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Magnetic properties of samples of the system $Ga_xFe_{1-x}[NiCr]O_4$ with frustrated magnetic structure

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Abstract

Magnetic properties of samples of the system $Ga_xFe_{1-x}[NiCr]O_4$ ($x = 0.0, 0.2, 0.4, 0.6, 0.8$) are investigated. The assumption is made that two magnetic phase transitions take place for the ferrites with $x \geqslant 0.2$: at T_C the transition from the paramagnetic state to a spin-glass state; and at T_t a second transition from a spin-glass state to a frustrated magnetic phase. This assumption is in good agreement with theoretical models. It is established that long-range magnetic ordering occurs at the temperature T_t.

It is suggested that a frustrated magnetic structure in one sublattice is necessary for the occurrence of anomalous dependences of the spontaneous magnetization on temperature $\sigma_s(T)$ of N, P or L type. It is established that if the frustrated magnetic structure is present in both sublattices of the ferrite, an anomalous $\sigma_s(T)$ curve of another type is formed.

Our conclusion is that the reason for the frustration of the magnetic connections in the samples of the system $Ga_xFe_{1-x}[NiCr]O_4$ with $x \leqslant 0.2$ is the presence of strong indirect interlattice interaction Fe^{3+}_A–O^{2-}–Cr^{3+}_B of positive sign.

1. Introduction

The ferrites with spinel structure can form a frustrated magnetic structure. As a rule, a frustrated magnetic structure is created by the dilution of the ferrite sublattices by non-magnetic ions [1]. In this case the frustrated magnetic structure consists of separate spontaneously magnetized areas formed due to long-range and short-range magnetic order. However, it is known that the probability of the formation of a frustrated magnetic structure in undiluted spinel ferrites is fairly high also, because they contain two or more types of magnetic cation with exchange interactions J_{AB}, J_{BB} and J_{AA} of different magnitudes and signs [2].

The present paper is devoted to the study of magnetic properties of polycrystalline samples of nickel ferrite–chromates $Ga_xFe_{1-x}[NiCr]O_4$ ($x = 0.0, 0.2, 0.4, 0.6, 0.8$). From Mössbauer

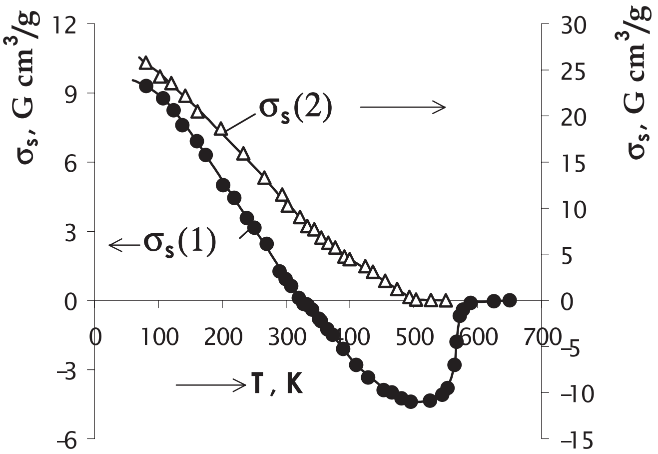

Figure 1. Temperature dependences of the spontaneous magnetization $\sigma_s(T)$ for the ferrites Ni[FeCr]O_4 (curve 1) and $Ga_{0.2}Fe_{0.8}$[NiCr]O_4 (curve 2).

measurements it is known that all the above-mentioned samples have a frustrated magnetic structure, including Ni[FeCr]O_4 [3].

2. Experiment

The samples of the system Ga_xFe_{1-x}[NiCr]O_4 ($x = 0.0, 0.2, 0.4, 0.6, 0.8$) were prepared using ceramic technology. A first anneal was carried out at the temperature of 1000 °C for 4 h; a second one was performed at the temperature of 1350 °C for 4 h with subsequent slow cooling. Both firings were carried out in air. X-ray diffraction patterns recorded at room temperature indicated that the samples were single-phase spinels.

The measurements of the magnetization σ and coercive force H_c were carried out by the ballistic method in magnetic fields up to 11 kOe in the temperature range 80–650 K. The magnetization was measured on a ball with a diameter of 7 mm. The remanent magnetization σ_r and coercive force H_c were derived from the shape of the hysteresis loops. The relative error in the magnetization measurements was about 3%.

3. Results and discussion

We found that the curve $\sigma_s(T)$ for nickel ferrite–chromate Ni[FeCr]O_4 has a compensation temperature $T_c = 325$ K and Curie temperature $T_C = 575$ K. However, the compensation temperature is absent for other samples of the system Ga_xFe_{1-x}[NiCr]O_4 ($x \geqslant 0.2$) having non-magnetic Ga^{3+} ions in the tetrahedral sublattice and the same concentration of Cr^{3+} ions in the octahedral sublattice. Measurements of remanent magnetization σ_r for the samples with $x \geqslant 0.2$ show that, over the whole temperature range investigated, σ_r does not change its sign, i.e. there is no compensation temperature for these samples. In figure 1, the temperature dependences of the spontaneous magnetization $\sigma_s(T)$ for the ferrites Ni[FeCr]O_4 (curve 1) and $Ga_{0.2}Fe_{0.8}$[NiCr]O_4 (curve 2) are presented.

We also obtained anomalous temperature dependences of the spontaneous magnetization σ_s and coercive force H_c for samples of Ga_xFe_{1-x}[NiCr]O_4 with $x \geqslant 0.2$. The value of σ_s was determined by extrapolating the linear part of the curve $\sigma(H)$ to the field $H = 0$. It turned out that a drop in spontaneous magnetization occurred at a temperature T_t lower

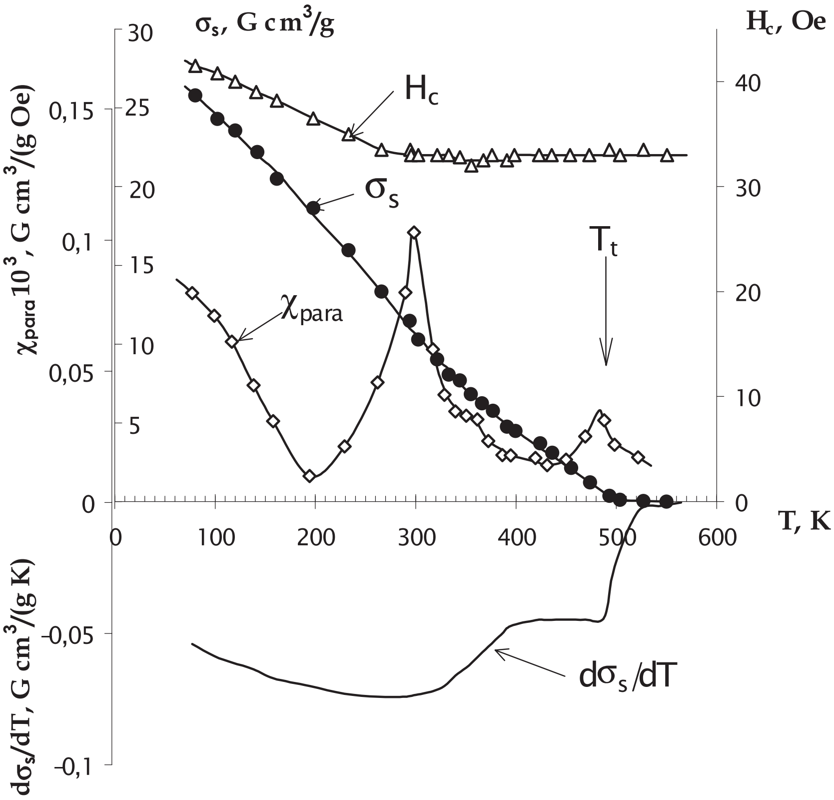

Figure 2. Temperature dependences of the spontaneous magnetization $\sigma_s(T)$, coercive force $H_c(T)$, derivative $(d\sigma_s/dT)(T)$ and paramagnetic susceptibility $\chi_{para}(T)$ for the sample $Ga_{0.2}Fe_{0.8}[NiCr]O_4$.

than the temperature T_C at which a decrease in coercive force must take place. In figure 2 temperature dependences of the spontaneous magnetization σ_s, coercive force H_c, derivative $d\sigma_s/dT$ and paramagnetic susceptibility χ_{para} are given for a sample with $x = 0.2$.

Moreover, the temperature dependences of the spontaneous magnetization $\sigma_s(T)$ for the ferrites with $x \geqslant 0.2$ differ strongly from the curve of Q type, according to Néel. For these compositions the curves $\sigma_s(T)$ are linear functions of temperature over a wide temperature range, so the behaviour of the derivative $d\sigma_s/dT$ is anomalous: the value of $d\sigma_s/dT$ increases with increasing temperature, remains constant over a certain temperature range and then decreases again.

Thus, we have established that, unlike non-frustrated ferrimagnets, the ferrites with concentration $x \geqslant 0.2$ with a frustrated magnetic structure have no maximum at T_C in the curve $(d\sigma_s/dT)(T)$. Also it is found that for these diluted ferrites the maximum paramagnetic susceptibility χ_{para} occurs at T_t and is absent at $T > T_t$ (figure 2).

We used a method of thermodynamic coefficients for definition of the temperature T_t, at which a long-range magnetic order occurs [4]. The magnetization isotherms for ferrites of the system $Ga_xFe_{1-x}[NiCr]O_4$ ($x = 0.0$–0.8) were investigated, i.e. the curves $(H/\sigma)(\sigma^2)$ are drawn. We obtained that $T_t \approx 573$, 490, 415, 300 and 100 K for the samples with $x = 0.0$, 0.2, 0.4, 0.6 and 0.8, respectively. It appeared that for samples with $x \geqslant 0.2$ these temperatures T_t are less than the Curie temperature T_C. For example, for the sample with

$x = 0.2$ it turned out that a long-range magnetic order appears at temperatures lower than the temperature $T_t \approx 490$ K. Unfortunately, we could not define the Curie temperatures T_C for the samples of the system $Ga_xFe_{1-x}[NiCr]O_4$ with $x \geqslant 0.2$, as the magnetization σ_s, being very small, smoothly decrease with increasing temperature above T_t. Thus the coercive force remains high at temperatures $T > T_t$, and the Curie temperature is the temperature at which both the magnetization σ_s and coercive force H_c vanish.

According to the conclusions of the theoretical model of Van Hemmen [5], if there is a transition from a paramagnetic to a spin-glass state in the magnetic composition, then at lower temperatures a second magnetic phase transition from a spin-glass state to another magnetic phase (ferromagnetic or frustrated magnetic) must take place. A similar conclusion has been reached in the theoretical work [6] in which a spin-glass model with short-range and long-range interactions was considered. According to this model a transition to spin-glass state takes place at higher temperatures than a transition to a ferromagnetic or antiferromagnetic phase.

Thus, on the basis of our experimental results and the conclusions of [5, 6], we have suggested that in the samples with $x \geqslant 0.2$ at the temperature T_C a transition from the paramagnetic state to a phase which consists of spontaneously magnetized areas, formed due to short-range order (a spin-glass state), occurs. A transition from spin-glass state to a state with frustrated magnetic structure is observed at the temperature T_t ($T_t < T_C$). In the frustrated magnetic phase there are fairly large spontaneously magnetized areas formed due to long-range magnetic order, which are chaotically arranged over the whole volume of the sample.

Also our assumption of two transitions at the temperatures T_C and T_t is proved to be true by the results of neutron diffraction investigations of the diluted sample $Co_{0.8}Mn_{0.2}Al_{1.6}Fe_{0.4}O_4$ [7]. It is established that this sample exhibits three phase transitions: at a temperature larger than 100 K, there is formation of magnetic spin clusters showing superparamagnetic-type behaviour before the true paramagnetic region is reached at about 200 K; a ferromagnetic long-range ordering is observed in the temperature range 50–100 K; and finally below 50 K there is a freezing of the magnetic spin clusters.

In figure 3(a), isotherms of magnetization $\sigma(H)$ at temperatures $T < T_t$ ($T = 80.5$ K) and at $T > T_t$ ($T = 493$ and 503.5 K) for the sample $Ga_{0.2}Fe_{0.8}[NiCr]O_4$ are presented. One can see that magnetization depends linearly on field for $H \geqslant 1$ kOe at temperatures $T = 498$ and 553 K, with attests that a spin-glass state occurs above T_t for this sample. In figure 3(b) the hysteresis loop for this sample at the temperature $T = 503.5$ K is presented.

Néel was the first to calculate that in ferrite–spinels anomalous temperature dependences of the spontaneous magnetization $\sigma_s(T)$ of N, P and L type can be observed [8].

Later, a few of authors found ferrites with anomalous curves $\sigma_s(T)$ of N type, i.e. with a compensation temperature: lithium chromates $Li_{0.5}Fe_{2.5-x}Cr_xO_4$ ($x = 1.0$–1.6) [9] and nickel chromates $NiFe_{2-x}Cr_xO_4$ ($x = 0.75$–1.5) [10]. These authors considered that the basic reason for the occurrence of the anomalous $\sigma_s(T)$ curves is the direct negative exchange interaction of Cr_B^{3+} and Cr_B^{3+} in the B sublattice, which results in a sharp reduction of the spontaneous magnetization of the octahedral sublattice $\sigma_{s\,\mathrm{oct}}(T)$ with increase of the temperature.

We believe that the anomalous $\sigma_s(T)$ curve of N type for the ferrite–chromates $Li_{0.5}Fe_{2.5-x}Cr_xO_4$ and $NiFe_{2-x}Cr_xO_4$ can be connected to another feature also. For example, $\sigma_s(T)$ curves for the ferrite–chromates $CoFeCrO_4$ [11] and $CuFeCrO_4$ [12] are not anomalous curves with a compensation temperature, whereas for the nickel ferrite–chromate $NiFeCrO_4$ [10] the curve $\sigma_s(T)$ is of N type with the same contents of Cr_B^{3+} ions in the B sublattice.

We suppose that the formation of a frustrated magnetic structure in one sublattice of a spinel ferrite must have a fundamental influence on the shape of the spontaneous magnetization $\sigma_s(T)$ curve. We suggest that the frustrated magnetic structure for the sample $Fe[NiCr]O_4$

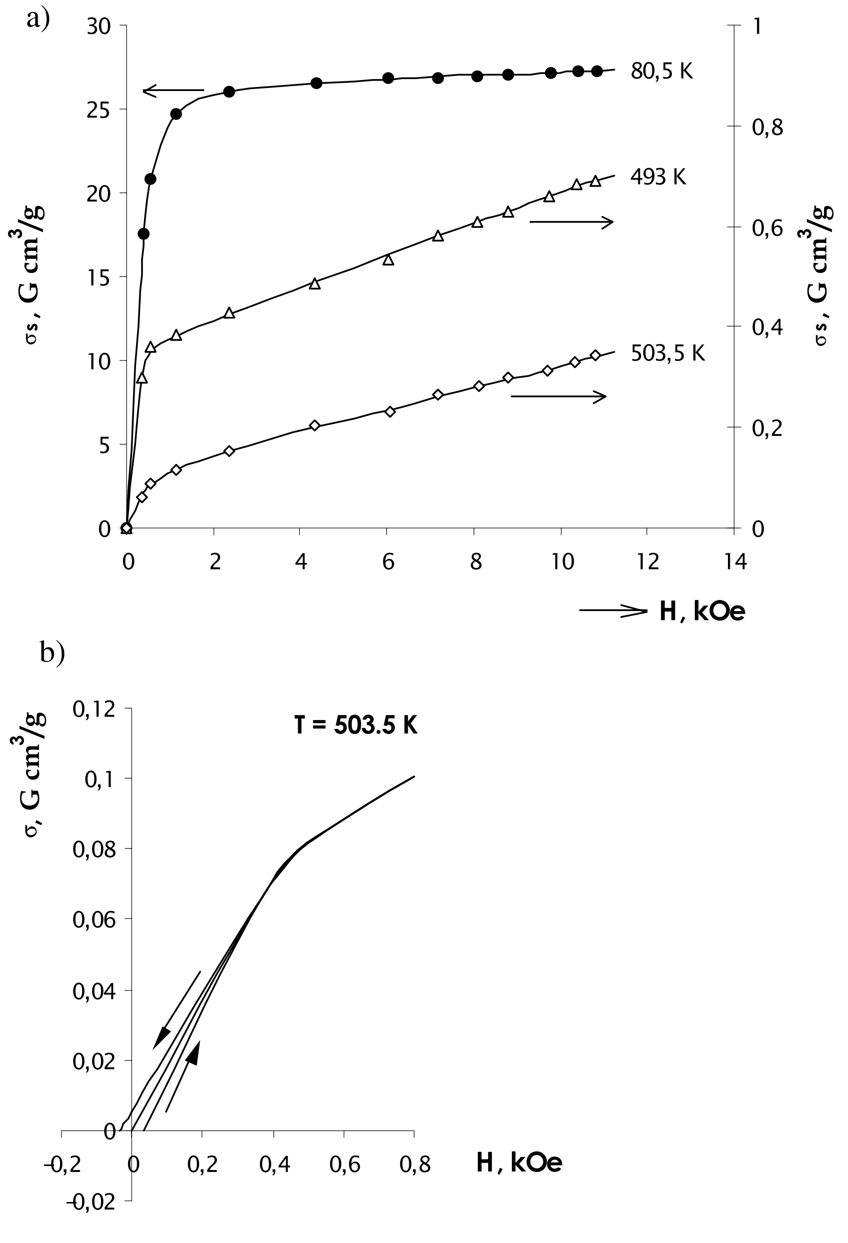

Figure 3. (a) Isotherms of magnetization $\sigma(H)$ for the sample $Ga_{0.2}Fe_{0.8}[NiCr]O_4$. (b) The hysteresis loop at the temperature $T = 503.5$ K.

occurs only in the octahedral sublattices, which are responsible for the magnetic moment of this ferrite below the compensation temperature T_c. At the same time, a frustrated magnetic structure is absent in the tetrahedral sublattices, which are responsible for the magnetic moment of the ferrite above T_c.

The formation of the frustrated magnetic structure in the tetrahedral sublattice of $Ga_xFe_{1-x}[NiCr]O_4$ samples ($x \geqslant 0.2$) is obviously connected to the introduction of non-magnetic Ga^{3+} ions.

Therefore, the formation of anomalous curves $\sigma_s(T)$ of the spinel ferrites can be interpreted in the following way. If the frustrated magnetic structure is absent in both sublattices of the spinel ferrites and the curves of spontaneous magnetization of both octahedral $\sigma_{s\,\mathrm{oct}}(T)$ and tetrahedral $\sigma_{s\,\mathrm{tetr}}(T)$ sublattices are of Q type, then the sum curve $\sigma_s(T)$ will obviously be of Q type (figure 4(a)). If a frustrated magnetic structure occurs in the octahedral sublattice, which is responsible for the magnetic moment of ferrite, while a frustrated magnetic structure is absent in the tetrahedral one, then the sum curve $\sigma_s(T)$ has an anomalous N-type shape (figure 4(b)). A P-type curve forms when a frustrated magnetic structure takes place in the tetrahedral sublattice but not in the octahedral sublattice (figure 4(c)). In that particular case, if the spontaneous magnetizations of the two sublattices are equal to each other at low temperatures, then the sum curve $\sigma_s(T)$ will be an anomalous curve of L type (figure 4(d)). Therefore, it may be stated that for the occurrence of anomalous shapes of the $\sigma_s(T)$ curve of N, P or L type, it is necessary that frustrated magnetic structure should be present in at least one of the two sublattices.

When a frustrated magnetic structure occurs in both sublattices, an anomalous curve of a new type forms, whose shape we obtained for the samples investigated from the system $Ga_xFe_{1-x}[NiCr]O_4$ with $x = 0.2$–0.8 (figure 4(e)).

Earlier, we obtained similar anomalous $\sigma_s(T)$, $H_c(T)$ and $(\mathrm{d}\sigma_s/\mathrm{d}T)(T)$ curves for copper ferrite–chromates $CuFe_{2-x}Cr_xO_4$ ($x = 1.0, 1.4, 1.6$) [12] and for samples of the systems $CuGa_xAl_xFe_{2-2x}O_4$ ($x \geqslant 0.4$) [13] and $CuGa_xAl_{2x}Fe_{2-3x}O_4$ ($x \geqslant 0.3$) [14] with a frustrated magnetic structure.

It is interesting to seek to understand the reasons for frustrated magnetic connections in the ferrite–chromates $Ga_xFe_{1-x}[NiCr]O_4$ with $x \leqslant 0.2$. The reason for these in spinel ferrites can be the dilution of ferrite by non-magnetic ions [1] or the presence of exchange interactions varying in sign and value in the samples [2]. Therefore it was necessary to estimate exchange interactions between ions, following [15].

In these samples, the following exchange interactions can take place: interlattice indirect exchange interactions Fe_A^{3+}–O^{2-}–Cr_B^{3+} and Fe_A^{3+}–O^{2-}–Ni_B^{2+}, intralattice indirect interactions Ni_B^{2+}–O^{2-}–Ni_B^{2+}, Ni_B^{2+}–O^{2-}–Cr_B^{3+} and Cr_B^{3+}–O^{2-}–Cr_B^{3+}, and also direct exchange interactions Cr_B^{3+}–Cr_B^{3+}. As always, it is possible to neglect the intralattice A–A interactions.

The $Fe_A^{3+}(e_g^2t_{2g}^3)$ ion forms a p_σ connection with the p orbital of oxygen. In its turn, the $Cr_B^{3+}(t_{2g}^3e_g^0)$ ion has only t_{2g} magnetic orbitals and forms a p_π connection with the same orbital of oxygen. Hence, the interaction Fe_A^{3+}–O^{2-}–Cr_B^{3+}, formed by p_σ–p_π connections, has a positive sign and moderate force [15]. The interaction Fe_A^{3+}–O^{2-}–Ni_B^{2+} between $Fe_A^{3+}(t_{2g}^3e_g^2)$ ions and $Ni_B^{2+}(t_{2g}^6e_g^2)$ ions is formed by p_σ–p_σ connections. Therefore, one expects this interaction to be of negative sign and strong.

The intralattice B–B interaction between $Ni_B^{2+}(t_{2g}^6e_g^2)$ ions formed by p_π–p_π connections has a positive sign and is weak. As the $Ni_B^{2+}(t_{2g}^6e_g^2)$ ion has magnetic e_g orbitals and the $Cr_B^{3+}(t_{2g}^3e_g^0)$ ion has magnetic t_{2g} orbitals, the interaction Ni_B^{2+}–O^{2-}–Cr_B^{3+}, formed by p_σ–p_π connections, will be negative and rather strong. The exchange Cr_B^{3+}–Cr_B^{3+} between $Cr_B^{3+}(t_{2g}^3e_g^0)$ ions will be direct, strong and of negative sign. The negative exchange Cr_B^{3+}–O^{2-}–Cr_B^{3-} is very weak and can, as a rule, be neglected.

For the first time, we have shown that in the diluted nickel ferrite–chromates $Ga_xFe_{1-x}[NiCr]O_4$ with $x \leqslant 0.2$ two interlattice exchange interactions of different sign take place: Fe_A^{3+}–O^{2-}–$Cr_B^{3+} > 0$ and Fe_A^{3+}–O^{2-}–$Ni_B^{2+} < 0$. However, the role of the first interaction will be amplified by negative intralattice exchange interactions Cr_B^{3+}–Cr_B^{3+} and Ni_B^{2+}–O^{2-}–Cr_B^{3+}. The presence of these exchange interactions also results in frustrated magnetic connections in octahedral sites of ferrite–chromates. Confirmation of this assumption is provided by the fact

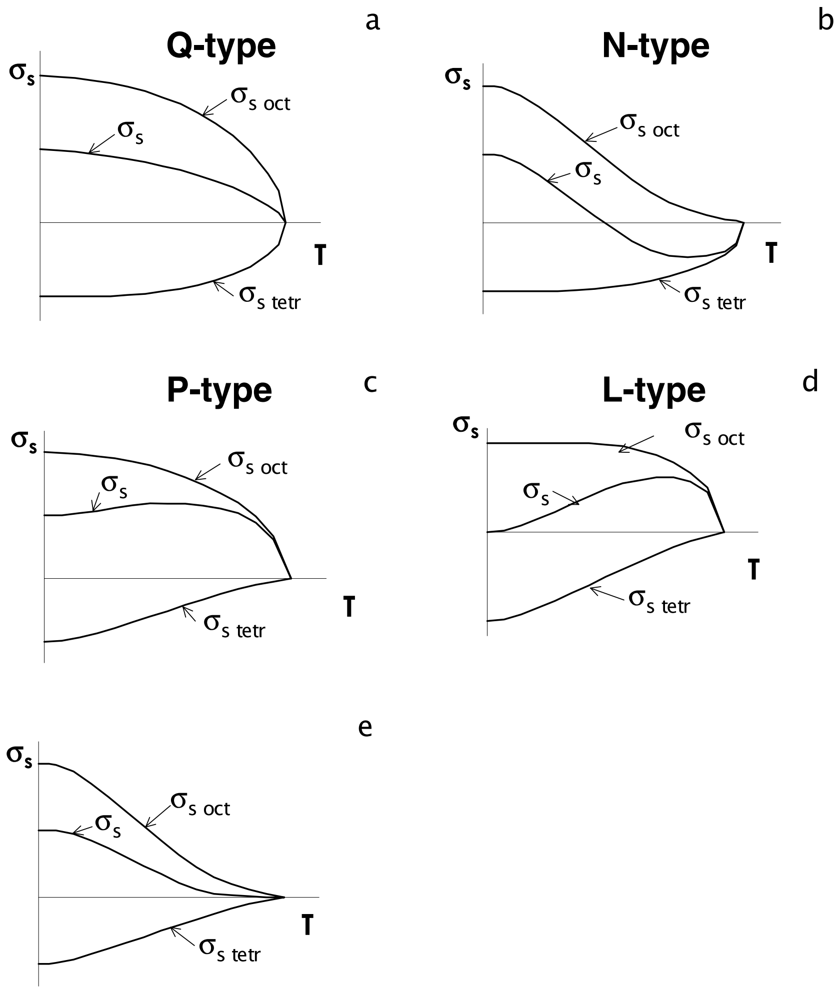

Figure 4. Schematic curves for the magnetization dependences of the B sublattice ($\sigma_{s\,\mathrm{oct}}(T)$) and the A sublattice ($\sigma_{s\,\mathrm{tetr}}(T)$) and the sum spontaneous magnetization ($\sigma_s(T)$).

that the frustrated magnetic structure is not found in the nickel chromate $Ni[Cr_2]O_4$. Hence, the large content of Cr_B^{3+} ions does not result in frustrated magnetic connections in $NiCr_2O_4$ chromate when the positive A–B exchange Fe_A^{3+}–O^{2-}–Cr_B^{3+} is absent.

4. Conclusions

It is established that for ferrites of the system $Ga_xFe_{1-x}[NiCr]O_4$ ($x = 0.2$–0.8) with frustrated magnetic structure, there is anomalous behaviour of the magnetization σ_s and coercive force H_c. So, the spontaneous magnetization $\sigma_s(T)$ depends linearly on temperature over a large temperature interval, and the reduction of σ_s occurs at a lower temperature than the reduction of the coercive force.

The assumption is made that at a temperature T_t ($T_t < T_C$) another phase transition takes place. First, there is a transition from a paramagnetic state to a cluster spin-glass structure at the Curie temperature T_C and, secondly, a transition from a cluster spin-glass structure to a frustrated magnetic structure at T_t caused by the long-range magnetic order. This assumption is in good agreement with theoretical models [5, 6].

Our conclusion is that the anomalous dependence of the spontaneous magnetization $\sigma_s(T)$ of N type for a sample of $NiFeCrO_4$ can be observed only in cases where frustrated magnetic structure is present in the B sublattice. It is established that for the occurrence of anomalous dependences of the spontaneous magnetization on temperature, $\sigma_s(T)$, of N, P or L type, it is necessary for at least one of the sublattices to exhibit frustrated magnetic structure.

It is found that the introduction of Ga^{3+} ions results in the disappearance of the compensation temperature T_c in the $\sigma_s(T)$ curve. It is shown that if there is frustrated magnetic structure in both sublattices of a ferrite, an anomalous $\sigma_s(T)$ curve of another type is formed.

It is found that, unlike the case for a non-frustrated ferrimagnet, a ferrite with frustrated magnetic structure has no maximum at T_C on the curve $(\mathrm{d}\sigma_s/\mathrm{d}T)(T)$. It is found that for a diluted ferrite with frustrated magnetic structure the maximum in the paramagnetic susceptibility χ_{para} is at T_t, and there is no maximum at T_C.

For the first time we have shown, thus, for the diluted nickel ferrite–chromates $Ga_xFe_{1-x}[NiCr]O_4$ with $x \leqslant 0.2$, that there are two interlattice exchange interactions of different sign: Fe^{3+}_A–O^{2-}–$Cr^{3+}_B > 0$ and Fe^{3+}_A–O^{2-}–$Ni^{2+}_B < 0$; however, the role of the first will be amplified by negative intralattice exchange interactions Cr^{3+}_B–Cr^{3+}_B and Ni^{2+}_B–O^{2-}–Cr^{3+}_B. The presence of these exchange interactions also results in frustrated magnetic connections in octahedral sites of ferrite–chromates.

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