The spin glass state and its suppression by indirect exchange via current carriers in the system of solid solutions $x\mathrm{CuCr_2Se_4}$–$(1-x)\mathrm{Cu_{0.5}Me_{0.5}Cr_2Se_4}$(Me = In, Ga)

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The magnetic and electrical properties of the spinel-like solid solutions $x\mathrm{CuCr_2Se_4}$–$(1-x)\mathrm{Cu_{0.5}Me_{0.5}Cr_2Se_4}$ (Me = In, Ga) have been studied experimentally. The compounds with $0 \leqslant x \leqslant 0.1$ are semiconductors with magnetic properties characteristic of spin glasses, namely a maximum in the initial magnetic susceptibility at $T = T_f$ and a dependence of magnetic properties on the thermomagnetic history of the specimen. The freezing temperature T_f depends on the frequency of the alternating magnetic field according to the Arrhenius law, the height of the potential barrier being of the same order as the activation energy determined from the temperature dependence of the electrical resistivity. The thermoremanence in these compounds appears not only below T_f but appreciably above T_f, up to $T \approx 3T_f$, unlike other materials with a spin glass (SG) state. Compounds with $x \geqslant 0.6$ (Me = In,Ga) are metallic amorphous ferromagnets, while those with $0.1 < x \leqslant 0.2$ are degenerate semiconductors with a mixed SG + ferromagnetic state which goes over to the SG state at low temperatures. In this system, indirect exchange via current carriers thus suppresses the SG state. The nature of the SG state in this system is discussed.

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INTRODUCTION

The spin glass (SG) state was first found in very dilute metallic alloys and its cause was considered to be the long-range oscillating interaction of the RKKY type. However, the SG state has recently been found in magnetically concentrated insulators, for example in $\mathrm{Eu_xSr_{1-x}S}$,[1] $\mathrm{Ga_{0.67}Cr_2S_4}$,[2] and $\mathrm{Cu_{0.5}In_{0.5}Cr_2S_4}$,[3] and this has necessitated a reappraisal of the nature of spin glasses. In addition, experimental results were obtained[4] which were paradoxical from the point of view of existing ideas about the nature of spin glasses: indirect exchange via current carriers not only does not promote the formation of a spin glass but, on the contrary, destroys it in the system of solid solutions $x\mathrm{CuCr_2S_4}$–$(1-x)\mathrm{Ga_{0.67}Cr_2S_4}$. In this system, compounds with $x < 0.5$ are insulators and spin glasses, but near the composition $x = 0.5$ a concentration insulator-metal transition takes place and a spontaneous moment arises in the solutions simultaneously, the magnitude of which corresponds to ferromagnetic ordering of the magnetic moments of the $\mathrm{Cr^{3+}}$ ions.

In the present work new semiconductor spin glasses in the chalcospinel system $x\mathrm{CuCr_2Se_4}$–$(1-x)\mathrm{Cu_{0.5}Me_{0.5}Cr_2Se_4}$ (Me = In,Ga) are described and it is shown that when Me is replaced by copper for $x > 0.1$, a transition from a SG to a ferromagnet (FM) takes place with a simultaneous change from a semiconductor to a metallic type of conduction. In the present system this transition takes place over a finite concentration range $0.1 < x \leqslant 0.2$ in which an SG + FM mixed state is found, and the material is a degenerate semiconductor, unlike the abrupt nature of the SG→FM transition which takes place simultaneously with the insulator-metal transition in the system $x\mathrm{CuCr_2S_4}$–$(1-x)\mathrm{Ga_{0.67}Cr_2S_4}$.[4]

The physical properties of the extreme compositions of this system are completely different. It is known that $\mathrm{CuCr_2Se_4}$ is a ferromagnet with *p*-type metallic conductivity,[5] while the compound $\mathrm{Cu_{0.5}Me_{0.5}Cr_2Se_4}$ (Me = In,Ga) is a semiconductor.[6] The latter compounds have been classified as antiferromagnets.[7] This conclusion was drawn by the authors only on the basis of the broad maxima observed in the magnetic susceptibility χ measured in a steady magnetic field. These maxima occurred at temperatures $T \approx 14$ K (Me = In) and $T \approx 7$ K (Me = Ga). However, no long range order was later found at $T = 4.2$ K in neutron diffraction studies of $\mathrm{Cu_{0.5}In_{0.5}Cr_2S_4}$.[8,9]

SPECIMENS AND EXPERIMENTAL METHOD

Polycrystalline specimens of the system of solid solutions $x\mathrm{CuCr_2Se_4}$–$(1-x)\mathrm{Cu_{0.5}Me_{0.5}Cr_2Se_4}$ (Me = In,Ga) were obtained by solid-phase synthesis from the starting materials which were $\mathrm{CuCr_2S_4}$ and $\mathrm{Cu_{0.5}Me_{0.5}Cr_2Se_4}$ (Me = In,Ga). The starting materials were synthesized from high-purity elements as described elsewhere.[10,11] The appropriate mixture of starting materials underwent a series of annealings (before each anneal it was ground, homogenized and pressed into pellets) in quartz tubes which were pumped out to 10^{-7} bar and then sealed.

X-ray investigations showed that the single phase region with spinel structure is observed for $0 \leqslant x \leqslant 0.2$ and $0.6 \leqslant x \leqslant 1$ for the system containing Ga, and for $0 \leqslant x \leqslant 0.2$ for the system with In.

A digital F5063 ferrometer was used to measure magnetic susceptibility in weak alternating magnetic fields. The specimens were ~1 mm diameter cylinders, 25 mm long. The demagnetizing effect was taken into account in calculating the susceptibility. The magnetization in static magnetic

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fields was measured either ballistically in a superconducting solenoid, or by a vibration magnetometer in an electromagnet.

EXPERIMENTAL RESULTS AND DISCUSSION

a) Magnetic susceptibility in a weak alternating field for compositions with SG state ($0 \leqslant x \leqslant 0.1$)

It has been shown in the present work that all the properties characteristic of SG are present for systems of the solid solutions $x\mathrm{CuCr_2Se_4}$–$(1-x)\mathrm{Cu_{0.5}Me_{0.5}Cr_2Se_4}$($\mathrm{Me} = \mathrm{In, Ga}$) with $0 \leqslant x \leqslant 0.1$. A peak in the temperature dependence of the magnetic susceptibility measured in a weak alternating field is found at the freezing temperature T_f. The peak is rounded and lowered under the action of a static magnetic field. This can be clearly seen in Fig. 1, which shows the $\chi(T)$ dependence for a specimen with $x = 0.05$ ($\mathrm{Me} = \mathrm{Ga}$) and the effect of a weak static field on it. The temperature T_f depends appreciably on the copper admixture to $\mathrm{Cu_{0.5}Me_{0.5}Cr_2S_4}$ (Table I) and increases with increasing x, although more slowly than linearly.

Both the magnitude of χ and the position of the maximum in the $\chi(T)$ curve depend on the frequency ν of the alternating field in which the susceptibility is measured. The temperature dependence of χ for the specimen with $x = 0.05$ ($\mathrm{Me} = \mathrm{Ga}$) obtained for various frequencies of the alternating field is shown in Fig. 2. It can be seen that as ν is increased, χ is reduced both above and below T_f, while the freezing temperature T_f itself increases.

We analyzed the frequency dependence of T_f using a simple superparamagnetic cluster model[5] to understand its nature. It was assumed that the magnetic moments of independent clusters can relax between different orientations separated by an energy barrier E_a, under the action of thermal excitations. The relaxation time is expressed by the Arrhenius law:

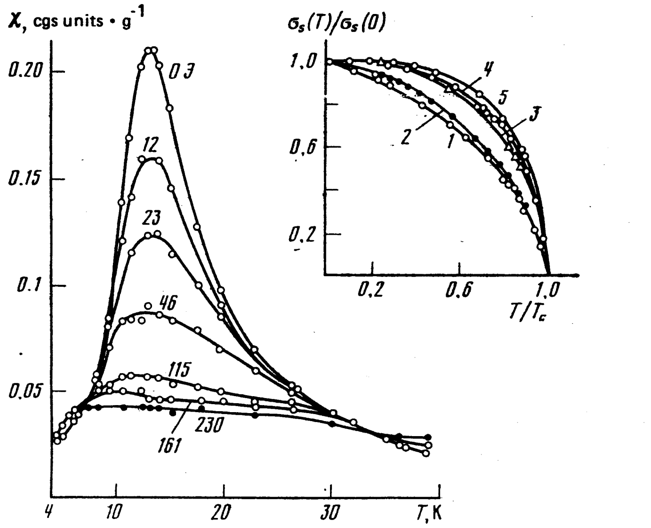

FIG. 1. $0.05\mathrm{CuCr_2Se_4}$–$0.95\mathrm{Cu_{0.5}Ga_{0.5}Cr_2Se_4}$. Temperature dependence of the magnetic susceptibility χ in an alternating magnetic field of frequency 8 kHz ($H_\sim = 0.06$ Oe) and the influence on it of a steady magnetic field. The inset shows the temperature dependence of the reduced spontaneous magnetization of gallium compounds with $x = 0.6$ (curve 1); 0.7 (2); 0.8 (3); 0.9 (4). For comparison the Brillouin function for $J = 3/2$ is shown (5).

TABLE I. Magnetic and electrical properties of the chalcogenide system $x\mathrm{CuCr_2Se_4}$–$(1-x)\mathrm{Cu_{0.5}Me_{0.5}Cr_2Se_4}$.

Compound	x	Magnetic moment at 4.2 K, μ_B mole^{-1}	Curie temperature T_c, K	Freezing temperature T_f, K	Asymptotic Curie temperature θ, K	Curie-Weiss constant, C	Effective magnetic moment calculated from C, μ_B mole^{-1}
Me=Ga	0	–	–	8.0	102	3.45	5.25
	0.03	1.77	–	8.6	145	2,74	4.68
	0.05	2.09	–	11.7	151	2.74	4.68
	0.10	2.85		19,5	179	2,63	4.59
	0.125	–	34	10.5	–	–	–
	0.15	–	56	9.3	–	–	–
	0.20	3.70	76.5	8.2	220	3.28	5.12
	0.60	5.14	365	–	–	–	–
	0.70	5.21	374	–	–	–	–
	0.80	5.28	427	–	–	–	–
	0.9	5.6	425	–	–	–	–
Me=In	0	2.68	–	10.5	97	3.73	5.46
	0,01	2.93	–	11.5	106	3.70	5.44
	0.03	3.10	–	12.4	117	3.65	5.4
	0.05	3.72	–	13.2	132	3.61	5.37
	0.10	4.83	–	18.7	244	3.51	5,30
	0.20	–	–	20.6	–	—	–

$$\tau=\tau_0 \exp\left(E_a/kT\right), \tag{1}$$

where τ_0 is a time constant characteristic of the material. It is assumed that at $\tau = 1/\nu$ the magnetic moments of the clusters are blocked or frozen-in. It is thus assumed in the superparamagnetism model that there is the following dependence of freezing temperature T_f on measuring frequency:

$$\nu=\nu_0 \exp\left(-E_a/kT_f\right), \tag{2}$$

where the frequency factor $\nu_0 \sim 10^9\ \mathrm{s}^{-1}$, or

$$\ln \nu-\ln \nu_0=-E_a/kT_f. \tag{3}$$

We plotted the dependence of $1/T_f$ on $\ln \nu$ for all the studied specimens with $x \leqslant 0.1$. It turned out that the experimental

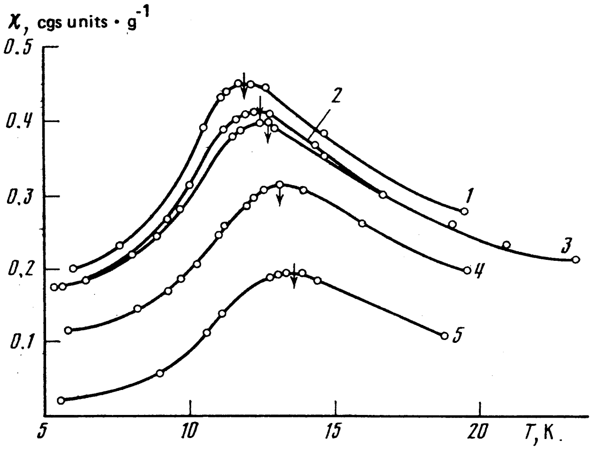

FIG. 2. Same specimen as Fig. 1. Temperature dependence of the magnetic susceptibility χ, obtained for different frequencies of the alternating field ν[Hz] = 200 (curve 1), 800 (2), 2000 (3), 5000 (4), 8000 (5). The amplitude of the alternating field $H_\sim = 1$ Oe. The freezing temperatures are shown by arrows.

TABLE II. Main characteristic of the system $x\mathrm{CuCr_2Se_4}$–$(1-x)\mathrm{Cu_{0.5}Me_{0.5}Cr_2Se_4}$, determined from the dependence of freezing temperature on measuring frequency and from the temperature dependence of the electrical resistivity.

Compound	x	Relative change in T_f with measuring frequency $\frac{\Delta T_f,}{T_f \Delta \lg \nu}$	Frequency factor ν_0, Hz	Model value for the energy barrier $25kT_f$, eV	Experimental value of the energy barrier from the Arrhenius law, E_a, eV	Activation energy E, eV, determined from the temperature dependence of resistivity
Me=Ga	0.05	0.08	$4.1\cdot10^{14}$	0.024	0.013	0.028
	0.10	0.16	$1.3\cdot10^{9}$	0.038	0.014	0.005
Me=In	0	0.05	$3.9\cdot10^{10}$	0.018	0.014	0.017
	0.01	0.06	$5.5\cdot10^{9}$	0.019	0.014	0.031
	0.03	0.05	$9\cdot10^{20}$	0.021	0.039	0.040
	0.05	0.05	$9\cdot10^{22}$	0.024	0.047	0.023
	0.10	0.16	$1.5\cdot10^{12}$	0.023	0.014	0.005

points lie well on a straight line at measurement frequencies from 0.02 to 8 kHz. We assumed a measurement frequency $\nu = 0.02$ Hz for studies of χ in static magnetic fields. We note that T_f determined from the maximum initial susceptibility in a static field also lies on this straight line, unlike in the spin glass insulators $\mathrm{Eu}_x\mathrm{Sr}_{1-x}\mathrm{S}$, for which this was not found.[13]

The values of ν_0 and $\Delta T_f/T_f\Delta \log \nu$ derived from plots of $T_f^{-1}(\ln \nu)$ are given in Table II. It can be seen that the energy barrier E_a changes from 166 to 547 K, which is of the same order as the value of $25\,kT_f$ of the model (T_f is here the temperature of the maximum in $\chi(T)$ in a static magnetic field). The frequency factor ν_0 for $x < 0.1$ lies mainly within the limits 1.3×10^9 to 4.1×10^{14} Hz, which does not differ as much as other spin glasses from the value 10^9 Hz which follows from the superparamagnetism model. Compounds with $x = 0.03$ and 0.05 are exceptions, ν_0 being respectively 9×10^{20} and 9×10^{22} Hz for them. We should note that ν_0 is completely unphysical for other spin glasses: for example it was $\sim10^{90}$ Hz for **PdMn** alloys[14] and $\sim10^{200}$ Hz in **CuMn**.[15] The relative change in T_f with changing frequency (the value of $\Delta T_f/T_f\Delta \log \nu$) is about the same as in $\mathrm{Eu}_x\mathrm{Sr}_{1-x}\mathrm{S}$,[13] but less than for $\mathrm{La}_{1-x}\mathrm{Gd}_x\mathrm{Al}_2$.[16] The values of $\Delta T_f/T_f\Delta \log \nu$ shown in Table II are about an order of magnitude greater than for **CuMn**[15] and several times larger than for **AuFe**[17,18] and **PdMn** alloys.[14] A strong frequency dependence of T_f is thus found in the compounds $x\mathrm{CuCr_2Se_4}$–$(1-x)\mathrm{Cu_{0.5}Me_{0.5}Cr_2Se_4}$ $(0\leqslant x\leqslant0.1)$. This, according to the superparamagnetism model is evidence of FM interaction between the nearest neighbors in the clusters.[12,19]

We also measured the temperature dependence of the resistivity ρ of the above compounds. For $x\leqslant0.1$ the $\rho(T)$ dependence was of semiconductor form (Fig. 3). The activation energy derived from the $\log\rho(1/T)$ curves (Fig. 3) is given in Table II. It is interesting that the magnitudes of the potential barriers E_a and the conduction activation energies are of the same order; we can suppose as a result of this that electronic processes have a basic role in the formation of FM clusters. This could occur, for example, if the clusters are of the ferronic type:[20] an electron is localized near an impurity or lattice defect, forming a ferromagnetic cluster around the impurity when its energy is lowered because of the gain in energy of s–d exchange. The conductivity of all the specimens was determined as p-type from the sign of the thermopower at 77 and 300 K.

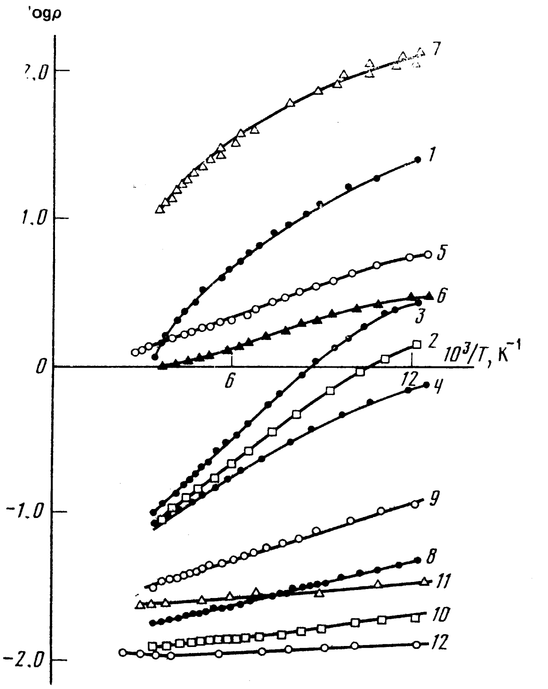

FIG. 3. Temperature dependence of the electrical resistivity of compounds with composition $x\mathrm{CuCr_2Se_4}$–$(1-x)\mathrm{Cu_{0.5}Me_{0.5}Cr_2Se_4}$:Me = In, with $x = 0$ (curve *1*), 0.01 (*2*), 0.03 (*3*), 0.05 (*4*), 0.10 (*5*), 0.20 (*6*); Me = Ga with $x = 0$ (*7*), 0.03 (*8*), 0.05 (*9*), 0.10 (*10*), 0.15 (*11*), 0.20 (*12*).

b) The dependence of magnetic properties on the thermomagnetic history of the specimens. Specimens with $0\leqslant x\leqslant0.1$

The low-temperature magnetic properties of compounds with $0\leqslant x\leqslant0.1$ are considerably dependent on the thermomagnetic history of the specimen. For example, the magnetization measured in a weak steady magnetic field depends appreciably on whether the specimen was cooled in the field or without it. Two curves of the magnetization σ of a specimen with $x = 0.01$ (Me = In) are shown in Fig. 4a as an example, obtained under different cooling conditions: curve *1*—the specimen was cooled to $T = 4.2$ K with no external field, the field was then switched on and the magnetization measured, after which the temperature was raised with the field on and the process was repeated; curve *2*—the specimen was slowly cooled from $T = 273$ K to 4.2 K while all the time in a field $H = 50$ Oe, and its magnetization was measured during this. The appreciable difference between curves *1* and *2* can be seen: curve *1* passes through a maximum at $T_f = 6$ K while there is no such maximum for curve *2*. There is a horizontal section below T_f on curve *2*. Curve *2* goes significantly above curve *1* for $T > T_f$, indicating the existence of thermoremanence considerably above the freezing temperature. Thermoremanence above the freezing temperature was also observed in other spin glasses, for example in dilute **AuFe** alloys.[21]

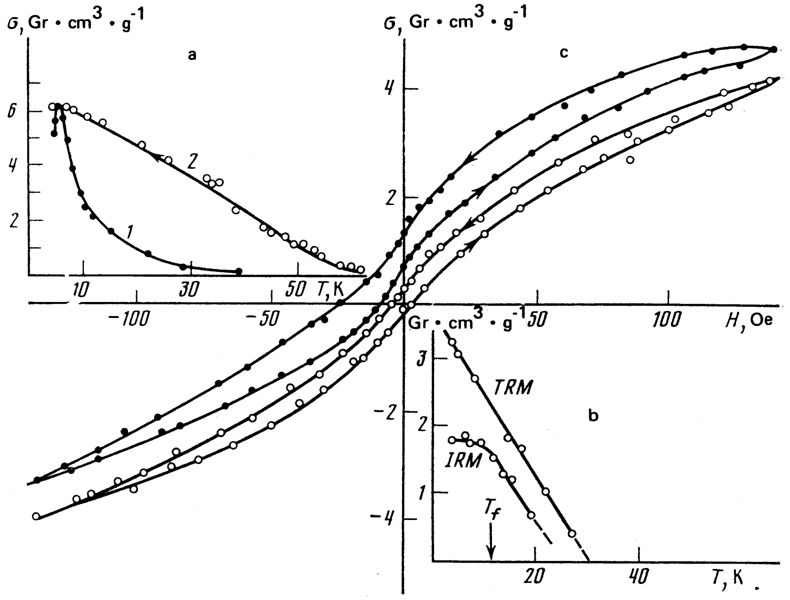

FIG. 4.a) $0.01CuCr_2Se_4$–$0.99\ Cu_{0.5}In_{0.5}Cr_2Se_4$ specimen. Temperature dependence of magnetization σ in a field of 50 Oe, obtained for various cooling conditions; b) $0.05CuCr_2Se_4$–$0.95Cu_{0.5}In_{0.5}Cr_2Se_4$ specimen. Temperature dependence of TRM and IRM measured after switching on a field $H = 200$ Oe; c) $0.03CuCr_2Se_4$–$0.97Cu_{0.5}Ga_{0.5}Cr_2Se_4$ specimen. Hysteresis loops obtained on cooling the specimen in a field of 138 Oe from $T > T_f$ to $T < T_f$ (●) and without a field (○).

We measured the remanent magnetization of specimens cooled in a weak steady magnetic field from $T > T_f$ (thermoremanent magnetization, TRM) and without a field (isothermal remanent magnetization, IRM). The dependence of IRM and TRM at $T = 4.2$ K on the magnitude of the magnetic field for the end points of the hysteresis loop for the specimen with $x = 0.01$ (Me = In) is shown in Fig. 5, and this is typical of other specimens with a SG state. It can be seen that the IRM curve goes considerably lower than the TRM curve: however, in a field $H \approx 1500$ Oe both curves saturate at the same value. The TRM curve passes through a maximum in the region of $H = 400$ Oe. We also obtained the magnetization σ_{irrev} and σ_{rev} under the same cooling conditions as those under which TRM and IRM were determined in a field H, on turining on of which TRM and IRM were measured; these curves are also shown in Fig. 5. For each value of field it was found that $\sigma_{\text{irrev}} - \sigma_{\text{rev}} = \text{TRM} - \text{IRM}$ within an accuracy of up to 16%. The temperature dependence of TRM and IRM for $H = 200$ Oe for the specimen with $x = 0.05$ is shown in Fig. 4b; it can be seen that TRM is observed over a temperature range nearly three times broader than T_f (T_f is shown by an arrow in the figure).

TRM was also observed earlier at temperatures appreciably above the freezing temperature in the spin-glass alloys **YPb**[22] and the insulator $Eu_{0.4}Sr_{0.6}S$,[23] but over a considerably narrower temperature range. The maximum temperature where TRM was still non-zero for $Eu_{0.4}Sr_{0.6}S$ was $\approx 1.55\ T_f$; it was about $3T_f$ for the compounds studied here. The existence of TRM above T_f favors the applicability of the superparamagnetism model for studying spin glasses rather than the existence of a phase transition at T_f. We note that for **AuFe** alloys[21] the temperature range above T_f where TRM is observed is almost an order of magnitude less than for the spin glass semiconductors considered here.

Cooling of the specimen in a magnetic field also has a considerable effect on the hysteresis loop. Hysteresis loops for the specimen with $x = 0.03$ (Me = Ga) cooled in a field $H = 138$ Oe and without a field are shown in Fig. 4c. It can be seen that the hysteresis loop in the second case is very narrow and symmetrical. When the specimen is cooled in a field the loop shifts in the direction of the applied field, and also along the σ axis, then broadens slightly, but remains fairly narrow. Such a hysteresis behavior is very similar to that observed in the spin glass metallic alloys **CuMn**, **AgMn** and **NiMn**[24] and is well explained on the model proposed by Beck.[25] On his assumption, magnetic clusters are frozen-in at random.

c) Magnetization in a strong steady field for the compounds with $0 \leqslant x \leqslant 0.1$

Magnetization isotherms of compounds with $x \leqslant 0.1$ measured in fields up to 50 Oe both above and below T_f are

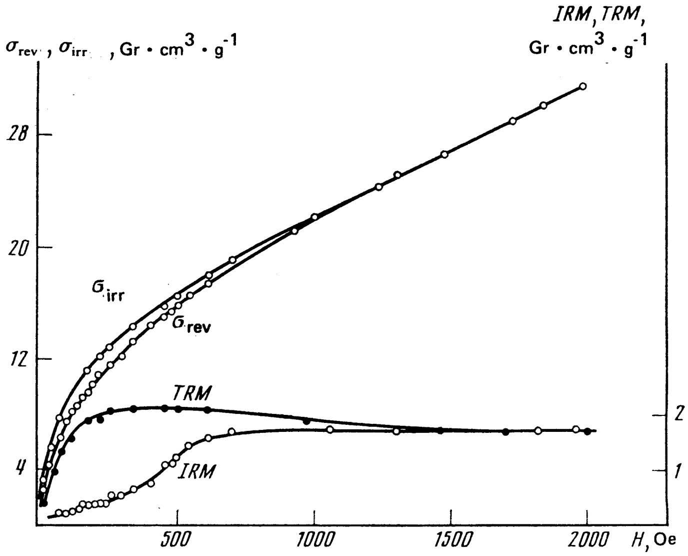

FIG. 5. $0.01\ CuCr_2Se_4$–$0.99Cu_{0.5}In_{0.5}Cr_2Se_4$ specimen. Field dependence of the magnetization σ and the residual magnetization of a specimen cooled in the field from $T > T_f$ to $T < T_f$ (curves σ_{irrev} and TRM) and cooled without a field (curves σ_{rev} and IRM).

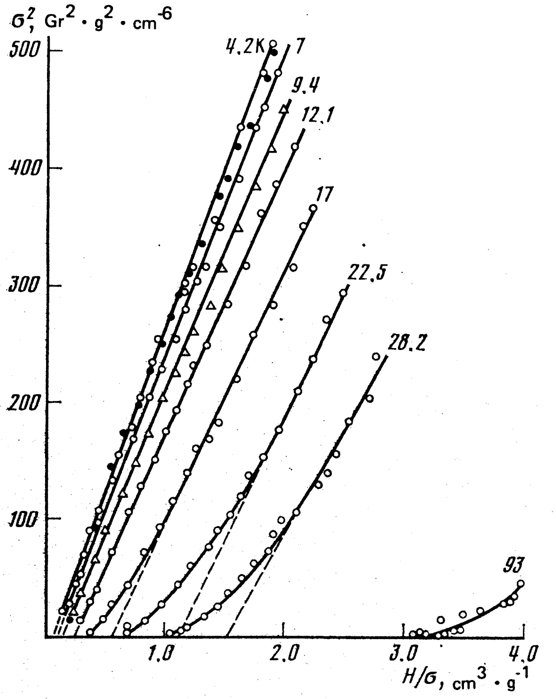

FIG. 6. $0.03CuCr_2Se_4$–$0.97Cu_{0.5}Ga_{0.5}Cr_2Se_4$ specimen. Belov-Arrot curves of $\sigma^2(H/\sigma)$ in the range of fields 1 KOe$\leqslant H \leqslant$50 kOe.

nonlinear. We show in Fig. 6 curves of $\sigma^2(H/\sigma)$ in both the weak field ($H \leqslant 500$ Oe) and strong field ($H \leqslant 50$ kOe) regions for $x = 0.03$ (Me = Ga). Extrapolation of the curves to the ordinate axis for weak and strong fields does not give positive intercepts on this axis, indicating the lack of long-range magnetic order in this material. A similar picture is also observed for other compounds with $x \leqslant 0.1$.

As we showed before,[3] the experimental curves of $\sigma(H/T)$ at $T > T_f$ for $x = 0$ (Me = In) lie satisfactorily on the Langevin curve with $J = \infty$,[12,26] with an effective moment of a magnetic cluster $m = 0.35 \times 10^{-18}$ erg·Oe^{-1} and specific saturation magnetization $\sigma_s = 28$ G·cm^3·g^{-1}. This shows the applicability of the cluster model for this compound at $T > T_f$. We also carried out a similar treatment of the experimental magnetization curves for compounds with $x \leqslant 0.1$. Only for $x = 0$ do we observe such good agreement between the $\sigma(H/T)$ curves for $T > T_f$ and the Langevin function; at $x \neq 0$ corrections have to be applied to the intramolecular field, and the temperature dependence of the magnetic moments of the clusters has to be taken into account. It turned out that the magnetic moment of the clusters decreases with increasing temperature while their concentration is raised. For example, for $x = 0.05$ the cluster moment falls from 60 to 22 μ_B on raising the temperature from 14 to 75 K and their concentration grows from 5×10^9 to 20×10^{10}.

d) The FM + SG mixed state in compounds with $0.1 < x \leqslant 0.2$

Magnetic properties in the concentration range $0.1 < x \leqslant 0.2$ differ considerably from those described above. The $\chi(T)$ dependence for compounds with $0.1 < x \leqslant 0.2$ (Me = Ga) measured in a weak alternating field is shown in Fig. 7, and the same dependence for $x = 0.2$ and the action of a steady magnetic field on it is shown in Fig. 8. It can be seen that the maximum value of χ is much higher for compounds in the SG state. In addition, the χ maximum in Fig. 8 is several times broader and is more rounded compared with the maximum in Fig. 1, while a weak steady field suppresses it appreciably more. This maximum is observed to be split in a weak field (Fig. 8), indicating that there are two transitions: at the Curie temperature T_c and at the freezing temperature T_f. We can propose by analogy with metallic alloys, for example AuFe, where a similar behavior of χ is observed,[27] that a mixed SG + FM phase is being observed in compounds with $0.1 \leqslant x \leqslant 0.2$, which goes over into SG at a temperature $T = T_f$ lying below the temperature of the maximum in χ (Fig. 7). We then determined T_f as the temperature at which the sharpest fall in χ starts (T_f for the compounds studied are indicated by arrows in Fig. 7).

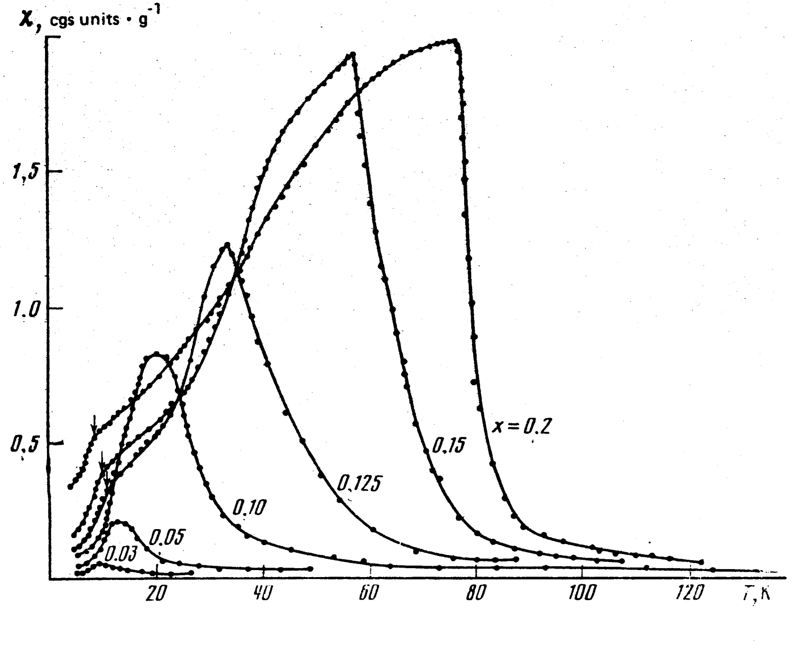

FIG. 7. Temperature dependence of the magnetic susceptibility in an alternating field ($\nu = 8$ kHz, $H_{\sim} = 1$Oe) of specimens of the system $xCuCr_2Se_4$–$(1-x)Cu_{0.5}Ga_{0.5}Cr_2Se_4$ ($0.03 \leqslant x \leqslant 0.2$). The arrows denote the transition temperature from the mixed state to the SG state.

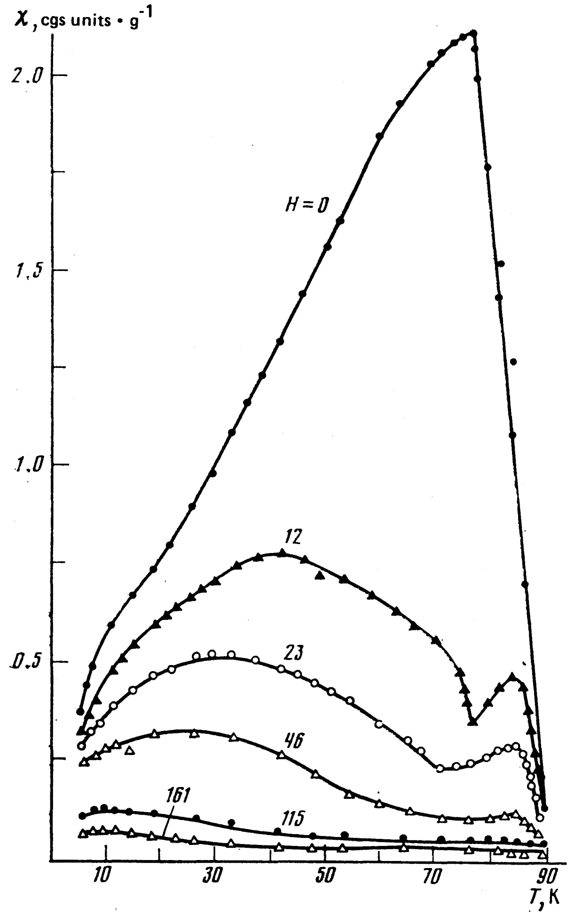

FIG. 8. $0.2CuCr_2Se_4$–$0.8Cu_{0.5}Ga_{0.5}Cr_2Se_4$ specimen. Temperature dependence of the magnetic susceptibility in a weak alternating field $\nu = 8$ kHz, $H_\sim = 0.06$ Oe) and the effect on it of a steady magnetic field (in Oe).

Values of the magnetic moment per molecule, measured in a field of 48 Oe are given in Table I for all the compounds. It can be seen that for $0.1 < x \leqslant 0.2$ these moments are considerably less than the value μ_B/mole, which would occur for ferromagnetic ordering of the moments of the Cr^{3+} ions, and is close to the values obtained for compounds with $x \leqslant 0.1$, where the SG state is observed. This suggests that at 4.2 K there is also an SG state for $0.1 < x \leqslant 0.2$. According to our measurements, the TRM and IRM curves for these compounds are then similar to those illustrated in Figs. 4b and 5 for compounds in the SG state. The difference between TRM and IRM disappears above T_f.

It can be seen from Table I that T_f falls as x increases for concentrations $0.1 < x \leqslant 0.2$. At the same time it is close to, but somewhat less than, the values of T_f for the SG state ($0 \leqslant x \leqslant 0.1$). A similar picture was observed earlier in AuFe alloys in the region of the percolation limit[28] and in the insulators $Eu_xSr_{1-x}S$ at $x \sim 0.5$.[29] In these systems the reduction in T_f with increasing concentration of the magnetically active atoms was explained by a reduction in cluster dimensions, similar to that observed in the material for lower concentrations of magnetically active atoms, due to the growth of the infinite cluster. It was assumed that an infinite cluster also exists below T_f in dilute AuFe alloys,[28] while in $Eu_xSr_{1-x}S$ it was found from neutron diffraction results[29] that long-range magnetic order disappears below T_f.

It can be seen from Fig. 3, where the temperature dependence of the electrical resistivity of the specimens investigated is shown, that compounds with $0.1 < x \leqslant 0.2$ are degenerate semiconductors.

The following behavior is thus observed in the system. Compounds with $0 \leqslant x \leqslant 0.1$ are semiconducting spin glasses, while compounds with $0.1 < x \leqslant 0.2$ are degenerate semiconductors in which the mixed SG + FM state is observed, which goes over to SG at low temperatures. The appearance of an infinite cluster is consequently accompanied by degeneracy of the semiconductor, i.e., practically by a transition to metallic conductivity.

e) Amorphous ferromagnetism in compounds with $0.6 \leqslant x \leqslant 0.9$ (Me = Ga)

We unfortunately did not have specimens with compositions $0.2 < x < 0.6$ (Me = Ga) and $x > 0.2$ (Me = In) because of the break in the single-phase region here. Compounds with $0.6 \leqslant x \leqslant 0.9$ (Me = Ga) have metallic type conductivity: as can be seen from Table I, their magnetic moments at 4.2 K are close to the value $6\mu_B$/mole for ferromagnetic ordering of the moments of the two Cr^{3+} ions in their chemical formula. The magnetization of these compounds is already saturated in fields ≈ 3 kOe. The Curie temperatures T_c determined for them by the thermodynamic-coefficients method are given in Table I. Their values are close to T_c of the metallic ferromagnet $CuCr_2Se_4$, where indirect exchange via the current carriers (holes) between the localized moments of the Cr^{3+} ions takes place.[5] At the same time, compounds with $0.6 \leqslant x \leqslant 0.9$ (Me = Ga) are evidently ferromagnets, as a result of which their magnetization is lower than calculated by the Brillouin function. This can be seen clearly in the inset of Fig. 1, which shows the temperature dependence of the reduced spontaneous magnetization $\sigma_s(T)/\sigma_s(0)$ for compounds with $0.6 \leqslant x \leqslant 0.9$ (Me = Ga) and the Brillouin function for $J = 3/2$.

Whereas it was previously assumed that indirect exchange was the main cause of SG formation, our results thus give evidence of the possibility of its role being exactly the opposite.

THE NATURE OF THE SPIN GLASS STATE. THE MECHANISM OF ITS DESTRUCTION BY INDIRECT EXCHANGE VIA CURRENT CARRIERS

The SG state cannot be connected with indirect exchange via conduction electrons because their concentration is too small for this. In fact, semiconductor type of conduction is a characteristic of compounds which are SG. We assume that SG formation in the unalloyed compound $Cu_{0.5}Me_{0.5}Cr_2Se_4$ (Me = In, Ga) is brought about by lattice frustration. We shall explain this in more detail. It is known[7,8] that 1:1 long-range crystallographic order is observed between Cu^{1+} and Me^{3+} ions in tetrahedral sites in the compounds $Cu_{0.5}Me_{0.5}Cr_2S_4$ and $Cu_{0.5}Me_{0.5}Cr_2Se_4$. Their nuclear space group is T_d^2 and not O_h^7 as in the typical spinel $MgAl_2O_4$, as a result of which we call these compounds spineloids. The ordering in the tetrahedral A sublattice leads to the point group symmetry of the octahedral or B sites occupied by Cr^{3+} being $3m$ and not $-\bar{m}$ as in a spinel, since the given site with neighbors at equal distance r_0 with O_h^7 symmetry is divided into two sites with distances respectively $r_0(1 \pm \Delta_0)$.

The magnetic structure of the compound $Cu_{0.5}In_{0.5}Cr_2S_4$ had been studied[8,30–32] and it was shown that the spins of the Cr^{3+} ions are directed parallel to the four cube diagonals formed by neighboring Cr^{3+} ions, and that the magnetic moments of all the Cr^{3+} ions interact antiferromagnetically with the resulting moments at a distance $r_0(1-\Delta_0)$ and ferromagnetically with moments of ions at a distance $r_0(1+\Delta_0)$. The magnetic interactions with more distant neighbors comprise no more than a few percent of the interactions with nearest neighbors.[33] If we consider each of the resulting four magnetic moments of nearest Cr^{3+} ions that interact ferromagnetically and form a tetrahedron as a simple spin localized at its center, then these "broadened" spins are connected in a simple face centered Bravais lattice with first-order antiferromagnetic (AFM) ordering (see Fig. 1 of Ref. 32). It is known that a certain type of frustration of the lattice bonds can lead to SG formation. The face-centered lattice with AFM interactions between nearest neighbors is one such lattice. A Monte Carlo analysis showed the possibility of spin glasses existing in such a lattice with high order degeneracy[34,35] and finite entropy at $T=0$.[36] It was deduced[32] from a study of the magnetic properties and neutron diffraction in the compound $Cu_{0.5}In_{0.5}Cr_2S_4$ that this is antiferromagnetic below 35 K and a spin glass above 35 K. It was shown that a strong magnetic field at $T<35$ K transforms the AFM order into a SG.

Since the degree of covalency in chalcogenide compounds increases on going from S to Se, it is higher than in $Cu_{0.5}Me_{0.5}Cr_2Se_4$ than in $Cu_{0.5}In_{0.5}Cr_2S_4$. From the semiempirical Goodenough-Kanamori rule it is known that 90-degree FM superexchange between nearest neighbors is little sensitive to the distance between the ions and increases with an increase in the degree of covalency. The AFM exchange between next-nearest neighbors falls quickly with increasing distance between them. Since the lattice constant in $Cu_{0.5}Me_{0.5}Cr_2Se_4$ is greater than in $Cu_{0.5}Me_{0.5}Cr_2S_4$, we expect a weakening in the AFM interaction between next-nearest neighbors in the former compared with the latter. At the same time the 90-degree FM interaction between nearest neighbors should be stronger in the first compound than in the second because of the larger degree of covalency. It follows from this that the same exchange interaction scheme as in $Cu_{0.5}In_{0.5}Cr_2S_4$ is maintained in $Cu_{0.5}Me_{0.5}Cr_2Se_4$, with the only difference that FM exchange within the tetrahedra[32] is greater while the AFM exchange between them is lower than in $Cu_{0.5}In_{0.5}Cr_2S_4$. As a result of this, there is already frustration of the bonds in $Cu_{0.5}Me_{0.5}Cr_2Se_4$ at $T<4.2$ K. Due to the lack of experimental results in this temperature range, it is not yet clear whether long range magnetic order exists in this compound at $T<4.2$ K.

Since the sign and magnitude of the superexchange integral depends on the type of nonmagnetic ion in the tetrahedral site, via which this superexchange takes place, replacement of part of the In(Ga) ions by Cu, or fluctuations in the distribution of In(Ga) and Cu ions in an unalloyed compound, should influence the magnetic properties of the system. As can be seen from Table I, the freezing temperature of the SG actually does increase with increasing x. The asymptotic Curie point, determined from the Curie-Weiss law for the high-temperature susceptibility also increases with increasing x, which reflects the growth in the ferromagnetic character of the exchange on increasing the copper content. The magnetic moment of the glass at 4.2 K in a field of 48 kOe also grows correspondingly.

The following orderings of the spins are thus achieved in the system of solid solutions $xCuCr_2Se_4$–$(1-x)Cu_{0.5}Me_{0.5}Cr_2Se_4$ (Me = In,Ga) as a function of x. In the unalloyed compound ($x=0$) at $4.2\ \mathrm{K} \leqslant T \leqslant T_f$ there is a SG state which can be realized by lattice frustration. On alloying it with copper, ferromagnetic clusters are formed in the spin-glass matrix, of which the following experimental facts described above are evidence: 1) strong frequency dependence of T_f obeying the Arrhenius law; 2) dependence of magnetic properties below T_f on the thermomagnetic history of the specimen; 3) the existence of thermoremanence appreciably above T_f; 4) coincidence of the experimental magnetization curves above T_f with the Langevin function for $J=\infty$, so that the magnetic moment of the clusters could be calculated; 5) the growth in the asymptotic Curie point with increasing alloying level, reflecting an increase in the FM character of the exchange. As was indicated above, these FM clusters are evidently of the ferronic type,[20] since the magnitude of the potential barrier, determined from the Arrhenius law, and the activation energy for conduction are of the same order of magnitude. The temperature dependence of the size and concentration of the clusters also supports this assumption, since it has such a character for ferrons.[20] The current carriers (holes) are then trapped in the ferrons while the spin glass-forming matrix is, on the contrary, depleted of them. There are, evidently, also ferromagnetic clusters in the unalloyed compound $Cu_{0.5}Me_{0.5}Cr_2Se_4$, since the experimental facts enumerated above, which confirm the existence of FM clusters, also apply to it. It is possible that their existence is produced by fluctuations in the positions of In(Ga) and Cu ions due to incomplete 1:1 crystallographic order in the A sublattice. For $Cu_{0.5}In_{0.5}Cr_2Se_4$ the degree of this order is about 87%.[3]

On going over to the mixed SG + FM state in compounds with $x>0.1$, the ferrons coalesce into one infinite cluster and metallic conductivity appears in the crystal. The SG region is now inside the FM matrix.

The appearance of an infinite cluster in compounds with $x>0.1$ at $T>T_f$ and $x \geqslant 0.6$ is accompanied by the appearance of metallic conduction in them. As was said above, the limiting composition of this system, $CuCr_2Se_4$ is a metallic ferromagnet with Curie point around 420 K, in which there is indirect exchange via the carriers (holes) between Cr^{3+} ions. The sharp strengthening of the ferromagnetic interaction, produced by the appearance of an infinite cluster in these compounds, is thus a consequence of the transition from a semiconductor to a metallic state, leading to the appearance of indirect exchange. The large value of the indirect exchange integral compared with the superexchange integral ensures a positive total exchange integral equal to the sum of the indirect exchange and superexchange integrals, regardless of the sign of the latter. Fluctuations in the sign of the superexchange integral, leading to SG in the insulating state, thus cease to manifest themselves in the sign of the total exchange integral after the indirect exchange begins, although they produce fluctuations in its magnitude. The latter leads to the crystal becoming an amorphous FM. In fact, as mentioned above and as follows from Fig. 1 (inset), the compounds with $0.6 \leqslant x \leqslant 0.9$ (Me = Ga) are amorphous FM.

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[1] H. Maletta and W. Felsch, Phys. Rev. B **20**, 1245 (1979).

[2] 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)].

[3] K. P. Belov, L. I. Koroleva, A. I. Kuz'minykh, and S. I. Usanin, Fiz. Tverd. Tela (Leningrad) **24**, 1298 (1982) [Sov. Phys. Solid State **24**, 738 (1982)].

[4] L. I. Koroleva, E. L. Nagaev, and N. A. Tsvetkova, Zh. Eksp. Teor. Fiz. **79**, 600 (1980) [Sov. Phys. JETP **52**, 303 (1980)].

[5] K. P. Belov, Yu. D. Tret'yakov, I. V. Gordeev, and Ya. A. Kesler, Magnitnye poluprovodniki—khal'kogenidnye shpineli (Magnetic semiconductor—chalcogenide spinels), MGU, Moscow (1981).

[6] H. Yokoyama and S. Chiba, J. Phys. Soc. Jpn. **27**, 505 (1969).

[7] H. L. Pinch, M. J. Woods and E. Lopatin, Mater. Res. Bull. **5**, 425 (1970).

[8] R. Plumier, F. K. Lotgering, and R. P. van Stapele, J. Phys. (Paris) **32**, C-1-324 (1971).

[9] C. Wilkinson, B. M. Knapp, and J. B. Forsyth, J. Phys. C **9**, 4021 (1976).

[10] K. P. Belov, Yu. D. Tret'yakov, I. V. Gordeev, L. I. Koroleva, A. V. Ped'ko, E. I. Smirnovskaya, V. A. Alferov, and Yu. G. Saksanov, Fiz. Tverd. Tela (Leningrad) **14**, 2155 (1972) [Sov. Phys. Solid State **14**, 1862 (1972)].

[11] K. P. Belov, Yu. D. Tret'yakov, I. V. Gordeev *et al.*, in: Ferromagnetizm (Ferromagnetism), K. P. Belov and Yu. D. Tret'yakov eds., MGU, Moscow (1975) p. 19.

[12] C. P. Bean and J. D. Livingston, J. Appl. Phys. **30**, 120S (1959).

[13] H. Maletta and W. Felsch, Phys. Rev. **20**, 1245 (1979).

[14] C. A. M. Mulder, A. J. van Duyneveldt, H. W. M. van der Linden, B. H. Verbeek, J. C. M. van Dongen, G. J. Nieuwenhuys, and J. A. Mydosh, Phys. Lett. A **83**, 74 (1981).

[15] C. A. M. Mulder, A. J. van Duyneveldt, and J. A. Mydosh, Phys. Rev. B **23**, 1384 (1981).

[16] H. V. Lohneysen, J. L. Tholence, and R. Tournier, J. Phys. (Paris) **39**, C6-922 (1978).

[17] F. Holtzberg, J. L. Tholence, H. Godfrin, and R. Tournier, J. Appl. Phys. **50**, 1717 (1979).

[18] G. Zibold, J. Phys. F **8**, L229 (1978).

[19] M. Hardiman, Bull. Am. Phys. Soc. **25**, 176 (1980).

[20] E. L. Nagaev, Fizika magnitnykh poluprovodnikov (Physics of Magnetic Semiconductors), Nauka, Moscow (1979).

[21] S. Oseroff, M. Mesa, M. Tovar, and R. Arce, J. Appl. Phys. **53**, 2208 (1982).

[22] S. P. McAlister, J. Appl. Phys. **52**, 1769 (1981).

[23] J. Ferré and J. Rajchenbach, J. Appl. Phys. **52**, 1697 (1981).

[24] H. Hiroyoshi and K. Fukamichi, J. Appl. Phys. **53**, 2226 (1982).

[25] P. A. Beck, J. Less-Common Met. **28**, 193 (1972).

[26] A. A. van der Giessen, J. Phys. Chem. Solids **28**, 343 (1967).

[27] B. V. B. Sarkissian, J. Phys. F **11**, 2191 (1981).

[28] B. R. Coles, B. V. B. Sarkissian, and R. H. Taylor, Philos. Mag. B **37**, 489 (1978).

[29] H. Maletta, J. Appl. Phys. **53**, 2185 (1982).

[30] M. Nauciel-Bloch and R. Plumier, Solid State Commun. **9**, 223 (1971).

[31] R. Plumier, M. Sougi, and M. Lecomte, Phys. Lett. A **60**, 341 (1977).

[32] R. Plumier, M. Sougi, M. Lecomte, and A. Miedan-Gros, Z. Phys. B **40**, 227 (1980).

[33] P. K. Baltzer, P. J. Wojtowicz, M. Robbins, and E. Lopatin, Phys. Rev. **151**, 367 (1966).

[34] M. K. Phani, J. L. Lebowitz, M. H. Kalos, and C. C. Tsai, Phys. Rev. Lett. **42**, 577 (1979).

[35] G. S. Grest and E. G. Gabl, Phys. Rev. Lett. **43**, 1182 (1979).

[36] A. Danielian, Phys. Rev. Lett. **6**, 670 (1961).

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