Spin glass state in the spinel families and stability conditions

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Abstract. The conditions of stability of the spin glass state and its percolation limit in the spinel families have been analyzed on the base of the de Almeida-Thouless theory. The temperature range was determined as a function of the antimony concentration for which the spin glass state is stable.

1. Introduction

A spin glass is a frustrated and random system. Such system contains dilute magnetic spins scattered in the bulk of the sample, so that the individual spin-spin couplings \( J_{ij} \) vary in a quasirandom way. Frustration leads to a Hamiltonian of the system that has no global minimum and the partition function is not dominated by the lowest energy spin configuration. Instead there is a large number of local minima which are metastable and form an energy landscape. In the Sherrington-Kirkpatrick model where the mean-field theory approximation is valid the spin glass has a line of transitions in an external magnetic field, the de Almeida-Thouless (AT) line. This line separates a high-temperature high-field paramagnetic phase from a low temperature low-field phase where the energy landscape has valleys separated by barriers in the thermodynamic limit. In the two spinel families: \( \text{CuCr}_{2-x}\text{Sb}_x\text{S}_4 \) \((x=0.3, 0.4, 0.5)\) and \( \text{Cu}_{1+x}\text{Cr}_{1.5+y}\text{Sb}_{0.5+z}\text{Se}_{4+t} \) \((0.02 \leq x \leq 0.01, 0.03 \leq y \leq 0.35, -0.2 \leq z \leq -0.02, 0.01 \leq t \leq 0.08)\) the spin glass states appear and it turned out that the concentrations of the antimony ions up to about 0.5 make the percolation limit of these spin glass states. Here we analyze the AT lines in these spinels and determine the temperature range as a function of the antimony concentration for which the spin glass state is stable (see also [1]).

The spin glass can be modelled by a statistical mechanical system whose degrees of freedom are \( N \) two-valued spins \( s_i = \pm 1 \) and the Hamiltonian \( H \):

\[
H = \sum_{i,j} J_{ij} s_i s_j. \tag{1.1}
\]

The partition function \( Z \) for the statistical system with the fixed set of couplings \( \{J_{ij}\} \) is the sum over spins \( s_i \):

\[
Z[\beta, J_{ij}] = \sum_{s_i} \exp \left[ - \beta H \right]. \tag{1.2}
\]
Thus the $Z$ is the function of $\beta=1/(kT)$ and the coupling constants $J_{ij}$. In the case of the spin glass the coupling constants are not fixed but are distributed randomly specified by giving a probability distribution $[DJ]$. In such system an expectation value of a variable $X$ depending on $s_i$ and $J_{ij}$ is defined as:

$$
\langle \langle X \rangle \rangle = \frac{\int DJ_{ij}}{Z(\beta, J_{ij})} \sum_{i,j} X(s_i, J_{ij}) \exp\left[-\beta H_{ij}\right],
$$

(1.3)

and is the function of $\beta$. As is well-known there exist four kind models of the spin glasses [e.g. 2]:

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

In the Sherrington-Kirkpatrick (SK) model all $J_{ij}$ are different from zero and the Gaussian probability distribution has variance $N^{-1/2}$. The coordination number $z$ is $N-1$. In the infinity limit of $N$ the mean field theory is valid. In the Bethe lattice (BL) model the spins live on a random lattice and only $Nz/2$ coupling constants $J_{ij}$ are different from zero with the variance $z^{-1/2}$. In the large range Edwards-Anderson (LREA) model the spins live on a finite dimensional lattice of dimension $D$. Only nearest spins at a distance less than $R$ interact and the variance of the $J$’s is proportional to $D^{-R/2}$. The Edwards-Anderson (EA) model is obtained when $R=1$. These models in appropriate limits lead to the SK model:

$$
\lim_{z \to \infty} BL = \lim_{R \to \infty} LREA = \lim_{D \to \infty} EA = SK.
$$

(1.4)

Compared to a real spin glass, the main simplification of the SK model is that there is neglected the spatial distribution of spins, in effect taking the limit of spins in infinite spatial dimensions. In the SK model the partition function $Z$ has two temperature regimes. At high temperature, the interactions are unimportant, and the spins are disordered. Conversely, at low temperature, there is ordering, but not detectable by a simple order parameter such as the average expectation value of the spins. This order is detected by the Edwards-Anderson order parameter $q_{EA}$:

$$
q_{EA} = \frac{1}{N} \sum_i \langle s_i \rangle^2,
$$

(1.5)

where $\langle s_i \rangle \equiv m_i$ means the local magnetization.

2. The AT line in the SK model

The order parameter $q$ for a spin-glass state in the SK model is given by the formula [3]:

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

(2.1)

where $J$ is a measure of a coupling constant for the interaction resulting in the spin-glass state, $H$ is an external magnetic field and $\mu$ 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 [4, 5]:

$$
\left(\frac{k_B T}{J}\right)^2 > \frac{1}{\sqrt{2\pi}} \int dz \exp(-z^2/2) \sec h\left(\frac{Jq^2z + \mu H}{k_B T}\right).
$$

(2.2)

One can rewrite the above formula introducing a new function $F$:
\[ F(J, H, T) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dz \exp(-z^2/2) \sec h \left( \frac{Jq^2z + \mu H}{k_B T} \right). \]  \tag{2.3}

Hence the condition (2.2) on stability of the spin glass state is: \((k_B T)^2 - J^2 F(J, H, T) > 0\).

In the case when the above bound is saturated: \((k_B T)^2 - J^2 F(J, H, T) = 0\) one can solve this equation (for fixed \(J\)) with respect to \(H\) so:

\[ H = A(J, T). \]  \tag{2.4}

The above relation is called the de Almeida-Thouless (AT) equation and 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 instabilities appear. Under assumption when coupling constant for a ferromagnetically ordered matrix is equal to \(J_0\) and at high temperatures \((T \to T_G)\) the AT equation can be solved and has the approximate form [5]:

\[ H = \frac{k_B T_G}{\mu S} \left[ 1 - \frac{J_0}{J} \left( 1 - \left( \frac{k_B T}{J} \right)^3 \right) \right], \]  \tag{2.5}

where the coefficient \(C(S)\) depends on spin \(S\) and has the following values: \(C(1/2)=5.333\), \(C(1)=2.828\) and \(T_G\) is the spin glass freezing temperature in zero field. The formula (3) is valid for the temperatures \(T\) which obey the relation \(J/k_B T \geq T\). In the considered compounds values of \(J_0/k_B\) are of the order of 100 K and the values of \(S\) are of the order of 1. The corresponding values \(J/k_B\) for these spinels are different. Thus for \(CuCr_{1.6}Sb_{0.4}S_4\) the ratio \(J/k_B = 31.55\) K (see Table 5 in [6]) and the corresponding AT line is expressed by the following equation:

\[ h = \left[ 1 - \frac{100}{31.55} \sqrt{2.828 \left( 1 - \left( \frac{T}{31.55} \right)^3 \right)} \right], \]  \tag{2.6}

where \(h = H_0/(k_B T_G)\).

The Fig. 1 on the left 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 \(CuCr_{1.5}Sb_{0.5}S_4\) with \(J/k_B = 20.70\) K (Table 5 in [6]) (dots 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 [6]). This negative value of the coupling constant corresponds to the experimental evidence of the collinear antiferromagnetism observed in this compound [7]. Thus in this case the AT line is described by the following equation:

\[ h = \left[ 1 + \frac{100}{1.85} \sqrt{2.828 \left( 1 + \left( \frac{T}{1.85} \right)^3 \right)} \right]. \]  \tag{2.7}
The below Fig. 2 presents the AT line for the spinel $CuCr_{1.5}Sb_{0.5}S_4$. Comparing the behaviour of the curves on Fig. 1 and Fig. 2 one can easily see that in Fig. 1 one deals with the temperature ranges of the stable spin glass states, whereas in Fig. 2 the AT line turns out to be divergent which indicates the absence of a spin glass state. This analysis is in a very good agreement with the experiment [6-9].

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 Eq. (2.5) and has the form:

$$T(J, h) = J - \frac{J}{\sqrt{C(S)}} \left( \frac{Jh}{J - J_0} \right)^{2/3},$$  \hspace{1cm} (2.8)

$J$ and $h$ have physical meaning only when $T>0$. If $J>0$, then the condition of the positive temperature $T>0$ is given by:

$$\left( C - h^2 \right) \left( J - \frac{\sqrt{C}J_0}{\sqrt{C - h}} \right) > 0.$$  \hspace{1cm} (2.9)

From the above inequality one gets two restrictions on $J$ for fixed $h$. The first one is for $C_h^2>0$

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

And the second one is for $C-h^2<0$: $\frac{\sqrt{C}J_0}{\sqrt{C + h}} > J > 0$. For $C(1)=2.828$ and $J_0/k_B=100$ K and for the fixed values of $h$ one obtains the corresponding plots temperature $T$ as the function of $J$.

On the left Fig. 3 presents four $T=T(J,h)$ dependencies for the 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.
As one can see from the Fig. 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 is 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 a 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 \( T = T(J) \) one has to solve the equation: \( dT/dJ = 0 \) which assumes the form:

\[
2 J^5 - 5 J^3 + 3 \left( \frac{C}{h^2} \right)^{1/3} = 0, \tag{2.10}
\]

where \( j = (J/J_0) \). One can obtain from Eq. (2.10) the parameter h as a function of J (or of j) for the maxima mentioned above:

\[
h = \frac{3 \sqrt{3C}}{\sqrt{(5 j^2 - 2 j^3)^{3/2}}}. \tag{2.11}
\]

The normalized field \( h \) is real when: \( 5j^2 - 2j^3 > 0 \). It means that: \( -\infty < j < 0 \) or \( 0 < j < (5/2)^{1/3} = 1.36 \). The plot \( h \) as a function of \( j \) is presented in Fig. 4 below.

One can see that in this figure is an extended minimum. The minimum value of \( h \) - calculated from (2.11) - 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 (tesla), if T is measured in Kelvin (K). Thus this is the minimum value of the external magnetic field \( H \) for the spin glass state to be stable. From Eqs. (2.8) and (2.10) one obtains the maximum freezing temperature \( T_{\text{max}} \) as a function of J in the form:

\[
T_{\text{max}}(J) = J - J_0 \left| \frac{J - J_0}{J_0} \right| \left( \frac{5}{3} \right)^{1/3}. \tag{2.12}
\]

Below on the Fig. 5 the temperature range of the existence of the spin glass state is presented. This temperature depends on J which is in turn dependent on Sb concentration. This range extends from 0 K to 100 K. On the other hand one can see in Fig. 5 that for the values of \( J/k_B \) greater than 130 K the spin glass state cannot exist. Such a situation is in a good agreement with the results obtained from the measurements of both the dc and ac magnetic susceptibility [6, 8].
3. Conclusions
In the considered compounds the percolation limit of the spin glass state in terms of Sb concentration is about 0.5. The maximum freezing temperature (Eq. (2.12) and Fig. 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 $J/k_B$ can serve as another criterion of the existence of the spin glass state. For instance, for the existence of the spin glass states in these compounds the values of $J/k_B$ should not be greater than 130 K. We also showed that a minimum value of the external magnetic field is necessary to stabilize the structure of the spin glass state. It seems that this stabilization consists in the partial but sufficient compensation of the thermal vibrations. The value of this field depends on the spin glass temperature $T_G$ as follows:

$$H_{\text{min}} = 3.46 \times 10^{-23}T_G \text{ [tesla]}.$$  

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