781 (1954).
[5]W. K. Unger, E. Wolfgang, H. Harms, and H. Haudek, J. Appl. Phys. **43**, 2875 (1972).
[6]Yu. S. Bersenev, N. P. Grazhdankina, and M. I. Oleinik, Prib. Tekh. Eksp. No. 5, 158 (1969).
[7]R. R. Heikes, Phys. Rev. **99**, 446 (1955).
[8]T. Chen and W. E. Stutius, IEEE Trans. Mag. **10**, 581 (1974).
[9]J. M. Noothoven van Goor and H. Zijlstra, J. Appl. Phys. **39**, 5471 (1968).
[10]C. D. Grahan and M. R. Notis, Proc. Internat. Conf. on Magnetism, MKM-73, Vol. 2, p. 186, Nauka, 1974.
[11]E. Kneller, Magnetism and Metallurgy, ed. by E. Bercowitz, Academic, 1969, p. 385.
[12]B. A. Vvedenskiĭ and G. S. Landsberg, Sovremennoe uchenie o magnetizme (Modern Studies of Magnetism), Gosizdat, 1929, p. 31.
[13]J. Becker, Trans. AIME **209**, 59 (1957).
[14]T. O. Paine in: Magnitnye svoĭstva metallov i splavov (Magnetic Properties of Metals and Alloys), S. V. Vonsovskiĭ, ed., IIL, 1961, p. 198.
[15]N. P. Grazhdankina and M. A. Novikov, Pis'ma Zh. Eksp. Teor. Fiz. **30**, 333 (1979) [JETP Lett. **30**, 308 (1979)].
[16]G. A. Samara and A. A. Giardini, in: Phys. of Solids at High Pressure, ed. by C. T. Tomizuka and R. M. Emrick, Academic, 1965, p. 308.
[17]Yu. P. Irkhin, Fiz. Met. Metallov. **6**, 214 (1958).

Translated by J. G. Adashko

# Destruction of the spin glass state by indirect exchange via conduction electrons in the $x CuCr_2S_4$–$(1-x)Ga_{2/3}Cr_2S_4$ solid-solution system

L. I. Koroleva, É. L. Nagaev, and N. A. Tsvetkova

*M. V. Lomonosov State University, Moscow*
(Submitted 7 February 1980)
Zh. Eksp. Teor. Fiz. **79**, 600–604 (August 1980)

An experimental investigation was made on the magnetic and electrical properties of solid solutions in the $x CuCr_2S_4$–$(1-x)Ga_{2/3}Cr_2S_4$ system. At low values of $x$ these solutions are insulators and exhibit properties typical of spin glasses (susceptibility peak, low-temperature magnetization hysteresis). However, when composition is varied an insulator–metal transition occurs near $x = 0.5$ and a spontaneous moment appears at the same time. A rapid rise of the magnetic ordering temperature accompanying this phase transition can be explained by the appearance of an indirect exchange via charge carriers, which suppresses the spin-glass state. Thus, in contrast to the earlier view that an indirect exchange is the main reason for the existence of a spin-glass state, the results obtained in the present study suggest a directly opposite role of this exchange in the case of insulating spin glasses. A theoretical analysis is used to show that an indirect exchange via charge carriers may destroy a spin-glass state also in spin glasses which are magnetic semiconductors. For certain values of the carrier density these materials may exhibit a heterophase state in which a crystal splits into a series of alternate spin-glass and ferromagnetic regions, with the carriers concentrated in the latter. Destruction of such a heterophase state by a magnetic field or by an increase in temperature may result in an insulator–metal phase transiton.

PACS numbers: 75.30.Et, 75.30.Kz, 75.25. + z

The existence of spin glasses was first discovered in metallic alloys and for this reason a view has been held that a spin-glass state is a consequence of an indirect exchange (via conduction electrons), whose integral in the RKKY theory is due to an oscillatory function of the separation between localized moments. Discovery of insulating spin glasses in the $Eu_xSr_{1-x}S$ solid-solution system[1] demonstrated that in any case the RKKY indirect exchange is not necessary for their existence. Moreover, a question arises whether an indirect exchange establishes a spin-glass ordering in a disordered conducting crystal. The reasons for these doubts are as follows. Firstly, since the Fermi surface of electrons in alloys is smeared by the scattering of electrons on the random potential, the indirect exchange integral in the RKKY theory decreases exponentially with distance[2] so that in many cases it is practically constant in sign. Secondly, oscillations of the indirect exchange integral are suppressed also in the case of narrow energy bands of width comparable with or less than the $s$–$d$ exchange integral,[3] which is typical of transition-element alloys.

We made an experimental observation which seemed paradoxical from the point of view of the existing ideas on the nature of spin glasses: an indirect exchange via charge carriers not only did not facilitate spin-glass ordering but destroyed a spin-glass state.

We investigated magnetic and electrical properties of polycrystalline samples of $xCuCr_2S_4-(1-x)Ga_{2/3}Cr_2S_4$ solid solutions prepared by a method described in Ref. 4. The terminal compositions of this system had very different properties: at $x = 1$ the material was a metallic ferromagnet,[5] whereas at $x = 0$ it was an insulating spin glass.[6] The solutions in the range from $x = 0$ to $x = 0.45$ were spin glasses. This was indicated by the following observations. 1) The magnetic susceptibility $\chi$ of these compositions measured in a weak static field

 0038-5646/80/080303-03$02.40  

as a function of temperature $T$ exhibited a peak at $T = T_f$ whose amplitude increased and width decreased on increase in the magnetic field $H$. The dependence of $\chi$ on $H$ was qualitatively similar to that shown in Fig. 2 of Ref. 6 for $x = 0$. 2) Below $T_f$ the magnetic moment depended on whether a sample was cooled from $T_1 > T_f$ to $T_2 < T_f$ in a magnetic field or in the absence of such a field.

The spin-glass state of $Ga_{2/3}Cr_2S_4$ was due to the disorder in the distribution of the nonmagnetic gallium ions, so that the integrals of the superexchange between the magnetic $Cr^{3+}$ ions fluctuated. Replacement of a small proportion of the Ga ions with Cu did not improve the crystallographic order but in fact reduced it (this was not true at high values of $x$—see below). Therefore, at moderately high Cu concentrations the spin-glass state should be retained and its stability should increase. Our data (Fig. 1) indicated that the temperature of freezing of a spin glass $T_f$ did indeed rise on increase in the Cu concentration: it was 4.5 °K for $x = 0$ and 17.6 °K for $x = 0.4$. The temperature $T_f$ was defined as the temperature corresponding to the magnetic susceptibility maximum in weak fields. The asymptotic Curie point, deduced from the Curie–Weiss law for the high-temperature susceptibility, also increased with $x$ from 10 to 65 °K (Fig. 1) indicating enhancement of the ferromagnetic nature of the exchange on increase in the copper content. There was also a corresponding increase with $x$ in the magnetic moment of the glasses at 4.2 °K measured in a field of 50 kOe (Fig. 2). (However, one of the samples with $x = 0$ had an anomalously large moment which was 1.5 times greater than that of a sample with $x = 0.4$; the reason for this anomaly was not clear.)

However, when $x$ reached the value 0.5, the magnetic and electrical properties of the solutions changed radically: the conductivity measured at 4.2 °K rose by 11 orders of magnitude in the interval between $x = 0.4$ and $x = 0.6$ (Fig. 2) and this was accompanied by the appearance of a spontaneous magnetization with the Curie point at $T_c = 240$ °K for $x = 0.6$ and also by an increase in $\Theta$ from 65 to 298 °K (Fig. 1). Thus, at $x \approx 0.5$ there was a composition-induced insulator–metal phase transition accompanied by a transition from the spin-glass state to an amorphous ferromagnet. (The relatively

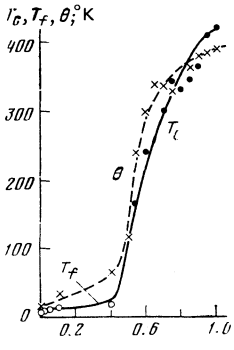


FIG. 1. Dependences of the magnetic ordering temperatures on $x$: the Curie point $T_c$, the freezing temperature $T_f$, and the asymptotic Curie temperature $\Theta$ for a system of $x = CuCr_2S_4$—$(1-x)Ga_{2/3}Cr_2S_4$ solid solutions.

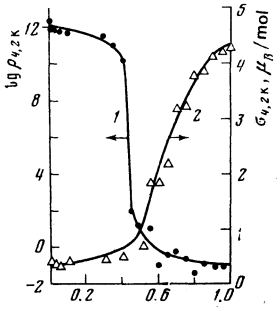


FIG. 2. Dependences of the logarithm of the electrical resistivity $\rho_{4.2\,°K}$ and of the magnetization $\sigma_{4.2\,°K}$ per molecule on $x$ obtained in a field of 50 kOe at 4.2 °K for the $x\,CuCr_2S_4$—$(1-x)Ga_{2/3}Cr_2S_4$ system: 1) spin-glass ordered region; 2) ferromagnetically ordered region.

low conductivity of the metallic materials shown in Fig. 2 was clearly due to the polycrystalline nature of the sample. According to Ref. 7, the conductivity of $CuCr_2S_4$ single crystals was 2–3 orders of magnitude higher than the values given in Fig. 2.) A further increase in $x$ caused $\Theta$ to rise to 390 °K, and $T_C$ to rise from 240 to 420 °K.

Undoubtedly, the magnetism in the metallic state was due to ordering of localized moments. This was indicated by the similarity of the values of the moment per molecule in a field of 50 kOe found at 4.2 °K (representing essentially the saturation moment) and of the effective moment deduced from the Weiss constant of pure $CuCr_2S_4$ (the values were 4.58 and 4.54 $\mu$B, respectively). Moreover, the superexchange between the localized moments in insulating chromium chalcogenide spinels $AC_2X_4$ (A = Cd, Hg; X = S, Se) were known to have much lower magnetic ordering temperatures (from 18 to 130 °K) than $CuCr_2S_4$. On the other hand, the Curie points reported not only for $CuCr_2S_4$ but also for other metallic ferromagnetic spinels $CuCr_2X_4$ (X = Se, Te) exceeded 360 °K (Ref. 7). Therefore, the very high value of $T_C$ obtained for $CuCr_2S_4$ could only be explained by an indirect exchange via charge carriers. (Although it is usual to talk of an indirect exchange via conduction electrons, one should speak here of an exchange via holes because conduction in $CuCr_2S_4$ is of $p$-type).

Hence, the strong enhancement of the ferromagnetic coupling between spins in the investigated alloys at the critical value $x_c \approx 0.5$ should be attributed to a transition from an insulating to a highly conducting state producing an indirect exchange. The high value of the indirect exchange integral compared with the superexchange integral ensures a positive sign of the total exchange integral equal to the sum of the indirect exchange and superexchange integrals, irrespective of the sign of the latter integral. Thus, fluctuations of the sign of the superexchange integral resulting in a spin-glass state in the insulating phase are suppressed so that they do not cause fluctuations of the sign of the total exchange integral when the indirect exchange is present but they still do cause fluctuations of the magnitude of the total integral. The latter fluctuations make the crystal an amorphous ferromagnet. This, in our opinion, is the mechanism of destruction of the

spin-glass state by the indirect exchange via charge carriers in the investigated system.

The destruction of the glass state at $x \sim 0.5$ is facilitated by the following circumstance. In contrast to the $x \ll 1$ case, replacement of gallium with copper in materials with high values of $x$ does not reduce but enhances the crystallographic order because of suppression of the disorder resulting from the fact that only some of the molecules have a cation (for $x = 0$ we find that there are only two Ga cations for every three molecules, whereas at $x = 1$ there is one Cu cation per each molecule). However, this cannot account for the destruction of the glass state. If we ignore the insulator–metal phase transition and consider only the enhancement in the cation ordering, we can describe the spin glass–amorphous ferromagnet transition using the percolation theory: $x_c \approx 0.5$ should be the critical percolation concentration at which the number of ferromagnetic bonds becomes sufficient to establish a ferromagnetic order in the crystal. However, the value of $\Theta$ in the vicinity of $x_c$ should be a smooth function of $x$ since the high-temperature magnetic susceptibility close to $x_c$ is practically independent of whether ferromagnetic clusters join one another or are isolated. However, the above data show that $\Theta$ rises very steeply in the interval $x = 0.4$–$0.6$ reaching directly 230 °K. This means that $x_c$ is not the critical percolation concentration but the concentration at which in the exchange mechanism becomes modified (an indirect exchange via conduction electrons appears in the system). Consequently, it is this indirect exchange which destroys the spin-glass state.

Naturally, this is not a universally valid conclusion but one which applies to the investigated system of solid solutions: it is valid only in the case of insulating spin glasses and not always even then.

In any case, we can identify another class of spin glasses in which an indirect exchange can destroy a spin-glass ordering: this class is represented by magnetic semiconductors. If such a semiconductor is doped with a donor (or acceptor) impurity, it becomes degenerate. Delocalized donor electrons are responsible for an indirect exchange which tends to establish a ferromagnetic order.[3] If the carrier density is insufficient to change the spin-glass to the ferromagnetic state throughout a crystal, this crystal may split into alternate regions with the spin-glass and ferromagnetic ordering and at $T = 0$ the carriers may become localized in the ferromagnetic regions.

This phenomenon is fully analogous to the situation in degenerate antiferromagnetic semiconductors described in Ref. 3. If the correlations between the directions of neighboring spins in a spin-glass state are unimportant, all the calculations made in Ref. 3 for antiferromagnetic semiconductors can be applied also to spin glasses. In particular, if a ferromagnetic phase in a two-phase material is in the form of isolated ferromagnetic regions inside a spin-glass matrix, the low-temperature conductivity of such a crystal should be very low. Destruction of this two-phase state by increasing the temperature or by applying a magnetic field should result in delocalization of the conduction electrons localized in the ferromagnetic regions, i.e., it should result in a jump in the conductivity of the kind expected for an insulator–metal phase transition. However, if the carrier density is sufficiently high for the ferromagnetic regions to merge into one system which contains spin-glass regions as inclusions, the field and temperature dependences of the conductivity should be weak and the low-temperature conductivity should be high.

The authors are grateful to K. P. Belov for discussing the results, and to I. V. Gordeev, Ya. A. Kesler, and V. V. Titov for preparing the samples and analyzing them.

[1]H. Maletta and W. Felsch, Phys. Rev. B 20, 1245 (1979).
[2]D. C. Mattis, The Theory of Magnetism, Harper and Row, New York, 1965 (Russ. Transl., Mir, M., 1967).
[3]É. L. Nagaev, Fizika magnitnykh poluprovodnikov (Physics of Magnetic Semiconductors), Nauka, M., 1979.
[4]L. I. Koroleva, N. A. Tsvetkova, V. V. Titov, Ya. Y. Kesler, I. V. Gordeev, and A. I. Kuz'minykh, Tezisy Vsesoyuzn. konf. po fizike magn. yavleniĭ (Abstracts of Papers presented at All-Union Conf. on Physics of Magnetic Phenomena), Kharkov, 1979, p. 176.
[5]F. K. Lotgering, Solid State Commun. 2, 55 (1964).
[6]K. P. Belov, L. I. Koroleva, N. A. Tsvetkova, Yu. F. Popov, I. V. Gordeev, Ya. A. Kesler, V. V. Titov, and A. G. Kocharov, Pis'ma Zh. Eksp. Teor. Fiz. 31, 96 (1980) [JETP Lett. 31, 87 (1980)].
[7]F. K. Lotgering, in: Proc. Intern. Conf. on Magnetism, Nottingham, England, 1964, publ. Institute of Physics, London, 1965, p. 533.

Translated by A. Tybulewicz