

# New semiconducting spin glass $\text{Fe}_{0.67}\text{Cr}_{1.33}\text{Sn}_{0.67}\text{S}_4$ with magnetically active ions in both the *A* and *B* sublattices

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(Submitted 23 December 1994)

Pis'ma Zh. Éksp. Teor. Fiz. **61**, No. 3, 209–213 (10 February 1995)

The new semiconducting compound  $\text{Fe}_{0.67}\text{Cr}_{1.33}\text{Sb}_{0.67}\text{S}_4$ , with the spinel structure, has magnetic properties characteristic of spin glasses. Specifically, there is a maximum in the initial susceptibility at the temperature  $T = T_f$ . This maximum is suppressed by a static magnetic field  $H$ , and the low-temperature magnetization depends on the thermomagnetic history of the sample. The functional dependence  $T_f(H, T)$  obeys the Almeida–Thouless relation. The dependence of  $T_f$  on the frequency of the alternating magnetic field is a power law, indicating the existence of a spin-glass–paramagnet phase transition. This is the first spin glass among the chalcospinels to have magnetically active ions in both the *A* and *B* sublattices. © 1995 American Institute of Physics.

A spin-glass state has so far been observed in chalcospinels with magnetically active ions in only one sublattice: either the octahedral sublattice (*B*) or the tetrahedral one (*A*). Spin-glass states have thus been described in  $\text{Ga}_{2/3}\text{Cr}_2\text{S}_4$  (Ref. 1),  $\text{Cu}_{0.5}\text{Me}_{0.5}\text{Cr}_2\text{Se}_4$  ( $\text{Me} = \text{In}, \text{Ga}$ ) (Ref. 2),  $\text{Cu}_{2/3}\text{Ge}_{1/3}\text{Cr}_2\text{S}_4$  (Ref. 3),  $\text{CdCr}_x\text{In}_{2-2x}\text{S}_4$  (Ref. 4),  $\text{ZnCr}_{2x}\text{Al}_{2-2x}\text{S}_4$  (Ref. 5), and  $\text{Zn}_{1-x}\text{Mn}_x\text{In}_2\text{S}_4$  (Ref. 6). There was interest in determining whether a spin-glass state can exist in chalcospinels in which magnetically active ions are in the *A* and *B* sublattices simultaneously. Since the intersublattice indirect antiferromagnetic exchange in spinels is much stronger than the exchange within sublattices, it is far from obvious that a spin-glass state could exist in such chalcospinels. According to the data of Ref. 7, for example, the values of the exchange integrals in the spinel  $\text{FeCr}_2\text{S}_4$  are  $J_{\text{Cr-Cr}} = \pm 1$  K and  $J_{\text{Cr-Fe}} = -10$  K.

In this letter we are reporting a study of magnetic and critical properties of spinels with the composition  $\text{Fe}_{0.67}^{2+}[\text{Cr}_{1.33}^{3+}\text{Sn}_{0.67}^{4+}]\text{S}_4^{2-}$ , which have been synthesized for the first time. As the chemical formula shows, the *B* sublattice in this compound is diluted with diamagnetic  $\text{Sn}^{4+}$  ions, while there is a deficiency of  $\text{Fe}^{2+}$  ions in the *A* sublattice. This compound turns out to be a *p*-type semiconductor. At  $T = 4.2$  K, its resistivity is  $\rho = 4.5 \times 10^7 \Omega \cdot \text{cm}$ , while that at  $T = 293$  K is  $\rho = 1.1 \times 10^2 \Omega \cdot \text{cm}$ .

The curves of the magnetization  $\sigma$  versus the field  $H$  do not exhibit saturation in the fields in which the measurements have been carried out: up to 35 kOe at  $T = 4.2$  K and up to 10 kOe at  $T \geq 77$  K. At the same time, this compound has magnetic properties which are characteristic of spin glasses. For example, the temperature dependence of the initial susceptibility  $\chi$  measured in an alternating magnetic field (measurements were carried out over the frequency interval  $0.3 \leq \omega \leq 2$  kHz) has a maximum at  $T = T_f$ . This maxi-

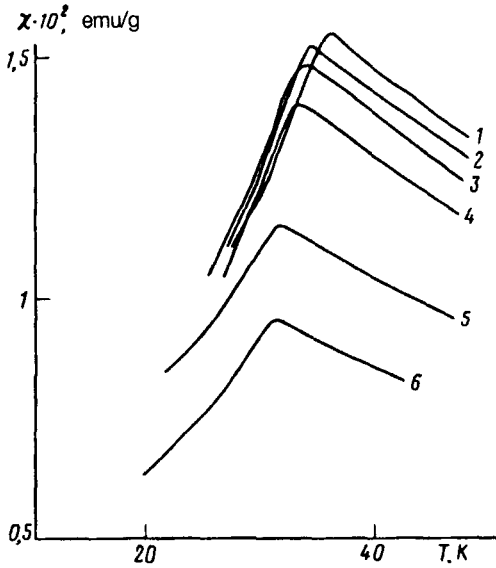


FIG. 1. Temperature dependence of the initial magnetic susceptibility  $\chi$  in an alternating magnetic field with a frequency of 500 Hz ( $H_{\sim} = 0.3$  Oe); effect of a static magnetic field  $H$  on this dependence.

num is suppressed fairly quickly by a weak static magnetic field applied parallel to the alternating field (Fig. 1). The magnetization in a static field  $H = 46$  Oe at  $T \leq T_f$  depends on the cooling conditions. For example, the  $\sigma(T)$  curve of a sample recorded after the sample has been cooled in the indicated field from  $T > T_f$  to  $T = 4.2$  K runs well below the  $\sigma(T)$  curve of a sample cooled to 4.2 K in the absence of a field (the latter curve was obtained during heating of the sample; the field was applied only during the measurements).

One of the basic problems of the spin-glass state, of course, is the question of the existence of a spin-glass-paramagnet phase transition in the real materials which are classified as spin glasses. In the mean-field theory of spin glasses it has been shown that there is a line on the  $(H, T)$  plane below which the Edwards-Anderson order parameter is unstable.<sup>8</sup> This is the so-called Almeida-Thouless line in the Ising model:

$$1 - \{T_f(H)/T_f(0)\} \sim H^{2/3}. \quad (1)$$

It turns out that in real spin glasses the  $T_f(H)$  dependence is described by relation (1). These experiments have been regarded as evidence that the mean-field theory is valid for these spin glasses, and that there is a phase transition at  $T_f$ , consistent with the theory.<sup>8</sup> In the present study we investigated the effect of a static magnetic field on the temperature dependence of  $\chi$  (Fig. 1). We see from Fig. 1 that  $\chi_{\max}$  decreases with increasing magnetic field, and that the maximum itself shifts down the temperature scale. The freezing point  $T_f$ , defined as the temperature of the maximum of the  $\chi(T)$  curve, is thus shifted by a magnetic field to a lower temperature. Figure 2 shows, in full logarithmic scale, a plot of  $\{1 - [T(H)/T(0)]\}$  versus the field  $H$  for the composition which we are discussing in the present paper. We see that the points conform satisfactorily to a straight line with a slope of 0.61. This figure is very close to the power of 2/3 in the Almeida-

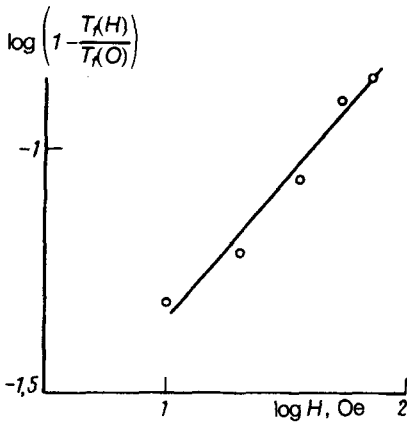


FIG. 2. Plot of  $\{1 - [T_f(H)/T_f(0)]\}$  versus  $H$  in full logarithmic scale.

Thouless relation. The satisfaction of the Almeida–Thouless relation for this spin glass can be taken as proof that a spin-glass–paramagnet phase transition occurs in it.

As it turns out, the freezing point of the spin glass  $\text{Fe}_{0.67}\text{Cr}_{1.33}\text{Sn}_{0.67}\text{S}_4$ , found from the maximum of the initial susceptibility in an alternating magnetic field, depends on the frequency of this field,  $\omega$ . We know<sup>8</sup> that in all real spin glasses except<sup>9</sup>  $\text{AgMn}$  the temperature  $T_f$  depends on the frequency. However, it turns out that in spin-glass materials the relaxation time  $\tau$  near the freezing point increases more rapidly than by an Arrhenius law, which is characteristic of superparamagnets. In several cases the behavior conforms to the empirical Vogel–Fulcher law:<sup>10</sup>

$$\tau = 1/\omega = \tau_0 \exp\{E/k(T_f - T_0)\}, \quad (2)$$

where  $\tau_0 \approx 10^{-12}$  is the minimum relaxation time, and  $E$  is a quantity with the dimensionality of an energy. Since the relaxation time  $\tau$  diverges at  $T = T_0$ , it has been suggested in several papers that  $T_0$  is the point of a spin-glass–paramagnet phase transition. At the same time, we know that if a phase transition occurs at a certain temperature  $T^*$ , then the relaxation time for magnetization fluctuations undergoes a critical slowing at  $T^*$ , and  $\tau$  obeys a power law<sup>11</sup>

$$\tau = \tau_0 [T/(T - T^*)]^{z\nu}. \quad (3)$$

Here  $z$  is a dynamic exponent, and  $\nu$  is the critical exponent of the Edwards–Anderson correlation length. A Monte Carlo numerical simulation undertaken by Ogielski<sup>12</sup> for an Ising spin glass with  $T^* \neq 0$  (the  $\pm J$  model, the 3D case) yielded the value  $z\nu = 7.2 \pm 1$ .

Binder and Young<sup>13</sup> suggested an alternative hypothesis, in which the temperature of the spin-glass–paramagnet phase transition is assumed to be zero. For  $\tau$  they found the following relation, which has come to be known as a “generalized Arrhenius law”:

$$\ln(\tau/\tau_0) = T^{-z\nu}. \quad (4)$$

A Monte Carlo numerical simulation carried out by Binder and Young for an Ising system (the  $\pm J$  model) yielded  $z\nu = 2$  for the 2D case and  $z\nu = 4$  for the 3D case.

TABLE I. Fits of various laws to the  $T_f(\omega)$  dependence.

Power law			Vogel–Fulcher law			Generalized Arrhenius law	
$\tau_0$ , s	$z\nu$	$T^*$ , K	$\tau_0$ , s	$E$ , meV	$T_0$ , K	$\tau_0$ , s	$z\nu$
$1.85 \times 10^{-10}$	7.6	32	$3.0 \times 10^{-12}$	23.3	23	$10^{-12}$	2.52
$2.0 \times 10^{-11}$	9.64	31	$1.5 \times 10^{-11}$	20.0	24	$10^{-9}$	3.76
$7.2 \times 10^{-12}$	10.68	30.5					

The  $T_f(\omega)$  dependence for several real spin glasses has been compared with the three laws listed above. Depending on the particular law which describes the dependence, a conclusion has been drawn about whether a spin-glass–paramagnet phase transition does or does not occur at  $T_f \neq 0$  for the given spin glass. In the present study we fitted the three laws written above to the  $T_f(\omega)$  dependence for the composition  $\text{Fe}_{0.67}\text{Cr}_{1.33}\text{Sn}_{0.67}\text{S}_4$ . For this purpose, we plotted experimental relations (2)–(4) in logarithmic scale, taking  $\tau$  to be the value of  $1/\omega$  and taking  $T$  to be  $T_f$  in the Vogel–Fulcher and power laws. The adjustable parameters were  $T_0$  in (2),  $T^*$  in (3), and  $\tau_0$  in (4). From the resulting plots we selected those on which the points conformed satisfactorily to straight lines. We used these lines to determine the values of  $\tau_0$  and  $E$  in the Vogel–Fulcher law,  $\tau_0$  and  $z\nu$  in the power law, and  $z\nu$  in the generalized Arrhenius law. Table I shows the values of  $\tau_0$ ,  $z\nu$ , and  $E$  found from the straight lines which are the best fits for each law.

When we fit an Arrhenius law

$$\tau = \tau_0 \exp(E_a/kT) \quad (5)$$

to the  $T_f(\omega)$  dependence, we find an unrealistically small value  $\tau_0 = 5.3 \times 10^{-27}$  s. (For an Arrhenius law we would have  $\tau_0 \approx 10^{-9}$  s.) It can be seen from Table I that the plots of  $T_f(\omega)$  correspond best to a power law with  $T^* = 31$  K. This value of  $T^*$  corresponds satisfactorily to the temperature of the maximum on the  $\sigma(T)$  curve of a sample cooled in the absence of a field (34.8 K). The Vogel–Fulcher law leads to an unrealistically small value of  $T_0$ , while the generalized Arrhenius law for the 3D case leads to a value of  $\tau_0$  which is far too low. The satisfaction of a power law for  $T_f(\omega)$  indicates that a spin-glass–ferromagnet phase transition occurs in this spin glass.

In summary, the experimental facts reported here indicate that a spin-glass state is observed in the compound  $\text{Fe}_{0.67}\text{Cr}_{1.33}\text{Sn}_{0.67}\text{S}_4$  at  $T \leq 31$  K. The basic cause of this state is a dilution of the *A* and *B* sublattices. The percolation threshold for the octahedral sublattice in a spinel structure is known to be<sup>14</sup>  $p_{co} = 0.401$ , while that for the tetrahedral sublattice is<sup>15</sup>  $p_{ct} = 0.428$ . It can be seen from the chemical formula for this compound that the ratio of the number of magnetically active ions to the total number of ions in the octahedral sublattice is  $p_o = 0.665$ , and that in the tetrahedral sublattice is  $p_t = 0.67$ . These values are only slightly higher than the threshold concentrations for the *A* and *B* sublattices given above. Upon dilution of the *A* and *B* sublattices, the  $\text{Fe}^{2+}$  and  $\text{Cr}^{3+}$  ions occupy the corresponding sublattices in a random fashion. Although strong antiferromag-

netic  $A-B$  interactions do occur between them, the bonds do not have a periodic structure. Consequently, a state with a long-range antiferromagnetic order cannot occur, and a spin-glass state arises.

This study was supported by the Russian Fund for Fundamental Research (Topic 94-02-03564).

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Translated by D. Parsons