion that dependence $\chi^{-1} = f(T)$ is practically linear at ~225-300K. Thus revealing the linear parts on the curves is not a simple problem.
Figure 6. Temperature dependence of the product of molar magnetic susceptibility ($\chi_{\text{mol}}$) on the temperature ($T$) for samples SmCo$_{1-x}$Ga$_x$O$_3$ in the temperature range 5-300K (a) and 10-60K (b).
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For SmCoO$_3$ linear dependence of $\chi_{\text{mol}}T$ on $T$ is observed in a broad range of temperatures (10-125K) (Figure 6(a), curve 1). Thus, the molar magnetic susceptibility of SmCoO$_3$ and SmCo$_{1-x}$Ga$_x$O$_3$ solid solutions in the temperature range 10-60K can be represented as a sum of two contributions: the first is described by the Curie-Weiss law ($\chi_{c,\text{mol}} = C_M/T$) and the second is temperature-independent one ($\chi_0$)

$$\chi_{\text{mol}} = C_M/T + \chi_0,$$

where $C_M$ is molar Curie constant.

From the Equation (1), it is resulted that

$$\chi_{\text{mol}}T = C_M + \chi_0T,$$

i.e., $\chi_{\text{mol}}T$ product depends linearly on the temperature.

By least-squares method for SmCo$_{1-x}$Ga$_x$O$_3$ samples coefficients $a$ and $b$ of the equation of linear dependence $\chi_{\text{mol}}T = aT + b$ are evaluated. Using the coefficients $a$ and $b$ of these equations molar Curie constants $C_M$ ($C_M = b$) and temperature-independent contributions $\chi_0$ ($\chi_0 = a$) were calculated. These contributions are due mainly to the polarization paramagnetism of Van-Vleck for Sm$^{3+}$ ions as well as diamagnetism of the Sm$^{3+}$, Co$^{3+}$, Ga$^{3+}$, O$^{2-}$ ions (Table 1). If we assume that cobalt Co$^{3+}$ ions below 60K for all SmCo$_{1-x}$Ga$_x$O$_3$ samples studied are mainly in the LS-state [8, 10] their magnetic susceptibility is due to the magnetic moment of samarium Sm$^{3+}$ ions. In this connection, the effective magnetic moment of samarium Sm$^{3+}$ ions ($\mu_{\text{eff,Sm}^{3+}}$) for SmCo$_{1-x}$Ga$_x$O$_3$ was calculated by the formula (3):

$$\mu_{\text{eff,Sm}^{3+}} = \sqrt{\frac{3k \cdot C_M}{N_A \cdot \mu_B^2}},$$

where $k$ is Boltzmann constant, $N_A$ is Avogadro constant, and $\mu_B$ is Bohr magneton.
The values obtained for the effective magnetic moment of Sm$^{3+}$ ions for SmCo$_{1-x}$Ga$_x$O$_3$ for the 10-60K temperature interval are given in the Table 1.

**Table 1.** Molar Curie constant ($C_M$), temperature-independent contribution in the magnetic susceptibility ($\chi_0$), the effective magnetic moment of Sm$^{3+}$ ions ($\mu_{\text{eff}, \text{Sm}^{3+}}$) for SmCo$_{1-x}$Ga$_x$O$_3$ in the temperature range 10-60K

| SmCo$_{1-x}$Ga$_x$O$_3$, $x$ | $C_M \times 10^2$, cm$^3$/mol | $\chi_0 \times 10^3$, cm$^3$/mol | $\mu_{\text{eff}, \text{Sm}^{3+}}$, $\mu_B$ |
|-----------------------------|-------------------------------|----------------------------------|----------------------------------|
| 0                           | 3.421                         | 1.221                            | 0.52                             |
| 0.1                         | 3.177                         | 1.237                            | 0.50                             |
| 0.2                         | 3.687                         | 1.679                            | 0.54                             |
| 0.3                         | 4.420                         | 1.838                            | 0.59                             |
| 0.4                         | 3.773                         | 2.078                            | 0.55                             |
| 0.5                         | 4.332                         | 2.231                            | 0.59                             |

These data show that the effective magnetic moment of Sm$^{3+}$ ions ($\mu_{\text{eff}, \text{Sm}^{3+}}$) in SmCo$_{1-x}$Ga$_x$O$_3$ ($0 \leq x \leq 0.5$) practically does not depend on the $x$ and its value ($0.50 - 0.59\mu_B$) is less than the theoretical value $0.84\mu_B$ [11] (for the free Sm$^{3+}$ ions without polarization paramagnetism of Van-Vleck). Note that for SmCoO$_3$ magnetic moment $\mu_{\text{eff}, \text{Sm}^{3+}}$ equals to $0.52\mu_B$ and this value is close to the corresponding value ($0.47\mu_B$) obtained in [10] for the temperatures above 20K. Contribution ($\chi_0$) in magnetic susceptibility of SmCo$_{1-x}$Ga$_x$O$_3$ for the temperature interval 10-60K gradually increases with increasing degree of substitution $x$ (Table 1). It means that an increase in the polarization paramagnetism of Van-Vleck takes place, caused, probably, by decrease in the gap between the ground and excited states of Sm$^{3+}$ ions during the magnetic dilution of the Co$^{3+}$ ions. It may be due to an increase of the parameters $a$, $b$, $c$
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as well as the degree of orthorhombic distortion of the perovskite structure \( (\varepsilon = (b-a)/a) \) : from \( 1.234 \cdot 10^{-2} \) for \( \text{SmCoO}_3 \) to \( 1.789 \cdot 10^{-2} \) for \( \text{SmCo}_{0.5}\text{Ga}_{0.5}\text{O}_3 \). For \( \text{SmCoO}_3 \) \( \chi_0 \) is equal to \( 1.221 \cdot 10^{-3} \text{cm}^3/\text{mol} \). This \( \chi_0 \) value is somewhat smaller than \( 1.46 \cdot 10^{-3} \text{cm}^3/\text{mol} \) value obtained in [10] for \( \text{SmCoO}_3 \) in the temperature range 10-300K, but considerably larger than the theoretical value \( 0.676 \cdot 10^{-3} \text{cm}^3/\text{mol} \) for the free \( \text{Sm}^{3+} \) ions [10]. The results of our study of the magnetic susceptibility for \( \text{SmCo}_{1-x}\text{Ga}_x\text{O}_3 \) show that the orientational contribution \( (\chi_{c,\text{mol}} = C_M/T) \), depending on the temperature according to the Curie law, is less while the polarization temperature-independent contribution \( (\chi_0) \) is more than those for the free \( \text{Sm}^{3+} \) ions. This indicates a “partial freezing” of the orbital angular moment and a large polarizability of the electron shell of \( \text{Sm}^{3+} \) ions in the crystal field of orthorhombically distorted perovskite structure.

Unfortunately in our opinion at present it is not possible to account for the above fact that modified Curie-Weiss law is valid only for narrow temperature intervals. It is the experimental fact.

If at temperatures below 300K the cobalt \( \text{Co}^{3+} \) ions in the samarium cobaltite \( \text{SmCoO}_3 \) are in the LS-state and they are diamagnetic, the molar magnetic susceptibility for this compound is determined by:

\[
\chi_{\text{mol,SmCoO}_3} = \chi_{c,\text{mol,Sm}^{3+}} + \chi_{0,\text{SmCoO}_3},
\]

where \( \chi_{0,\text{SmCoO}_3} \) is the sum of contributions due to the diamagnetism of the \( \text{Sm}^{3+}, \text{Co}^{3+}, \text{Ga}^{3+}, \text{O}^{2-} \) ions and Van-Vleck paramagnetism of \( \text{Sm}^{3+} \) ions; \( \chi_{c,\text{mol,Sm}^{3+}} \) is temperature dependent (according to the Curie-Weiss law) contribution of the \( \text{Sm}^{3+} \) ions.
For the 10-60K temperature range the effective magnetic moment of samarium Sm$^{3+}$ ions for SmCo$\text{1-}_x\text{Ga}_x\text{O}_3$ ($0 \leq x \leq 0.5$) varies only slightly (Table 1). Therefore, one can assume that a gradual increase in molar magnetization ($\sigma_{\text{mol}}$) (Figure 4) and molar magnetic susceptibility ($\chi_{\text{mol}}$) (Figure 5(a)) observed at a certain temperature for solid solutions SmCo$\text{1-}_x\text{Ga}_x\text{O}_3$ with increasing ($x$) is caused both an increase of the contribution ($\chi_0$) and the presence of Co$^{3+}$ ions in the IS-state. According to this assumption, the molar magnetic susceptibility for SmCo$\text{1-}_x\text{Ga}_x\text{O}_3$ ($\chi_{\text{mol}},\text{SmCo}_{\text{1-}}\text{Ga}_x\text{O}_3$) at a certain temperature may be expressed by the equation:

$$\chi_{\text{mol}},\text{SmCo}_{\text{1-}}\text{Ga}_x\text{O}_3 = \chi_{c,\text{mol}},\text{Sm}^{3+},\text{SmCo}_{\text{1-}}\text{Ga}_x\text{O}_3 + \chi_{c,\text{Co}^{3+}},\text{SmCo}_{\text{1-}}\text{Ga}_x\text{O}_3 + \chi_{0,\text{mol}},\text{SmCo}_{\text{1-}}\text{Ga}_x\text{O}_3 ,$$  \hspace{1cm} (5)

where $\chi_{0,\text{mol}},\text{SmCo}_{\text{1-}}\text{Ga}_x\text{O}_3$ is the sum of temperature-independent contributions due to the diamagnetism of the Sm$^{3+}$, Co$^{3+}$, Ga$^{3+}$, O$^{2-}$ ions and Van-Vleck paramagnetism of Sm$^{3+}$ ions for SmCo$\text{1-}_x\text{Ga}_x\text{O}_3$. Since in the 10-60K temperature range $\chi_{c,\text{mol}},\text{Sm}^{3+},\text{SmCo}_{\text{1-}}\text{Ga}_x\text{O}_3 = \chi_{c,\text{mol}},\text{Sm}^{3+},\text{SmCo}_x\text{O}_3$, then from Equations (4) and (5), one can obtain:

$$\Delta\chi_{\text{mol}} = \chi_{\text{mol}},\text{SmCo}_{\text{1-}}\text{Ga}_x\text{O}_3 - \chi_{\text{mol}},\text{SmCoO}_3 = \chi_{c,\text{Co}^{3+}},\text{SmCo}_{\text{1-}}\text{Ga}_x\text{O}_3 + \Delta\chi_0 .$$

Hence it appears that

$$\chi_{c,\text{Co}^{3+}},\text{SmCo}_{\text{1-}}\text{Ga}_x\text{O}_3 = \Delta\chi_{\text{mol}} - \Delta\chi_0 , \text{ where } \Delta\chi_0 = \chi_0,\text{SmCo}_{\text{1-}}\text{Ga}_x\text{O}_3 - \chi_0,\text{SmCoO}_3 .$$  \hspace{1cm} (6)
Calculations of $\chi_{c,Co^{3+},SmCo_{1-x}Ga_xO_3}$ conducted by means of (6) in the temperature range 10-60K showed that for the samples $SmCo_{1-x}Ga_xO_3$ at $x = 0.3$ (Figure 7, curve 1); 0.5 the $\chi_{c,Co^{3+},SmCo_{1-x}Ga_xO_3}$ values were positive.

For $SmCo_{0.7}Ga_{0.3}O_3$ for the 5-60K temperature interval magnetic susceptibility $\chi_{c,Co^{3+}}$ was calculated by using Equation (6) (Figure 7, curve 1). Reciprocal value $(1/\chi_{c,Co^{3+}})$ within 5-40K interval varied linearly (Figure 7, curve 2). By the least squares method equation of linear dependency $(\chi^{-1}_{c,Co^{3+},SmCo_{1-x}Ga_xO_3} = a + bT)$ was obtained. Using coefficients $a$ and $b$, constants $C_M$ and $\Theta$ were calculated ($C_M = 0.012 cm^3 / mol$ and $\Theta = -2.9 K$). The effective magnetic moment of the paramagnetic Co$^{3+}$ ions $\mu_{eff,Co^{3+}}$ for $SmCo_{0.7}Ga_{0.3}O_3$ (for 1 mol of Co$^{3+}$ ions, taking into account that $1 - x = 0.7$) was calculated by the formula (3) and it was equal to 0.37$\mu_B$. 

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Figure 7. Temperature dependence of magnetic susceptibility \((\chi_{c,\text{Co}^{3+}})\) (curve 1) and reciprocal magnetic susceptibility \((1/\chi_{c,\text{Co}^{3+}})\) (curve 2) in the temperature range 5-60K for SmCo_{0.7}Ga_{0.3}O_3.

A fraction of Co^{3+} ions in the IS-state relative to the total content of Co^{3+} ions in SmCo_{0.7}Ga_{0.3}O_3 \((y)\) was evaluated by the Equation (7):

\[
\mu_{\text{eff,Co}^{3+}}^2 = (1 - y)\mu_{\text{eff,Co}^{3+}\text{LS}}^2 + y\mu_{\text{eff,Co}^{3+}\text{IS}}^2
\]  

\text{(7)}

where \(\mu_{\text{eff,Co}^{3+}} = 0.37\mu_B, \mu_{\text{eff,Co}^{3+}\text{LS}} = 0, \) and \(\mu_{\text{eff,Co}^{3+}\text{IS}} = 2.828\mu_B\). It is obtained that \(y\) equals to 1.71%.

Therefore, increase of the molar magnetic susceptibility at increasing of the substitution degree \(x\) of Co^{3+} ions by diamagnetic Ga^{3+} ions in SmCoO_3 with the formation of solid solutions SmCo_{1-x}Ga_xO_3 \((0 \leq x \leq 0.5)\) on the whole is due to the increase of the temperature
independent contribution stipulated by Van-Vleck paramagnetism \((\chi_0)\) of the \(\text{Sm}^{3+}\) ions. A fraction of the \(\text{Co}^{3+}\) ions being in a paramagnetic state is insignificant at 10-60K.

4. Conclusion

Synthesis of the samarium cobaltites-gallates \(\text{SmCo}_{1-x}\text{Ga}_x\text{O}_3\) \((x = 0; 0.1; 0.2; 0.3; 0.4; 0.5)\) is carried out by a conventional solid-state reaction method at 1523K. X-ray diffraction analysis showed that within the above range of \(x\) solid solutions were formed. Parameters \(a, b, c\) of the orthorhombically distorted perovskite crystal lattice increased linearly at \(x\) increase. Molar magnetic susceptibility \(\chi_{\text{mol}}\) for \(\text{SmCo}_{1-x}\text{Ga}_x\text{O}_3\) is determined in the temperature range 5-300K in a magnetic field of 0.8 T. It is found that increasing \(x\) for \(\text{SmCo}_{1-x}\text{Ga}_x\text{O}_3\) does not lead at a certain temperature to the absence of change or to a decrease of \(\chi_{\text{mol}}\) as it should be observed at invariability of the magnetic state of \(\text{Sm}^{3+}, \text{Co}^{3+}\) ions but on the contrary to the increase of \(\chi_{\text{mol}}\). This implies that the magnetic state of \(\text{Sm}^{3+}, \text{Co}^{3+}\) ions for solid solutions \(\text{SmCo}_{1-x}\text{Ga}_x\text{O}_3\) differs from their state in a pure \(\text{SmCoO}_3\). In this paper, it is confirmed by the analysis of the values of the effective magnetic moment of \(\text{Sm}^{3+}\) ions \((\mu_{\text{eff}, \text{Sm}^{3+}})\) and temperature-independent contribution \((\chi_0)\) due to the Van-Vleck polarization paramagnetism for the \(\text{Sm}^{3+}\) ions in \(\text{SmCo}_{1-x}\text{Ga}_x\text{O}_3\) within the temperature range 10-60K. It is found that for the samples \(\text{SmCo}_{1-x}\text{Ga}_x\text{O}_3\) for the 10-60K temperature interval the effective magnetic moment of \(\text{Sm}^{3+}\) ions \((\mu_{\text{eff}, \text{Sm}^{3+}})\) practically does not depend on the degree of substitution \(x\) and it equals to \((0.50 - 0.59)\mu_B\).
It is also observed, that increase of the $\chi_{\text{mol}}$ at growth of the substitution degree $x$ in $\text{SmCoO}_3$ with the formation of solid solutions $\text{SmCo}_{1-x}\text{Ga}_x\text{O}_3$ $(0 \leq x \leq 0.5)$ takes place. It may be due to the increase of the contribution $\chi_0$ of the $\text{Sm}^{3+}$ ions. A fraction of the $\text{Co}^{3+}$ ions being in a paramagnetic state is insignificant at 10-60K.

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