Percolation limit and stability conditions for the spin glass state in the spinel families based on the two matrices $CuCr_2S_4$ and $CuCr_2Se_4$ doped by Sb ions

Percolation limit and stability conditions for the spin glass state in the spinel families based on the two matrices CuCr$_2$S$_4$ and CuCr$_2$Se$_4$ doped by Sb ions

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Abstract
The percolation limit of the appearance of the spin glass state in the compounds under study has
been obtained experimentally. The conditions of stability of the spin glass state have been
analyzed here on the basis of the de Almeida–Thouless theory for two spinels differing in the
magnetic coupling constants. It turned out that for the higher value of the coupling constant the
magnetic field influences the freezing temperature more strongly. Moreover, the greater the
coupling constant the broader the range of the possible values of freezing temperatures, in other
words the greater the temperature range of the appearance of the spin glass states. It was proved
that for the stability of the spin glass state the existence of a small magnetic field is necessary.
In our case the value of this field is equal to $3.46 \times 10^{-23} T_G$. For the compounds under study
the value of the magnetic coupling constant J cannot exceed 130 K for the spin glass state
to appear.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The last two decades have shown a renaissance of interest
in the spinel compounds. This is because of the variety
of physical properties in these materials, for instance giant
magnetoresistance (e.g. [1–6]), spin glass state (e.g. [7–17])
and thermoelectric effect (e.g. [18]). The first two effects can
be useful in the switching facilities and in spintronics. As
concerns the third one, the spinels belong to the group of
materials which can be used both in thermopower generators
and in electronic refrigerators.

Both spinel matrices, i.e. CuCr$_2$S$_4$ and CuCr$_2$Se$_4$,
mentioned in the title of the paper are strong ferromagnets with
the p-type metallic conductivity. For both these compounds the
Curie temperatures T_C as well as the Curie–Weiss temperatures
Θ_{C-W} are of the order of 500 K. On the base of these

matrices two spinel families were obtained via substitution
in the B sites of the magnetic chromium ions by the
nonmagnetic antimony ions, namely the stoichiometric family
CuCr$_{2-x}$Sb$_x$S$_4$ ($x = 0.3, 0.4, 0.5$) and the non-stoichiometric
family Cu$_{1+x}$Cr$_{1.5+y}$Sb$_{0.5+z}$Se$_{4+t}$ (where:$-0.02 \leqslant x \leqslant 0.01$,
$0.03 \leqslant y \leqslant 0.35$, $-0.2 \leqslant z \leqslant -0.02$, $0.01 \leqslant t \leqslant 0.08$).
Such a dilution of the magnetic subarray by the nonmagnetic
ions leads to the variety of effects in the spinel families
mentioned above. In the compounds of both these series the
spin glass states were observed [12, 13]. From the extended
magnetic studies it follows that

(1) for the stoichiometric compounds with the sulfur anions
the freezing temperature T_G of the spin glass state changes
from 47.4 K for $x = 0.3$ to 30 K for $x = 0.4$, whereas in
the compound with $x = 0.5$ the spin glass state disappears.
T_G is here the temperature of the spin glass state in

zero magnetic field. In experimental terms T_G is the temperature below which the ZFC and FC hysteresis of the temperature dependence of the dc magnetic susceptibility takes place (ZFC—zero field cooling, FC—field cooling). Thus the Sb ions substituted in the octahedral sites of the spinel structure change the magnetic ordering from ferromagnetism for $CuCr_2S_4$, via the spin glass state for $x = 0.3$ and 0.4, to collinear antiferromagnetism for $x = 0.5$ with the Néel temperature $T_N = 23.5$ K (see table 5 in [13]), the latter temperature being experimentally defined as the temperature at which a sharp maximum of the temperature dependence of the magnetic susceptibility appears;

(2) for the non-stoichiometric compounds with the selenium anions a slight increase of the freezing temperature was observed from $T_G = 36.1$ K for $z = -0.02$ to $T_G = 42.2$ K for $z = -0.20$, i.e. with decreasing Sb content. This means that the non-stoichiometry does not significantly influence the freezing temperature (see table 5 in [13]).

On the other hand, from the electrical measurements it follows that the giant negative magnetoresistances appear, which coexist with the spin glass states mentioned above. For instance, for the compounds with the sulfur anions the negative giant magnetoresistance reaches -74% at the external magnetic induction of 38 T at liquid helium temperature [14]. In the case of the compounds with the selenium anions even a jump-like phase transition from the colossal negative to the colossal positive magnetoresistance takes place [13]. It turned out that concentrations of the antimony ions up to about 0.5 give the percolation limit of the spin glass states in both the spinels with sulfur and selenium [12, 13].

The main aim of this work is to discuss in terms of the de Almeida–Thouless theory the percolation limit and the stability conditions for the cluster spin glass states in the compounds under study.

As is well known, there exist four spin glass models [19]:

(1) the Sherrington–Kirkpatrick model,
(2) the Bethe lattice model,
(3) the long range Edwards–Anderson model and
(4) the Edwards–Anderson model.

In all four models one can apply the mean field theory under certain conditions [19]. The SK model allows the validity of mean field theory, because the coordination number z tends to infinity with total number of lattice points N ($z = N - 1$), which means that it tends to the thermodynamic limit, which is here the case. In the last three models the free energy tends to the free energy of the SK model under the following conditions, namely, (i) for the Bethe lattice model if the coordination number z tends to infinity, (ii) for the long range Edwards–Anderson model if the range of the interaction R tends to infinity, (iii) for the Edwards–Anderson model if the lattice dimension D tends to infinity. The cluster spin glass states appearing in the compounds under study reveal in a natural way high coordination numbers because of the spread of the magnetic coupling over the whole volumes of

these clusters. It is the high values of the coordination numbers that qualify our approach to the application of the SK model and in turn to the application of the mean field theory.

2. Stability conditions for the spin glass state

The order parameter q for a spin glass state is given by the formula [15]

$$q = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} dz \exp\left(-z^2/2\right) \tanh^2\left(\frac{Jq^2z + \mu H}{k_B T}\right), \tag{1}$$

where J is a measure of a coupling constant for the interaction resulting in the spin glass state (which means that it is a resultant of all the competing magnetic interactions), H is an external magnetic field and μ is the magnetic moment of an ion. The integration variable z is related to the Gaussian probability distribution. The spin glass state is stable if the following condition holds [16, 17]:

$$\left(\frac{k_B T}{J}\right)^2 > \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} dz \exp\left(-z^2/2\right)$$
$$\times \operatorname{sech}^4\left(\frac{Jq^2z + \mu H}{k_B T}\right). \tag{2}$$

The above relations define at the plane (T, H) a curve called the de Almeida–Thouless (AT) line. This line separates the region where the spin glass state is stable from the region where an instability appears.

The equations determining the AT line were derived in [16] in the case when a coupling constant J_0 is taken for a purely ferromagnetic ordering in the matrix (which means that other kinds of magnetic interactions do not appear here). In this case and at high temperatures (when $T \to T_G$) the AT line has the approximate form [17]

$$H = \frac{k_B T_G}{\mu S}\left|1 - \frac{J_0}{J}\right|\sqrt{C(S)\left(1 - \frac{k_B T}{J}\right)^3}, \tag{3}$$

where the coefficient $C(S)$ depends on spin S and has the following values:

$$C(1/2) = 5.333, \qquad C(1) = 2.828.$$

The formula (3) is valid for the temperatures T which obey the relation $J/k_B \geqslant T$ under the condition that $J_0 < J$. Moreover, this formula usually describes the stability of the spin glass state. In our case one deals with the cluster spin glass states, which means that there here exist both ferromagnetic and antiferromagnetic clusters. The magnetic interaction inside a particular ferromagnetic cluster is connected with the coupling constant J_0, whereas the corresponding coupling constant for an antiferromagnetic cluster is equal to J_0'. On the other hand the average coupling constant of the magnetic interaction for any pair of clusters is equal to J. Therefore, the general relation between the three coupling constants looks as follows: $J_0' < J < J_0$. Thus our attempt to use the de Almeida–Thouless theory consists in the extension of this theory and its application to the case of the cluster spin glass state. The
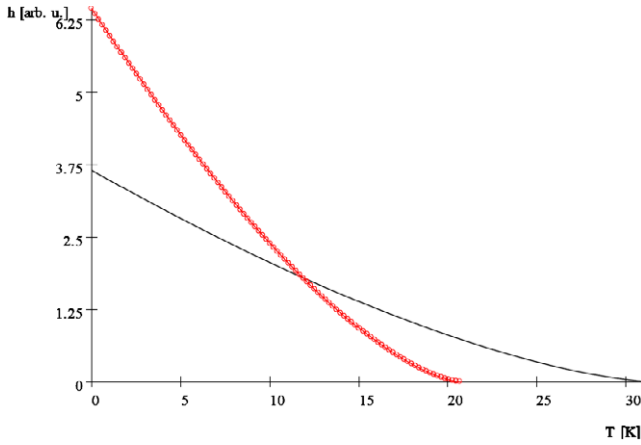
Figure 1. Stability (AT) lines of spin glass states for two spinels: CuCr$_{1.6}$Sb$_{0.4}$S$_4$ (solid line; $J/k_B = 31.55$ K) and CuCr$_{1.7}$Sb$_{0.3}$S$_4$ (dotted line; $J/k_B = 20.70$ K). h denotes the reduced magnetic field. J denotes the magnetic coupling constant.

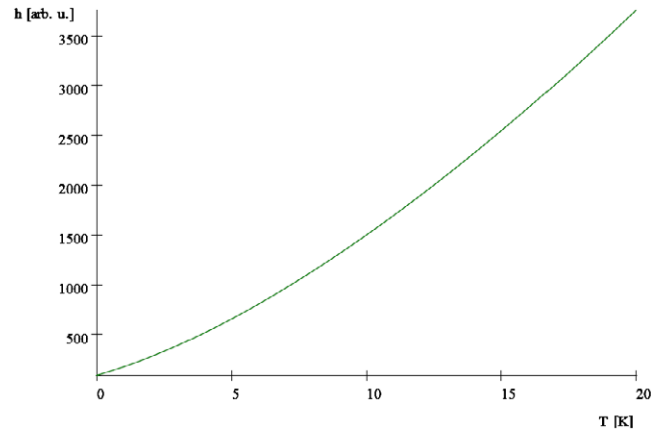**Figure 2.** Plot of equation (3) for the spinel CuCr$_{1.5}$Sb$_{0.5}$S$_4$ ($J/k_B = -1.85$ K) on the (h, T) plane. One can see that the spin glass state cannot appear in this compound.

results of such an application are here compared with our experimental results.

　　To apply the above considerations to the compounds under study one has first to take into account that for both their matrices the well known values of J_0/k_B are of the order of 100 K and the values of S are of the order of unity. The corresponding values J/k_B for the spinels under study are different. Thus for CuCr$_{1.6}$Sb$_{0.4}$S$_4$ $J/k_B = 31.55$ K (see table 5 in [13]) and the corresponding AT line is expressed by the following equation:

$$h = \left| 1 - \frac{100}{31.55} \right| \sqrt{2.828 \left(1 - \frac{T}{31.55} \right)^3},$$

where $h = H\mu/(k_B T_G)$. Figure 1 presents the AT lines for the spinel CuCr$_{1.6}$Sb$_{0.4}$S$_4$ with $J/k_B = 31.55$ K (solid line) and for the spinel CuCr$_{1.7}$Sb$_{0.3}$S$_4$ with $J/k_B = 20.70$ K (see table 5 in [13]) (dotted line).

　　On the other hand for the spinel CuCr$_{1.5}$Sb$_{0.5}$S$_4$ the magnetic coupling constant J/k_B is equal to -1.85 K (see table 5 in [13]). This negative value of the coupling constant corresponds to the experimental evidence of the collinear antiferromagnetism observed in this compound [20]. Thus in this case the AT line is described by the following equation:

$$h = \left| 1 + \frac{100}{1.85} \right| \sqrt{2.828 \left(1 + \frac{T}{1.85} \right)^3}.$$

Figure 2 presents the AT line for the spinel CuCr$_{1.5}$Sb$_{0.5}$S$_4$. Comparing the behavior of the curves in figures 1 and 2 one can easily see that in figure 1 one deals with the temperature ranges of the stable spin glass states, whereas in figure 2 the AT line turns out to be divergent, which indicates the absence of a spin glass state. This analysis is in very good agreement with the experiment [12–14, 20].

　　Taking into account that here J can be considered as a variable which depends on the Sb concentration, let us consider the temperature T as a function of J and H (or h). In this case the temperature T can be interpreted as the freezing

temperature of a spin glass state. This function has been obtained from equation (3) and has the form

$$T = J - \frac{J}{\sqrt[3]{C(S)}} \left(\frac{Jh}{J - J_0} \right)^{2/3}. \tag{4}$$

J and h have physical meaning only when $T > 0$. If $J > 0$, then

$$\sqrt[3]{C(S)} > \left(\frac{Jh}{J - J_0} \right)^{2/3}. \tag{5}$$

In another form,

$$\left(C - h^2 \right) \left[J - \frac{\sqrt{C} J_0}{\sqrt{C} - h} \right] \left[J - \frac{\sqrt{C} J_0}{\sqrt{C} + h} \right] > 0. \tag{6}$$

If $C - h^2 > 0$ and J values in equation (6) are taken for fixed h, then

$$J > \frac{J_0}{\sqrt{C} - h} > 0. \tag{7}$$

If $C - h^2 < 0$, then

$$\frac{J_0}{\sqrt{C} + h} > J > 0. \tag{8}$$

　　For $C(1) = 2.828$ and $J_0/k_B = 100$ K and for fixed values of h one obtains the corresponding plots $T = T(J)$ (see figure 3).

　　As follows from the plots presented in figure 3, the higher the value of the external magnetic field (h) the narrower both the T and J ranges in which the spin glass state can exist. The physical sense of this result indicates that the external magnetic field leading to a magnetic ordering in the sample liquidates the randomness of the orientation of the magnetic moments. In this way the spin glass state disappears in the sample. This result is in good agreement with the experimental data (see above) for the compounds under consideration.

　　In order to determine the maxima of T on all the curves $T = T(J)$ the following analysis has been made. The
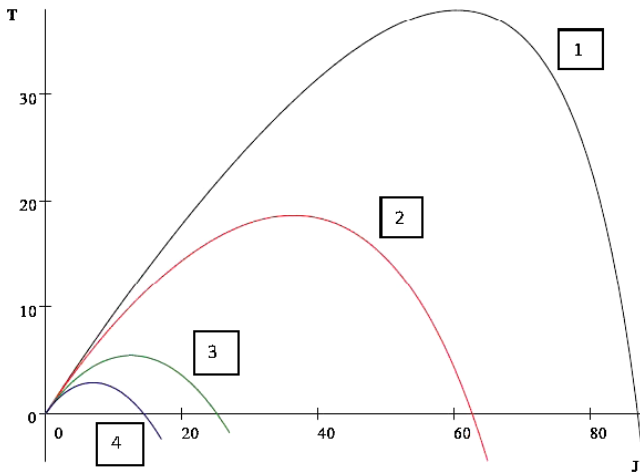
Figure 3. Four $T = T(J)$ dependences for fixed values of h. Curve 1 corresponds to $h = 0.25$, curve 2 corresponds to $h = 1$, curve 3 corresponds to $h = 5$ and curve 4 corresponds to $h = 10$. Note that on every curve presented there appears a maximum.
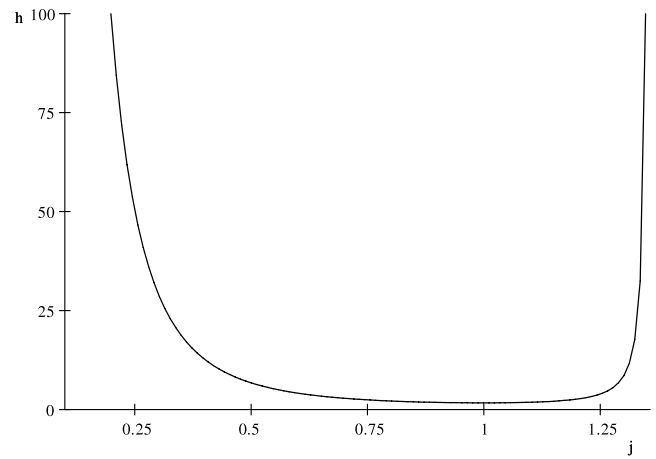
extremum of the expression in equation (4) is given by the solution of the equation

$$\frac{\mathrm{d}T}{\mathrm{d}J} = 0,$$

which assumes the form

$$2j^5 - 5j^2 + 3\left(\frac{C}{h^2}\right)^{1/3} = 0, \qquad (9)$$

where $j = \left(\frac{J}{J-J_0}\right)^{1/3}$. One can obtain from equation (9) the parameter h as a function of J (or of j) for the maxima mentioned above:

$$h = \frac{3\sqrt{3C}}{\sqrt{\left(5j^2 - 2j^5\right)^3}}. \qquad (10)$$

The normalized field h is real when

$$5j^2 - 2j^5 > 0. \qquad (11)$$

This means that: $-\infty < j < 0$ or $0 < j < (5/2)^{1/3} = 1.36$. The plot of h as a function of j has the form presented in figure 4. One can see in this figure that this plot reveals an extended minimum. The minimum value of h—calculated from the corresponding derivative—is equal to 1.68. For this value the minimum of the real field H assumes the value of $3.46 \times 10^{-23} T_G$ T. Thus this is the minimum value of the external magnetic field H for the spin glass state to be stable.

From equations (4) and (9) one obtains the maximum freezing temperature $T_{\max}$ as a function of J in the form

$$T_{\max}(J) = J - J\left|\frac{1 - \frac{J_0}{J}}{1 - \frac{5}{3}\frac{J_0}{J}}\right|. \qquad (12)$$

As follows from figure 5, the temperature range of the existence of the spin glass state in the case of the compounds under study depends on J, which is in turn dependent on
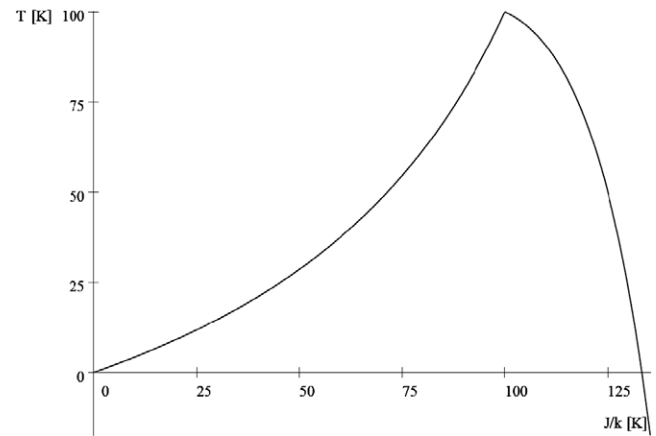

Figure 4. Plot $h = h(j)$ based on equation (10). j denotes the reduced magnetic coupling constant.

Figure 5. The phase diagram of stability of the spin glass state on the (T, J) plane.

Sb concentration. This temperature range extends from 0 to 100 K. On the other hand, one can see in figure 5 that for values of J/k greater than 130 K the spin glass state can not exist. Such a situation is in good agreement with the results obtained from the measurements of both dc and ac magnetic susceptibility [12, 13].

3. Conclusions

From the experimental results cited in section 1 it follows that for all the compounds under study the percolation limit of the spin glass state in terms of Sb concentration is about 0.5. The maximum freezing temperature (see equation (12) and figure 5) turned out to be not greater than about 100 K. This temperature can be interpreted as the stability limit of the spin glass state in the compounds under study. The values of J/k can serve as another criterion for the existence of the spin glass state. For instance, for the existence of the spin glass states in the compounds under study the values of J/k should not be greater than 130 K. As follows from figure 4, a minimum value of the external magnetic field is necessary to stabilize the structure of the spin glass state. This stabilization consists in the partial but

sufficient compensation of the thermal vibrations. The results obtained of the calculations based here on the extended de Almeida–Thouless theory turned out to be in good agreement with our experimental ones mentioned above. The approach described here can be applied to all the cluster spin glass states which occur in the compounds possessing in their crystal structure both the tetra- and octahedral positions and for which one can determine from experiment the values of T_G, J and J_0.

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