Spin-glass state in alloys of copper with manganese, iron, and cobalt

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The electrical resistivity, the magnetic susceptibility, and the anomalous Hall effect are investigated in alloys of copper with manganese, iron, and cobalt. The observed extrema of the kinetic characteristics are explained within the framework of "noise" theory. It is shown that spin-orbit interaction of the conduction electrons with localized moments of the impurity plays an essential role in the formation of a "spin-glass" state in alloys of copper with *d* elements.

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INTRODUCTION

Phase transitions and similar critical phenomena in macroscopic systems have in recent years attracted considerable attention from investigators. If "localization" of an isolated magnetic impurity in a nonmagnetic matrix leads to a Kondo effect, then the sign-variable interaction between impurities may insure "local magnetic order" and produce a "spin-glass" state. The view that has now developed[1] is that in systems with short-range sign-variable exchange interaction, the ground state is strongly degenerate ("frustration"); the critical dimension of such systems is four, which indicates the absence in them of a phase transition of the spin-glass type. For systems with Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction, the question remains open; doubly degenerate modes, either ferro- or antiferromagnetic, may exist in the substance.[2]

The classical approach to the theory of spin glasses[3,4] assumed as elements in the interaction either localized spins or gigantic superparamagnetic clusters. Such a representation precluded the simultaneous consideration of "Kondo" and spin-glass states. Statistical "noise" theory[5] made it possible to separate these states on the basis of the parameter $\gamma=\Delta_c/T_K^{\text{eff}}$, where Δ_c is the value of the interimpurity interaction and where T_K^{eff} is the effective temperature of the Kondo system. The approach developed made it possible to include in the treatment, in the role of spin glasses, such alloys as lanthanum-cerium, molybdenum-iron, copper-iron, copper-cobalt, etc.

EXPERIMENTAL TECHNIQUE

In this work we investigated alloys of copper with manganese, iron, and cobalt, over the concentration range, for the alloying impurities, from 0.48 to 3.71 at.%. The mixtures were melted in a vacuum induction furnace, from metals of purity not less than 0.997.

The Hall effect was measured by the standard method, described in Ref. 6. The specimens were foil of thickness 20-40 μm, annealed at 800 °C for one hour in a vacuum ~1.33 · 10⁻³ Pa, with subsequent cooling at rate ~ –100 deg/min. Use of such thick specimens made it possible to record a Hall emf signal of the order of tens of nanovolts in magnetic fields of induction from 0.04 to 0.1 T. The sensitivity of the apparatus for measurement of the Hall effect was $\sim 10^{-9}$ V. The Hall contacts were spot-welded by electric spark. Assymetry of the contacts was checked by a potentiometric method. Even effects (Nernst, Righi-Leduc, etc.) were eliminated by commutation of the current and of the direction of the magnetic field. The averaged values of the Hall emf were processed on a computer with confidence coefficient $P=0.95$. The relative error of the measurement of Hall emf did not exceed 5%.

The magnetic susceptibility was investigated on cylinder specimens of diameter 2.2-3.0 mm and length 10 mm, by the "compensated transformer" method, in alternating magnetic fields of frequency from 38 to 1200 Hz and amplitude from 0.1 to 5 G. The relative error of the measurement did not exceed 3%.

Measurements of the Hall emf and of the magnetoresistivity in strong magnetic fields ($1\ \mathrm{T} \leq B \leq 13\ \mathrm{T}$), at the boiling temperature of liquid helium, were made on the "Solenoid" apparatus of the Physical Institute of the USSR Academy of Sciences. For specimens, we used both foil of thickness 20-30 μm and a wire of diameter 0.2 mm. The relative errors of the measurement of Hall emf and of magnetoresistivity did not exceed 3%.

RESULTS AND DISCUSSION

We shall estimate the characteristic parameters of the copper-manganese, copper-iron, and copper-cobalt alloys using a modified noise theory.[5] For the parameter T_m, the temperature of the maximum of the resistivity in copper-iron alloys, we shall use the values obtained by us earlier.[7] On using the expressions for the noise temperature or the jump-over energy Δ_c,

$$\Delta_c=\frac{2T_m/i_0}{(s(s+1))^{1/2}/\pi i_0+\ln F_n(T_m/T_K)}, \tag{1}$$

$$F_n=\left(1+\sum_1^{n+1}\alpha_n\Gamma^n\right)\Big/\left(1+\sum_1^{n}\beta_n\Gamma^n\right), \tag{2}$$

where T_K is the Kondo temperature of the isolated im-

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purities, s is the spin of an impurity, and i_0, α_n, β_n, and F_n are the characteristic functions of the noise theory, and on using also the experimental values of T_m and retaining only the first two terms in the order Γ $(n=1)$, for $s=2-5/2$ we find that Δ_c in copper-manganese alloys varies from 0.7 to 18 K with increase of the manganese concentration from 0.15 to 3.17 at.%; the effective Kondo temperature T_K^{eff} remains practically unchanged and equal to $T_K=0.012$ K (see Table I). The alloy is a typical spin glass with $\gamma=\Delta_c/T_K^{eff}\gg 1$ (Ref. 5). In copper-iron alloys, a somewhat different picture is observed. With change of the iron concentration from 0.6 to 3.71 at.%, the energy of interimpurity interaction rises from 6.8 to 21 K, with substantial decrease of the effective Kondo temperature. Thus the comparability in size of the parameters Δ_c and T_K^{eff} in the alloy Cu + 0.6 at.% Fe is removed in the copper-iron alloys because of increase of the interimpurity interaction with increase of the iron concentration. At $C=0.6$ at.% Fe, the Cu + Fe alloy goes over to a spin-glass state $(\gamma>1)$. An interesting conclusion that follows from Table I is a theoretical basis for the absence of a maximum of the resistivity in copper-iron alloys at concentration $C_{Fe}<0.6$ at.%[7,8]; this follows directly from the comparability of Δ_c and T_K^{eff}. Equality of the parameter γ to unity, in the noise theory, imposes a prohibition on the spin-glass state in the system.

A transition from the Kondo state to the spin-glass state, just as in copper-iron alloys, occurs in copper-cobalt alloys with increase of the impurity concentration.[9] The ratio Δ_c/T_K^{eff} in the alloy Cu + 1.96 at.% Co is 5.3.

We shall calculate the **s-d** exchange integrals, the values of the RKKY interactions, and the effective Kondo temperatures of the systems by using the following relations of noise theory:

$$\begin{gathered}\Delta_{\mathrm{RKKY}}\approx CI^2 s(s+1)/\varepsilon_F,\\ kT_K^{eff}=D\exp(-1/n|I|),\\ T_K^{eff}=T_m\exp\{-[\pi^3/14\zeta(3)]T_m/\Delta_c\},\end{gathered}\tag{3}$$

where E_F is the Fermi energy, $D\sim 10^5$ K is the half-width of the conduction band, $n\approx 0.294$/atom is the density of states on the Fermi surface for copper, $\zeta(x)$ is a special function, and I is the exchange integral. We shall estimate the values of the internal molecular fields in the Kondo theory[10] according to a standardized $Q_S(S/S_0)$ curve:

$$S(H^i,T)=S_0Q_S(x),\quad x=2\mu_B H^i/kT,\tag{4}$$

where S_0 is the characteristic thermal emf at $T=0$. We note that the alloy Cu + 1.96 at.% Co is, with respect to the interaction parameters, close to the alloy Cu + 1.71 at.% Fe. The values obtained for the quantities Δ_c and H^i are compatible with those calculated by Schilling and Klein.[11,12] The relatively small change of the **s-d** exchange integrals in copper-manganese alloys over the range of manganese concentrations from 0.15 to 3.17 at.% is probably due to the insignificant change of the density of states on the Fermi surface for low alloys.

TABLE I. Interaction parameters in alloys of copper with manganese, iron, and cobalt, estimated by noise theory.

C, impurity at. %	T_m, K	T_K^{eff}, K	$\lvert I^{s-d}\rvert$, eV	Δ_c, K	Δ_{RKKY}, K	T_f, K	H^i, kOe
0.15 Mn	2.42 *	0.012 *	0.213 *	0.72	0.98	–	13.1
0.35 Mn	9.1 *	0.012 *	0.391 *	2.32	3.16	–	28.4
0.48 Mn	13.2	0.012	0.405	3.36	4.54	4.8	48.4
0.98 Mn	27.5	0.012	0.546	5.48	7.39	9.5	70.6
1.22 Mn	34.1	0.012	0.568	6.74	8.90	11.0	85.4
2.04 Mn	52.8	0.012	0.597	12.10	16.49	15.3	94.8
3.17 Mn	75.4	0.012	0.611	18.85	21.36	21.0	98.5
0.6 Fe	5.9	6.1	1.96	6.8	6.6	4.9	78.3
1.14 Fe	6.5	4.9	2.74	8.5	8.7	6.0	105.7
1.71 Fe	12.2 **	3.8	2.78	13.9	14.6	12.0	113.4
2.05 Fe	14.0 **	3.4	2.82	16.0	16.5	16.1	117.8
2.85 Fe	22.0	3.2	2.90	19.6	20.8	19.8	119.1
3.71 Fe	24.0	2.9	2.96	21.0	22.4	23.2	121.0
1.96 Co	12.1	3.2	2.85	17.1	19.4	24.6	114.0

*According to data of Ref. 9.

**According to data of Ref. 8.

As was indicated above, the characteristic temperatures T_m of the maximum of the electrical resistivity and T_f of spin-glass "freezing" were determined experimentally. Figure 1 shows the concentration dependences $T_f(C)$ and $T_m(C)$ for the copper-manganese and copper-iron alloys. The dependences of the characteristic temperatures on the impurity concentration can be described by the laws:

$$\begin{gathered}T_m\sim C\quad\text{at}\quad C_{\mathrm{Mn}}<6\ \text{at.}\%,\\ T_m\sim C^\alpha\quad\text{for}\quad 6\ \text{at.}\%\leqslant C_{\mathrm{Mn}}\leqslant 28\ \text{at.}\%,\quad 0.5\leqslant\alpha\leqslant 0.7.\end{gathered}\tag{5}$$

$$\begin{gathered}T_f\sim C\quad\text{for}\quad C_{\mathrm{Mn}}<3\ \text{at.}\%,\\ T_f\sim C^{0.5}\quad\text{for}\quad 3\ \text{at.}\%\leqslant C_{\mathrm{Mn}}\leqslant 16\ \text{at.}\%.\end{gathered}\tag{6}$$

For copper-iron alloys, $T_f\sim C$ at iron concentration $C_{Fe}\lesssim 1.5$ at.%. At larger iron content, the linear law if not obeyed. For the parameter T_m in Cu + Fe alloys, the directly proportional relation $T_m=kC_{Fe}$, where k is a constant, is satisfied at iron concentration $C_{Fe}\lesssim 3$ at.%. Relations $T_f(C)$ and $T_m(C)$ of the type (5) and (6) correspond to those predicted in the classical theory of spin glasses.[13] The deviation of the curves from a linear law at large concentrations of the impurity apparently indicates the formation of superclusters, containing more than two atoms. It is noteworthy that in all the alloys investigated, $T_m>T_f$; this is a distinguishing trait of spin glasses with RKKY interaction. The inset in Fig. 1 shows the temperature dependence of the magnetic susceptibility of the alloy Cu + 1.96 at.% Co, taken at frequency 120 Hz at magnetic-field amplitude $B=0.1$ G. On the $\chi(T)$ curve at temperature $T_f\sim 24$ K, the maximum that is characteristic of a spin glass is observed. We note that for an alloy of the same composition, there are observed on the curve of EPR signal intensity vs temperature, at $T\sim 30$ K, anomalies characteristic of a spin-glass state.[18] With decrease of the frequency of the alternating external magnetic field, the peak of the magnetic susceptibility becomes sharper, while its position on the temperature scale remains practically unchanged. With increase of the frequency of the external magnetic field to 10^6 kHz, the freezing point T_f shifts to the right by 1 - 2 degrees. Such behavior of the magnetic susceptibility with frequency is well de-

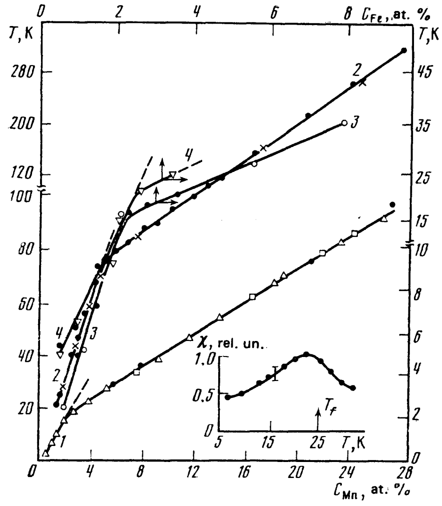

FIG. 1. Characteristic temperatures of copper-manganese and copper-iron alloys. "Freezing" points (T_f): 1, Cu-Mn; 3, Cu-Fe. Maxima of resistivity (T_m): 2, Cu-Mn; 4, Cu-Fe. ⊏, Ref. 14; △, Ref. 15; ×, Ref. 16; ○, Ref. 17. Inset: temperature dependence of the magnetic susceptibility of the alloy Cu + 1.96 at.%Co; f = 120 Hz, B = 0.1 G.

scribed by Fulcher's law[19,20]:

$$T_f=T_0+E_a/k(\ln\nu_0-\ln\nu), \tag{7}$$

where T_0 is the "true" freezing point of the spin glass, $1/\nu_0=\tau_0$ is the relaxation time, and E_a is the activation energy of the system. For example, for the alloy Cu + 8 at.% Mn, $T_0=36.5$ K, $\tau_0=10^{-13}$ s, $E_a/k=71$.

On the temperature dependences $\chi(T)$ of the magnetic susceptibility and $E^H(T)$ of the Hall emf, for the alloys investigated, maxima were observed at temperatures that differed from each other by 1 – 3 degrees.[7,18] Since the Hall emf has the form

$$E^H=R_0(1+4\pi\chi)H^z+R^a4\pi\chi^aH^z, \tag{8}$$

the maxima of E^H are probably dependent on the anomalous part of the magnetic susceptibility χ^a. This can be easily shown by use of the expressions for the anomalous Hall coefficient[21]:

$$R^a=\lambda A[V^2+I^2B_1(T,s)+I^3B_2(T,s)], \tag{9}$$

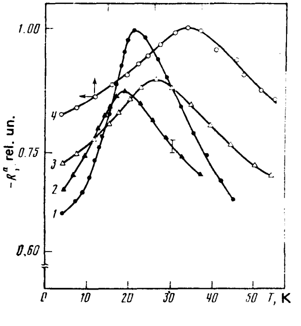

FIG. 2. Temperature dependence of anomalous Hall-effect "constant" for alloys: 1, Cu + 6.08 at.%Mn; 2, 2.85 at.%Fe; 3, 1.96 at.% Co; 4, 22.1 at.% Mn.

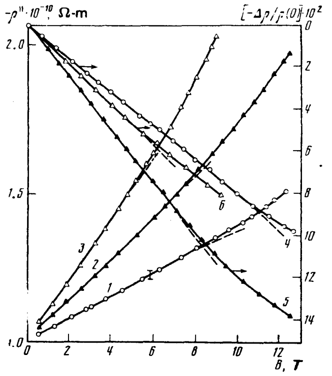

FIG. 3. Isothermal field dependence of the Hall resistivity and of the transverse magnetoresistivity of alloys (T = 4.2 K): 1 and 4, Cu + 6.08 at.% Mn; 2 and 5, 2.85 at.% Fe; 3 and 6, 1.96 at.% Co.

$$R^a=\sigma_{xy}^{(1)}/4\pi\sum_n\langle s_n{}^z\rangle\sigma_{xx}{}^2, \tag{10}$$

where A is a constant independent of the impurity concentration C and of the temperature; λ is the spin-orbit interaction parameter; $R_1(T,s)$ and $B_2(T,s)$ are the characteristic functions that determine the Hall effect in the Kondo systems; and σ^1_{xy} is the asymmetric part of the electrical conductivity tensor that is linear in the spin-orbit interaction. Since B_1 and B_2 are independent of the concentration of the magnetic impurity for low-alloy systems, R^a also is independent of C. This is due to the fact that $\sigma^1_{xy}/\sigma^2_{xx}\sim C$ but also the magnetization $\langle s^2_n\rangle\sim C$. Thus finally, $E^H\sim\chi^a\sim C$. Proportionality of E^H to the concentration of the magnetic impurity is observed experimentally.[7,22] The $\chi(T)$ and $E^H(T)$ laws obtained made it possible to construct graphically the temperature behavior of the anomalous Hall-effect constant (Fig. 2), on which maxima are clearly observed at the points of transition to a spin-glass state. The relative value of the maxima of $\chi(T)$ reaches 30-35%. This fact indicates the determinative role of spin-orbit interaction in the formation of a spin-glass state in low alloys of copper with iron, manganese, and cobalt.

The isothermal variations of the impurity Hall resistivity and of the transverse magnetoresistivity of the alloys Cu + (Mn, Fe, Co), in magnetic fields of induction up to $B=13$ T, are shown in Fig. 3. The transverse magnetoresistivity of all the alloys investigated is negative. The value of $\Delta\rho/\rho(0)$ at $B=13$ T and $T=4.2$ K reaches a maximum value ~14% in the alloy Cu + 2.85 at.% Fe. While the magnetoresistivity of the alloy Cu + 6.08 at.% Mn at $B\gtrsim 8$ T shows a tendency toward "saturation," at larger impurity content, in strong magnetic fields, $d\rho_1/dB$ is positive[23]; this is probably due to the clearly expressed exchange anisotropy of the system copper-manganese.[24] In copper-iron and copper-cobalt alloys, a tendency of the magnetoresistivity to saturate shows up in magnetic fields $B\gtrsim 5-8$ T; this is apparently caused by gigantic magnetic clusters.[8] The field dependence of the Hall resistivity at $B=5$ T indicates predominance of the mechanism of Béal-Monod and Weiner[25] in the scattering of conduction electrons by localized magnetic moments of the impurity.

CONCLUSION

Calculation of the interaction parameters of alloys of copper with manganese, iron, and cobalt, in noise theory, has substantiated the possibility of separating the systems into typical spin glasses, for example copper-manganese, and atypical spin glasses, where the parameter $\gamma = \Delta_c/T_K \lesssim 1$. The absence of a maximum of the electrical resistivity in copper-iron alloys for $C_{Fe} < 0.6$ at.% is explained by the comparability of the parameters of interimpurity interaction with the value of the effective temperature of the Kondo system. The experimental results on the concentration dependence of the characteristic temperatures in alloys of copper with manganese and iron are explained within the framework of the classical theory of spin glasses. In strong magnetic fields, of induction up to $B = 13$ T, a "spin component" of the anomalous Hall effect is separated out.

The observed extrema of the anomalous Hall-effect constant at temperatures close to the freezing point of the spin glass indicate the determinative role of spin-orbit interaction in the formation of a spin-glass state in low alloys of copper with the *d* metals (Fe, Mn, Co).

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