THE CONCENTRATION MAGNETIC PHASE TRANSITION IN $Cu[Cr_{2-x}Gd_x]S_4$ ($0.0\leq x\leq 1\cdot 0$)

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The investigation results of temperature dependence of paramagnetic susceptibility of new magnetoordered system $Cu[Cr_{2-x}Gd_x]S_4$ ($0.0\leq x\leq 1\cdot 0$) are carried out. It is established, that the concentration phase transition ferromagnetic-ferrimagnetic takes place at x=0.2 and Curie temperature essentially decreases with increase of gadolinium concentration.

The obtaining and investigation of physic properties of new magnetic materials with favorable parameters are the main actual tasks in the region of solid body physics. In the given paper the experimental results on phase transition ferromagnetic-ferrimagnetic in the system $Cu[Cr_{2-x}Gd_x]S_4$, firstly synthesized by us, are given. The data on synthesis and investigation results of some kinetic and magnetic properties of this system had been presented by us earlier in the ref. [1-3].

According to ref [2] the $Cu[Cr_{2-x}Gd_x]S_4$ system in interval ($0.0\leq x\leq 1\cdot 0$) has the spinel structure and lattice parameter decreases linearly in practices with the increase of gadolinium concentration.

The paramagnetic susceptibility of homogeneous and one-phase samples was investigated in temperature interval 200K≤T≤700K by Faraday method. It is established, that system $Cu[Cr_{2-x}Gd_x]S_4$ is ferromagnetic material at $x\leq 0.2$, and it is ferromagnetic one at big concentrations of gadolinium (x=0.4; 0.6; 1.0). Curie paramagnetic temperature (θ_p) for each composition was defined from the temperature dependence of paramagnetic susceptibility in $\chi^{-1}=f(T)$ coordinates, by extrapolation to temperature axis.

Curie ferro-(ferri-) magnetic temperature (T_c) was defined on strict decay of the signal from the differential coil at sample heating. The corresponding data are given in the table.

Table
Curie temperatures (T_c and θ_p) and electrical conduction (σ) of $Cu[Cr_{2-x}Gd_x]S_4$ system.

x	T_c,K	θ_p,K	σ, ohm^{-1}, cm^{-1} (300K)	ΔT_c,K	$\Delta T_c/\Delta x$
0	417	429	104	-	-
0.2	372	388	15.4	-45	225
0.4	340	355	1.80	-32	160
0.6	306	318	0.99	-34	170
1.0	245	259	0.51	-61	152.5

As it is followed from the table, the ferro- (ferri-) magnetic Curie temperature essentially decreases with increase of gadolinium concentration. It is need to mention specially the concentration phase transition, revealed by us in $Cu[Cr_{2-x}Gd_x]S_4$ system: data on the susceptibility show, that system, investigated by us is ferromagnetic at $CuCr_2S_4$, i.e. the ferromagnetic order, which is suitable for $x\leq 0.2$ (fig. curve 1) is saved at these concentrations. The temperature dependence of paramagnetic susceptibility of cation-replaced compositions ($x>0\cdot 2$) is described by Neel hyperbola (fig. curve 2). The transition of temperature susceptibility from the linear one to hyperbolic one takes place at $x\approx 0.2$. This means, that concentration magnetic phase transition ferromagnetic→ferrimagnetic takes place at this gadolinium concentration.

The magnetic phase transition ferromagnetic-ferrimagnetic probably is connected with the amplification 180° negative anti-ferromagnetic super-exchange with the increase of gadolinium concentration. However, the unique mechanism of concentration phase transition ferromagnetic-ferrimagnetic in $Cu[Cr_{2-x}Gd_x]S_4$ can be established by only direct neutron-graphical or magnetic-resonance methods.

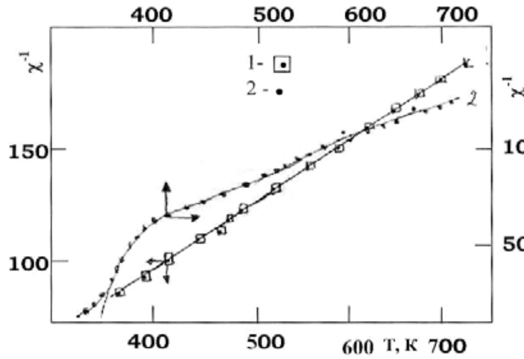

Fig. The temperature dependence of paramagnetic susceptibility of $Cu[Cr_{2-x}Gd_x]S_4$, 1 – x=0.2; 2 – x=0.4 system

Curie paramagnetic temperature (θ_p) for each composition was defined by the extrapolation of experimental dependence $\chi^{-1}=f(T)$. These data are given in the table.

As it follows from the table, that Curie paramagnetic temperature is just bigger, than ferro- or ferromagnetic one for all compositions. This circumstance supposedly connects with presence of magnetic short range ordering in paramagnetic region. The influence of the short range ordering on the paramagnetic temperature firstly was theoretically considered in ref [6]. According to ref [6], the short range ordering promotes to the fact, that dependence curve $\chi^{-1}=f(T)$ decays just slowly, than hyperbolic dependence, obtaining on Neel theory at the approximation to Curie point. Therefore, the correct ferrimagnetic Curie point is always situated just below the temperature, found by the way of extrapolation of hyperbolic temperature dependence $1/\chi$ to the value $(1/\chi)=0$ (i.e. below so-called “paramagnetic” Curie point). The short range ordering, appearing higher Curie point because of the correlations of the exchanged forces, significantly increases the entropy of the spin system (S). As the entropy monotone increases at the decrease of the sublattice magnetization, it is obviously, that curve inclination $S=S(M)$, i.e. the $(\partial S/\partial M)$ derivative, decreases at this. In the result the curve inclination $1/\chi^{-1}=f(T)$ decreases too, as

$$\frac{\partial(1/\chi)}{\partial T}=\frac{1}{M}\left(\frac{\partial H}{\partial T}\right)=-\frac{1}{M}\left(\frac{\partial S}{\partial M}\right) \qquad (1)$$

The decrease of Curie temperature (T_c) with increase of the gadolinium concentration can be explained by the presence of the negative (anti-ferromagnetic) exchange, parallel with ferromagnetic 90° cation exchange and its amplification with the increase of gadolinium concentration.

In principle, T_c decrease at the Cr^{3+}-Gd^{3+} displacement can be explained by the weakness of positive indirect exchange by conduction electrons. Indeed, as was shown by us in the ref [3], the system electrical conduction $Cu[Cr_{2-x}Gd_x]S_4$ decreases with the increase of the gadolinium concentration. If we suppose, that this decrease mainly takes place because of the concentration of charge carriers, then it is naturally to expect the correlation between Curie temperature and carriers' concentration.

According ref [7] Curie ΔT_c temperature shift because of the charge carriers in degenerate magnetic semiconductors at small concentrations of the carriers is defined by the expression:

$$\Delta T_c = (\frac{\pi}{6})^{2/3} J_{s-d} \cdot S \cdot \nu / a_0 q_0 \quad , \tag{2}$$

where J_{s-d} is energy of *s-d* exchange, $\nu = \frac{n}{N}$ is carriers' number falling at one magnetic atom (*n* and *N* are concentrations of charge carriers and magnetic ions in volume unity correspondingly); a_0 is lattice parameter; $q_0 = \sqrt{2m^* \cdot J_{S-d} S}$, *m** is carriers' effective mass.

As it is seen, T_c shift is linear on concentration at small carriers' concentration. The dependence ΔT_c on ν becomes weak at the following *n* increase:

$$\Delta T_c = 0{,}4\sqrt{T_c^0 \cdot J_{s-d}} \cdot S \cdot \nu \tag{3}$$

(T_c is Curie temperature in the absence of charge carriers), the transition from the linear increase (2) to the root increase takes place at the following concentrations:

$$\nu \sim \frac{J}{W} \sim \frac{ZT_c^0}{S \cdot W} \tag{4}$$

where *Z* is number of the nearest neighbors; *W* is band width, on which the conduction is carried out. As it follows from the formulas (2) and (3) T_c increases, that is in the quality agreement with our data in all cases with the increase of the concentration of charge carriers. However, according to ref. [8], T_c shift in cuprum selen-chrome spinels is impossible to quantitatively explain only by change of carriers' concentration, as, since Curie temperature of $CuCr_2Se_4$ shifts on 346K at the change of carriers' concentration on one order, whereas, the shift, estimated on theory [7] is only ~50K. As $CuCr_2S_4$ and $CuCr_2Se_4$ are isostructure compounds and both are degenerate semiconductors, then probably T_c shift is caused by exchanges of RCCI type and negative super-exchange of anions because of charge carriers and in $CuCr_{2-x}Gd_xS_4$ system.

Thus, the concentration magnetic phase transition ferromagnetic-ferrimagnetic in $Cu[Cr_{2-x}Gd_x]S_4$ at $x \approx 0{\cdot}2$ probably is caused by amplification of anti-ferromagnetic super-exchange cation-anion-cation, and Curie temperature decrease is caused by joint action of above mentioned super-exchange and indirect exchange through charge carriers at Cr^{3+}-Gd^{3+}replacement.

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$Cu[Cr_{2-x}Gd_x]S_4$ ($0.0 \le x \le 1{\cdot}0$) SİSTEMİNDƏ MAQNİT FAZA KEÇİDİ

İşdə maqnitnizamlı, yeni, $Cu[Cr_{2-x}Gd_x]S_4$ ($0.0 \le x \le 1{\cdot}0$) sisteminin paramaqnit qavrayıcılığının temperatur asılılığına dair nəticələr nəzərdən keçirilir. Müəyyən olunmuşdur ki, qadoliniumun konsentrasiyasının artması ilə Küri temperaturu ciddi azalır və x=0.2- də ferromaqnit-ferrimaqnit maqnit faza keçidi baş verir. Bu keçid qadoliniumun konsentrasiyasının artması ilə kation–anion–kation antiferromaqnit ifrat mübadiləsinin güclənməsi ilə izah olunur.

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КОНЦЕНТРАЦИОННЫЙ МАГНИТНЫЙ ФАЗОВЫЙ ПЕРЕХОД В $Cu[Cr_{2-x}Gd_x]S_4$ ($0.0 \le x \le 1{\cdot}0$)

Приводятся результаты исследования температурной зависимости парамагнитной восприимчивости новой магнитоупорядоченной системы $Cu[Cr_{2-x}Gd_x]S_4$ ($0.0 \le x \le 1{\cdot}0$) . Установлено, что при x=0.2 имеет место концентрационный фазовый переход ферромагнетик - ферримагнетик и с увеличением концентрации гадолиния температура Кюри существенно уменьшается.

Received: 10.10.06