# Cluster spin glass state in dilute ferrimagnets

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An experimental check of the "exchange model" for the formation of the spin glass state in systems with short-range competing exchange is made by studying the static properties of the model ferrimagnetic system $Li_{0.5}Ga_xFe_{2.5-x}O_4$ ($0.9 \leqslant x \leqslant 2.0$). The polytherms $\sigma_H(T)$ and isotherms $\sigma_T(H)$ of the magnetization are measured at temperatures from 4.2 to 500 K and fields up to 50 kOe. An analysis of these curves yields conclusions as to the magnetic states that arise under certain $(x,H,T)$ conditions and permits construction of the concentration-temperature phase diagram. For $x \geqslant 1.3$, a cluster spin glass state arises at low temperatures; on increasing temperature it goes over to a paramagnetic ($x \geqslant 1.6$) or ferrimagnetic ($x < 1.6$) state. For $x \leqslant 1.2$ a long-range ferrimagnetic order coexisting with the clusters is observed at all temperatures $T < T_c$.

## INTRODUCTION

The problem of disordered magnets, and spin glasses in particular, is the subject of an ever increasing number of theoretical and experimental studies. The reason for this interest is, first of all, that conclusive answers have yet to be found for such important physical questions as the existence and nature of the phase transition to the spin glass state at the freezing temperature $T_f$, the type of order parameter, the influence of the various mechanisms on the properties of the spin glass, and, finally, whether individual spins or spin clusters are the "structural units" of the spin glass.[1,2] At the same time, the characteristic indicators of the spin glass state have been detected in many types of magnets, including industrial magnetic materials, and so the problem of disordered magnets has acquired a practical significance as well. For example, it has become obvious that when using the traditional method of obtaining new materials by varying the composition, one must consider the possibility that disordered states and, hence, qualitatively new physical properties will arise.

Unarguably, the specific conditions under which the spin glass state arises in various magnets and its inherent behavioral features must be studied further in order to solve the problem of disordered magnetic states in solids. The least studied materials in this regard are magnetic insulators and semiconductors, including ferrimagnets. Of the early models for disordered dilute ferrimagnets, the one that best agrees with our current understanding is the statistical-canting-angle model of Rozencwaig,[3] which has subsequently been developed by other authors.[4]

The most general model-free approach to dilute systems is to use percolation theory. According to the ideas of percolation theory, dilute ferrimagnets can have, depending on the concentration of magnetic ions, various cluster states coexisting with long-range order, a spin glass state, a superparamagnetic state, and, in particular, statistical canting.[5]

It is of interest to elucidate the possibilities and causes of the formation of the spin glass state in dilute ferrimagnets and to ascertain the features of this state for the following reasons. The classical objects which display the indicators of the spin glass state are highly dilute alloys of noble and transition metals, in which, according to the prevailing ideas, the mechanism of formation of the spin glass state stems primarily from the presence of a long-term exchange interaction of fluctuating sign—the RKKY interaction.[1,2,6] In addition, the overwhelming majority of theoretical papers have considered a model with an infinite interaction radius.[1] Although the mechanisms responsible for the transition to the spin glass state and for shaping the properties of this state (e.g., random anisotropy) continue to be actively studied, many investigators believe that the transition in the presence of a long-range interaction is a cooperative phenomenon.[1,6–8]

A different situation exists for ferrimagnets. A prerequisite for the onset of a disordered state, including the spin glass, on dilution is the presence of competing intrasublattice and intersublattice exchange interactions. However, the superexchange in ferrimagnets is short-ranged. Although certain dilute insulator and semiconductor systems have been found experimentally to exhibit properties analogous to those observed in classical spin galsses,[1,2,7] the specific mechanisms giving rise to the spin glass and the question of whether the transition at $T = T_f$ is of a cooperative nature in systems with a short-range exchange remain open to debate.[1,9]

To elucidate whether a spin glass state can arise as a result of a competition between short-range exchange interactions, in the present study we have investigated the magnetic states in the system of dilute ferrimagnets $Li_{0.5}Fe_{2.5-x}Ga_xO_4$ ($0.9 \leqslant x \leqslant 2.0$).

The chosen system is a good model object: the isomorphic substitution $Fe^{3+} \longleftrightarrow Ga^{3+}$ is possible over wide limits; there is only one kind of magnetic ion, $Fe^{3+}$, which is found in the $S$ state, i.e., the prerequisites for random crystallographic anisotropy are not met; the intrasublattice and interasublattice exchange interactions $Fe^{3+}$–$O^{2-}$–$Fe^{3+}$ are negative; the introduction of $Ga^{3+}$ ions only insignificantly

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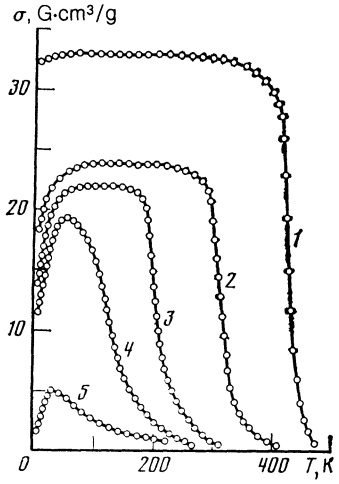


FIG. 1. Magnetization polytherms for $Li_{0.5}Fe_{2.5-x}Ga_xO_4$ samples in a field $H = 500$ Oe: 1) $x = 0.9$; 2) $x = 1.2$; 3) $x = 1.3$; 4) $x = 1.4$; 5) $x = 1.6$.

(through a change in the lattice parameter) alters the values of the exchange integrals, so that the ratio of the intersublattice to intrasublattice exchange integrals can be considered constant ($J_{ij}/J_{ii} \sim 2$; Ref. 10) over the entire range of $Ga^{3+}$ concentrations.

By using wide ranges of substitutions, magnetic fields (up to 50 kOe), and temperatures (4.2–500 K), we were able to study the change of the magnetic states as a function of concentration, temperature, and external magnetic field.

## MEASUREMENT TECHNIQUES AND EXPERIMENTAL RESULTS

In solving the problem set forth above, i.e., to ascertain whether a spin glass state can arise in dilute ferrimagnets, we based our study on the characteristic spin-glass indicators that find expression in peculiar behavior of the termperature dependence of the low-field magnetization: the vanishing of $\sigma_H(T)$ as $T \to 0$ K (due to the absence of a spontaneous magnetization in the spin glass state), the presence of a peak at $T \approx T_f$, and a change in the position and shape of this peak with increasing field.[1,2] In addition to measurements of the low-field magnetization, the program of study included measurements of the isotherms $\sigma_T(H)$ and polytherms $\sigma_H(T)$ of the magnetization at temperatures in the range 4.2–500 K and in fields up to 50 kOe.

The objects of study were polycrystalline samples obtained by ordinary ceramic technology. The samples were checked by x-ray diffraction to ensure that they contained a single phase. The diffraction patterns of all the samples exhibited superstructure reflections corresponding to an ordering of the $Li^+$ ions in sublattice $B$. The $Ga^{3+}$ cation distribution was estimated from the values of the magnetization at 4.2 K as obtained by extrapolation of an infinitely large field. The corresponding data for the cation distribution in the ferrimagnets $Li_{0.5}Fe_{2.5-x}Ga_xO_4$ with $0.9 \leqslant x \leqslant 2.0$ ($\alpha_A$ and $\alpha_B$ are the percent content of the magnetic ions $Fe^{3+}$ in sublattices $A$ and $B$, respectively; the uncertainty is $\pm 3\%$) are:

| $x$ | 0.9 | 1.2 | 1.3 | 1.35 | 1.4 | 1.6 | 1.7 | 1.9 | 2.0 |
|---|---|---|---|---|---|---|---|---|---|
| $\alpha_A$ | 45 | 33 | 33 | 36 | 40 | 33 | 30 | 30 | 30 |
| $\alpha_B$ | 58 | 48 | 40 | 35 | 35 | 28 | 25 | 18 | 15 |

The magnetization measurements [i.e., the $\sigma_H(T)$ and $\sigma_T(H)$ curves] in the temperature range 4.2 K $\leqslant T \leqslant$ 150 K were taken with a ballistic magnetometer (sensitivity $10^{-2}$ G·cm³/g); the relative error was $\pm 2\%$. A magnetic field of up to 50 kOe was produced by a superconducting solenoid.

For 77 K $\leqslant T \leqslant$ 500 K the magnetization was measured with a pendulum magnetometer. A field of up to 16 kOe was produced by an electromagnet. The sensitivity of the apparatus was 0.3 G·cm³/g; the relative error was 5%.

The formation of the magnetic states is influenced by three factors, namely the composition, field, and temperature; it is therefore convenient to study the experimental results by analyzing the influence of only two of these factors, treating the third as constant.

Figure 1 shows the temperature dependence of the magnetization $\sigma_H(T)$ of samples with a $Ga^{3+}$ content of $0.9 \leqslant x \leqslant 1.6$ in a field $H = 500$ Oe. We see that in all cases the $\sigma_H(T)$ curve falls off at both low temperatures and high temperatures. With increasing $Ga^{3+}$ content the sharp decrease in the magnetization at high temperatures in the sample with $x = 0.9$ (see curve 1 in Fig. 1) goes over to a smoother curve with a "high-temperature tail." This is especially evident in the samples with $x \geqslant 1.6$ (see curve 5 in Fig. 1 for $x = 1.6$) at temperatures above the temperature of the peak. The decrease in magnetization on decreasing temperature is more pronounced with increasing $Ga^{3+}$ concentration, so that, beginning with $x = 1.3$, the magnetization goes to zero as $T \to 0$ K. Thus, according to whether the low-field magnetization vanishes for $T \to 0$, we can divide the system of samples into two groups: I) $0.9 \leqslant x \leqslant 1.2$; II) $1.3 \leqslant x \leqslant 2.0$.

The differences in the behavior of these two groups of samples are seen just as clearly on the magnetization isotherms for 4.2 K (Fig. 2). The $\sigma_T(H)$ curves for samples with $0.9 \leqslant x \leqslant 1.2$ are the typical fundamental curves for magnetically soft materials: spontaneous-magnetization saturation is observed for $H \gtrsim 5$ kOe (without allowance for the demagnetizing factor). For $x = 0.9$ the high-field suscepti-

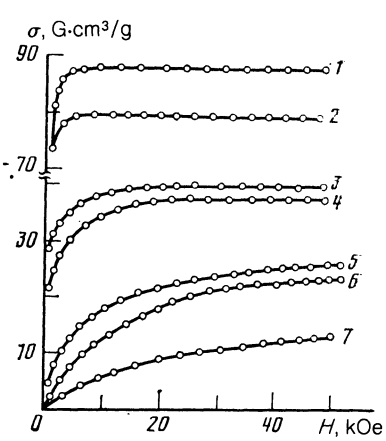


FIG. 2. Magnetization curves for $Li_{0.5}Fe_{2.5-x}Ga_xO_4$ samples at $T = 4.2$ K: 1) $x = 0.9$; 2) $x = 1.2$; 3) $x = 1.35$; 4) $x = 1.4$; 5) $x = 1.6$; 6) $x = 1.7$; 7) $x = 2.0$.

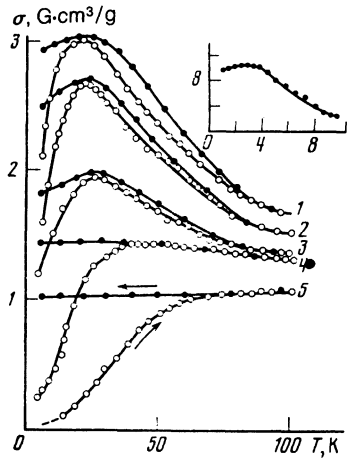


FIG. 3. Magnetization polytherms of $Li_{0.5}Fe_{0.9}Ga_{1.6}O_4$ sample: 1) $H = 300$ Oe; 2) $H = 200$ Oe; 3) $H = 100$ Oe; 4) $H = 50$ Oe; 5) $H = 25$ Oe. The inset is for $H = 2$ kOe. The light circles were taken on heating of the sample, the dark ones on cooling.

bility is nonzero ($\chi \approx 3 \cdot 10^{-5}$), whereas for $x = 1.2$ this is not observed. As we see from Fig. 2, for $x \geqslant 1.3$ the character of the $\sigma_T(H)$ curves, especially in fields $H < 20$ kOe, undergoes a substantial qualitative change: although the shape of the $\sigma_T(H)$ curves of different samples varies somewhat, they all behave like the magnization curves of a superparamagnet.[11]

Without considering in detail the influence of the temperature on the behavior of the magnetization isotherms of individual samples, we nontheless note the following. Group I: For $x = 0.9$ the behavior of the $\sigma_T(H)$ isotherms does not change substantially with increasing temperature, and only in a narrow region ($\approx 30$ K) near the Curie point $T_c$ does it take on a "superparamagnetic" character. For $x = 1.2$ an increase in temperature has the same effect on the $\sigma_T(H)$ curves as does an increase in the $Ga^{3+}$ concentration at 4.2 K: for temperatures $T \geqslant 70$ K on up to $T \geqslant T_c$ the behavior of the magnetization isotherms is superparamagnetic. For the group II samples ($x \geqslant 1.3$) the character of the $\sigma_T(H)$ curves remains unchanged with increasing temperature.

Since the vanishing of the low-field magnetization for $T \to 0$ is one of the indicators of a transition to the spin glass state, let us stop to analyze the behavior of the group II samples.

Let us first give a general outline of the behavior. For all the samples except $x = 1.4$ there is no peak in the $\sigma_H(T)$ for low fields; the peak appears only when the field is increased to $H \approx 400$ Oe for $x = 1.35$, to $H \approx 100$ Oe for $x = 1.6$, and to $H \approx 100$ Oe for $x = 1.7$. For $x = 1.4$ a rather broad peak appears beginning at $H = 5$ Oe. On the whole, the peaks of the $\sigma_H(T)$ curves are more pronounced at large $Ga^{3+}$ contents; with increasing field the peaks shift to lower temperatures and broaden out (Figs. 3 and 4).

A characteristic feature of the group II dilute ferrimagnets is the presence of magnetic viscosity (irreversibility of the magnetization polytherms on heating and cooling, transient effects) not only at low temperatures but also in a wide region $T > T_f$ [$T_f$ denotes the temperature of the peak on the $\sigma_H(T)$ curves; at low fields this is the temperature at which the irreversibility of $\sigma_H(T)$ on heating and cooling vanishes]. It should be noted that at low ($T < T_f$) temperatures the viscosity effects are suppressed by a comparatively weak field ($H < 3$ kOe), whereas for $T > T_f$ they persist all the way to $H \approx 10$ kOe.

The behavior of the group II samples showed the following differences. For samples with $1.3 \leqslant x \leqslant 1.4$, $T_f$ increases with increasing concentration, and the influence of the field on the position of the peaks becomes stronger with increasing $x$. In fields $H > 500$ Oe the $\sigma_H(T)$ curves are convex in the region $T > T_f$. For samples with $1.6 \leqslant x \leqslant 1.9$ the values of $T_f$ decrease with increasing $Ga^{3+}$ content, while the influence of the field on the position and shape of the peaks becomes weaker; for $T > T_f$ the $\sigma_H(T)$ curves are concave at all values of the field (see Figs. 1 and 4).

Thus the group II samples, which exhibit the indicators of a spin glass, can in turn be divided on the basis of the behavioral differences described above into two subgroups: a) $1.3 \leqslant x \leqslant 1.4$, and b) $1.6 \leqslant x \leqslant 1.9$.

For the $x = 2.0$ sample, because of the small magnetization, the measurements were made in fields $H \geqslant 1$kOe. Under these conditions the $\sigma_H(T)$ curves did not exhibit a peak at temperatures $T \geqslant 4.2$ K.

## DISCUSSION OF THE RESULTS

These studies have yielded definite evidence that the investigated system of dilute ferrimagnets occurs in different types of magnetic states depending on the concentration of nonmagnetic ions, the temperature, and the strength of the applied field. On the basis of the entire set of experimental data we have constructed the phase diagram shown in Fig. 5, which shows the magnetic states that arise in the investigated system of dilute ferrimagnets at difference concentrations of the nonmagnetic $Ga^{3+}$ ions and different temperatures for $H \approx 0$.

Curve 1 is the line of Curie points, which are clearly determined from the region of maximum decay of the low-field magnetization (see Fig. 1) or by the Belov-Arrott method of thermodynamic coefficients (Fig. 6). Curve 2

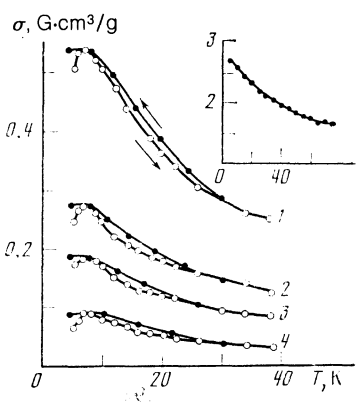


FIG. 4. Magnetization polytherms of $Li_{0.5}Fe_{0.6}Ga_{1.9}O_4$ sample: 1) $H = 50$ Oe; 2) $H = 300$ Oe; 3) $H = 200$ Oe; 4) $H = 100$ Oe. The inset is for $H = 5$ kOe. The light circles were taken on heating of the sample, the dark ones on cooling.

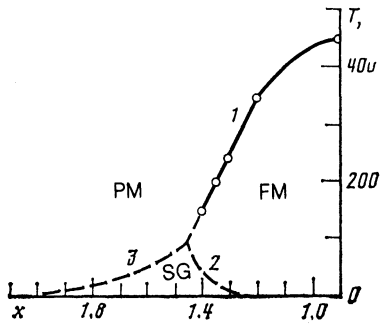


FIG. 5. Phase diagram for the dilute ferrimagnets $Li_{0.5}Fe_{2.5-x}Ga_xO_4$ ($0.9 \leqslant x \leqslant 2.0$).

separates the region with long-range ferrimagnetic (FM) order the spin glass (SG) region; it was constructed from the values of the temperature $T_f$ corresponding to the vanishing of the irreversibility of the low-field magnetization on heating and cooling of the samples at the lowest values of the applied field (see Fig. 3). Curve 3, which is the temperature boundary of the paramagnetic (PM) and SG states, was constructed in the same way.

The absence of long-range ferrimagnetic order at $Ga^{3+}$ concentrations $x \geqslant 1.6$ at all temperatures $T > 0$ K and fields $H < 15$ kOe is illustrated by the data in Fig. 6, which shows the Belov-Arrott curves for the samples with $x = 1.4$ (filled points) and $x = 1.6$ (open points). In contrast to the $x = 1.4$ sample, for which the linear parts of the Belov-Arrott curves for $T > T_f$ intersect the $\sigma^2$ axis in the positive region (and only for $T > T_c$ intersect in the negative region), for the sample with $x = 1.6$ the $\sigma^2$ axis is intersected in the negative region at all temperatues. Thus the sample groups distinguished earlier, viz., I, IIa, and IIb, belong to different regions of the phase diagram.

The paramagnetic and ferrimagnetic regions are not homogeneous. Directly beside lines 1 and 3 in the paramagnetic region is a region with pronounced short-range order; this region becomes wider in temperature with increasing $Ga^{3+}$ concentration. The existence of short-range order at $T \geqslant T_c$ ($T \geqslant T_f$) is implied by the presence of high-temperature tails on the $\sigma_H(T)$ curves (see Fig. 1) and by the behavior of the magnetization isotherm $\sigma_T(H)$, which deviates substantially from the linear dependence that is characteristic of paramagnets in weak fields. In the ferrimagnetic region the long-range ferrimagnetic order coexists with clusters. The latter are considered to be regions with a rather strong interaction inside and a weakened interaction at the boundary. For the group I samples ($x < 1.3$) the presence of clusters withing the region of long-range ferrimagnetic order, with moments which are frozen in arbitrary directions at low temperatures and which fluctuate at high temperatures, is consistent with the decrease of the magnetization at low temperatures $T \to 0$ K (see Fig. 1) and with the superparamagnetic character of the magnetization curves $\sigma_T(H)$ at high temperatures.

It follows from percolation theory that the probability of cluster formation increases sharply as the concentration approaches the percolation threshold. According to Ref. 5, for a two-sublattice ferrimagnet with one kind of magnetic ion the threshold for percolation through each of the sublattices corresponds to a magnetic ion content of $\approx 33\%$, while the boundary for percolation through the crystal as a whole corresponds to a magnetic ion content of less than 33% in each of the sublattices; for a cation distribution like that obtained in the group IIb samples, a disordered state of the spin glass type can form in the system.

Thus, with allowance for the cation distribution in the investigated samples (see the table above), the onset and enhancement of cluster effects and the transition to the spin glass state are perfectly normal in the context of percolation theory. Taking into account the entire set of experimental results for the system as a whole, we can conclude that for the group II samples ($x \geqslant 1.3$, the SG region on the phase diagram) at low temperatures ($T < T_f$), the magnetic state consists of a system of interacting clusters with magnetic moments frozen in arbitrary directions and thus has a zero spontaneous magnetization. The data on the cation distribution imply that all the samples correspond to the concentration region above the threshold for percolation through the crystal, and so there should be an exchange coupling between clusters.

From the point of view that the spin glass state in dilute ferrimagnets is of a cluster nature, it is entirely natural that the behavior of samples with different $Ga^{3+}$ contents should be different. For example, the more pronounce peaks on the low-field magnetization curves $\sigma_H(T)$ for samples with a large $Ga^{3+}$ content and the relatively weak influence of the field on the shape and position of these peaks are due to the large inhomogeneity of the cluster structure here. The inhomogeneity of the cluster structure also can be explained by the observed absence of peaks in weak fields $H \approx 0$. (For the sample with $x = 1.4$ the presence of a peak in weak fields is accidental in the sense that it is due solely to the relative proximity of the temperatures $T_f$ and $T_c$.) We note that the possibility that the shape of the peaks on the magnetization polytherms and the change in their position in an external field depend on the principal interactions in the crystal (exchange, anisotropy) has been considered, for example, in Ref. 12.

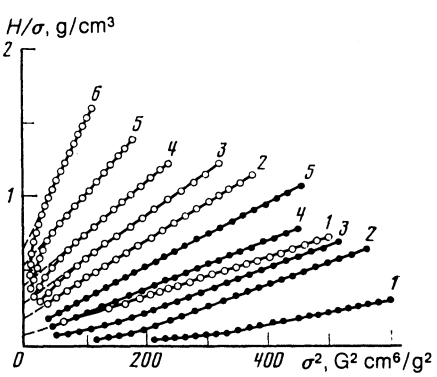


FIG. 6. Determination of the Curie points by the Belov-Arrott method for $Li_{0.5}Fe_{0.9}Ga_{1.6}O_4$ (light circles): 1) $T = 4.2$ K; 2) $T = 60$ K; 3) $T = 80$ K; 4) $T = 100$ K; 5) $T = 110$ K; 6) $T = 130$ K and for $Li_{0.5}Fe_{1.1}Ga_{1.4}O_4$ (dark circles): 1) $T = 110$ K; 2) $T = 120$ K; 3) $T = 140$ K; 4) $T = 150$ K; 5) $T = 160$ K.

In addition to the absence of a peak in weak fields, the behavior of these samples for $T > T_f$. As we have mentioned, near the phase transition lines 1 and 3 (see Fig. 5) there is a region of strong short-range order, which is essentially due to the existence of rather large clusters.[13] The viscosity for $T > T_f$ is thus analogous to that observed in superparamagnets.[11] It is extremely important that the viscosity effects are different for $T < T_f$ and $T > T_f$. Of the above experimental results, the difference is seen in the fact that for $T < T_f$ the viscosity effects (irreversibility) are suppressed by a relatively weak field, while for $T > T_f$ they persist all the way up to $H \approx 10$ kOe.

## CONCLUSION

The major part of this study has been a direct experimental check of the exchange model for the formation of the spin glass state in dilute systems with short-range competing exchange. The experimental results show convincingly that for $x \geqslant 1.3$ the dilute ferrimagnets $Li_{0.5}Fe_{2.5-x}Ga_xO_4$ have a cluster spin glass state in the low-temperature region. In view of the model nature of this system and the good agreement between the results and percolation theory calculation, we can draw the following conclusions:

1) In dilute two-sublattice systems with competing short-range exchange of the antiferromagnetic type, a spin glass state forms for magnetic-ion concentrations in the region above the threshold for percolation through the crystal as a whole.

2) The spin glass state has a cluster nature, with an exchange coupling between clusters.

3) The ratio of the competing exchange interactions, which depends on the magnetic ion content in each of the sublattices, has a decisive influence on the sequence of states which arise on decreasing temperature: paramagnetic–spin-glass or paramagnetic–ferrimagnetic–spin-glass.

4) A double paramagnetic–ferrimagnetic–spin-glass transition occurs if the magnetic ion concentrations in the sublattices are close to (higher than or equal to) the threshold values for both sublattices simultaneously.

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