Influence of Cu, Ga and Au Dopants and Technology Conditions on the Magnetic Interactions in HgCr$_2$Se$_4$ Single Crystals

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For single crystals HgCr$_2$Se$_4$ doped by nonmagnetic Cu$^+$, Au^{2+} and Ga^{3+} ions and single crystals of HgCr$_2$Se$_4$ matrix growing in different synthesis conditions both the dc and ac magnetic susceptibility as well as the magnetization have been measured. As it follows from the analysis of the obtained results, paradoxically, the dopants strengthen the long range magnetic interactions of the ferromagnetically ordered single crystals under study, evidenced by the higher values of the ordering temperature in comparison with those ones for pure matrix. An influence of the technological processes connected with deficiency and/or excess of Hg on the long range magnetic interactions was not observed.

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1. Introduction

It is well known that in the ferromagnetic spinel compound HgCr$_2$Se$_4$ (where T_C and θ_{CW} are of order of 100 K and 150 K, respectively) the divalent Hg^{2+} ions occupy tetrahedral positions only, whereas trivalent Cr^{3+} ions are located only in octahedral positions. Ferromagnetic coupling of the magnetic moments in this compound is realized via superexchange magnetic interactions [1]. It is also well known that the full substitution in the tetrahedral positions of the divalent Hg^{2+} ions by the monovalent, e.g. Cu$^+$ ions, leads to both the mixed valence of the chromium ions (i.e., Cr^{3+} and Cr^{4+} in the ratio 1:1) and to the appearance and domination of another mechanism of the magnetic coupling giving very strong ferromagnetic coupling, namely double exchange interaction. In this case both T_C and θ_{CW} become of order of 400 K [2, 3]. However, the substitution of the Hg^{2+} ions by the trivalent ions, e.g. Ga^{3+}, leads to the collinear antiferromagnetism being the result of the superexchange interaction only, with the concentration of Ga^{3+} ions up to 50%.

The one aim of this work is to investigate how the substitution of Hg^{2+} ions by Cu$^+$, Au^{2+} and Ga^{3+} ones influences on the magnetic interactions in the sample, when the concentration of the substituting ions is lower than 10%. Another aim concerns the influence of technology conditions on magnetic properties in the sample.

2. Experimental

Using the chemical transport method the single crystals of HgCr$_2$Se$_4$ doped with gold (2%), copper (7%) and gallium (8%) were obtained. Additionally, the two non--doped single crystals of HgCr$_2$Se$_4$ were prepared in different synthesis conditions. One of them was synthesized with the deficiency of Hg (this procedure produces vacancies), another one with Hg excess (this procedure brings to elimination of vacancies).

For all crystals under study both the dc and ac magnetic susceptibility were measured in the temperature range of 4.2–250 K. The dc measurements were carried out with the use of the Cahn magnetic balance and SQUID susceptometer, whereas the ac measurements were done with the aid of the Lake Shore 7225 magnetometer.

3. Results and discussion

Figure 1 presents the magnetization isotherms for HgCr$_2$Se$_4$ containing 2% Au. As it follows from this picture at the liquid helium temperature the sample magnetizes very easily and reaches the magnetic saturation, but the value of the saturation magnetic moment per formula unit is equal to 5.55 μ_B. Let us note that the theoretical value of the saturation magnetic moment per formula unit for HgCr$_2$Se$_4$ is equal to 6 μ_B. On the other hand, at the temperature of 70 K, which is here much below the

Curie temperature (T_C = 110 K), magnetizing processes are already not so easy. It testifies to that the introducing Au^{++} ions in place of Hg^{++} ions into $HgCr_2Se_4$ matrix causes the strengthening of the antiferromagnetic coupling with the simultaneous weakening of the ferromagnetic one in superexchange magnetic interactions between magnetic moments localized on the chromium ions. In Fig. 2, which presents the temperature dependences of both zero-field cooled (ZFC) and field cooled (FC) dc magnetic susceptibility for $HgCr_2Se_4$+2% Au and $HgCr_2Se_4$+8% Ga, the small hysteresis of those dependences is quite good visible, especially for the sample doped with Ga. Such hysteresis points to the existence of a frustration of magnetic coupling in these samples. Figure 3 presents the dc magnetic susceptibility and its reciprocal vs. temperature for all doped single crystals under study. The fitting procedure of the Curie–Weiss law [4, 5] revealed (see Table) the paramagnetic temperature independent contributions of the magnetic susceptibility both for $HgCr_2Se_4$+2% Au. and $HgCr_2Se_4$+8% Ga as well as a diamagnetic one both for $HgCr_2Se_4$+7% Cu and $HgCr_2Se_4$ matrixes with deficiency and excess of Hg.
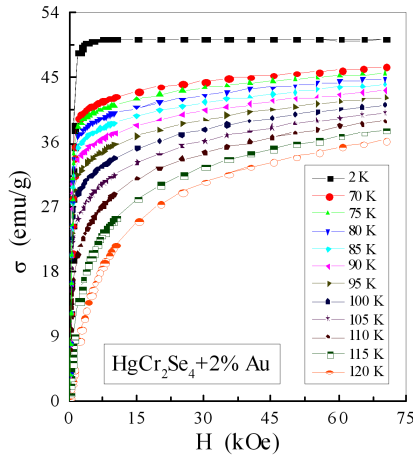

Fig. 1. Magnetization σ versus magnetic field H for $HgCr_2Se_4$ containing 2% Au.

The greatest value of T_C obtained at the external magnetic field equal to 1156 Oe is for the sample with Cu and somewhat lower one for the sample with Ga (see Table). On the other hand, Fig. 4 presents the temperature dependences of the ac magnetic susceptibility taken at the alternating magnetic field equal to 1 Oe. From this figure it follows that the values of T_C for compounds with Au and Ga are little lower in comparison with the ones obtained at 1156 Oe. It confirms the strong ferromagnetic coupling in the spinels under study because the stronger magnetic field shifts the ordering temperature to the higher temperatures. Figure 4 shows also that the imaginary part of ac magnetic susceptibility for crystal containing Au is practically equal to zero, whereas, for the sample with Cu both the real and imaginary part of
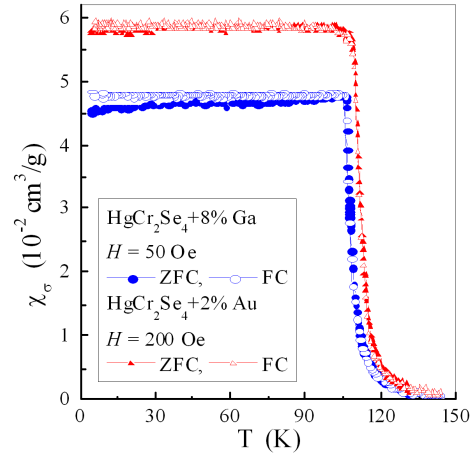

Fig. 2. ZFC and FC dc magnetic susceptibility χ_σ versus temperature T for $HgCr_2Se_4$+8% Ga and $HgCr_2Se_4$ + 2% Au.
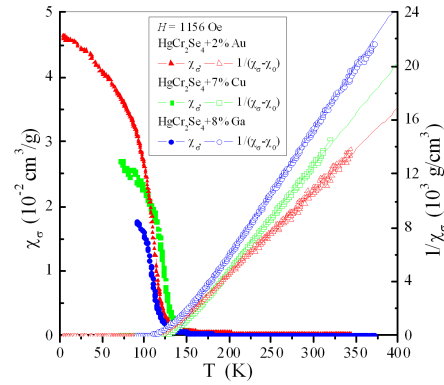

Fig. 3. Dc magnetic susceptibility χ_σ and its reciprocal $1/(\chi_\sigma - \chi_0)$ versus temperature T for $HgCr_2Se_4$+2% Au, $HgCr_2Se_4$+7% Cu and $HgCr_2Se_4$+8% Ga. The solid lines, $(T - \theta_{CW})/C_\sigma$, indicate the Curie–Weiss behavior after fitting, which includes all temperature independent contributions of magnetic susceptibility χ_0.

TABLE

The most important magnetic parameters. C_σ is the Curie constant, χ_0 is the temperature independent component of magnetic susceptibility, T_C is the Curie temperature and θ_{CW} is the paramagnetic Curie–Weiss temperature. Symbols (1) and (2) denote the samples with deficiency and excess of Hg.

Spinel	C_σ [K cm³/g]	χ_0 [cm³/g]	T_C [K]	θ_{CW} [K]
$HgCr_2Se_4$(1)	1.150×10^{-2}	-9.744×10^{-6}	110	133
$HgCr_2Se_4$(2)	1.384×10^{-2}	-9.749×10^{-6}	110	125
$HgCr_2Se_4$+2%Au	1.616×10^{-2}	2.035×10^{-4}	121	127
$HgCr_2Se_4$+7%Cu	1.407×10^{-2}	-1.014×10^{-5}	125	135
$HgCr_2Se_4$+8%Ga	1.069×10^{-2}	2.455×10^{-5}	119	136

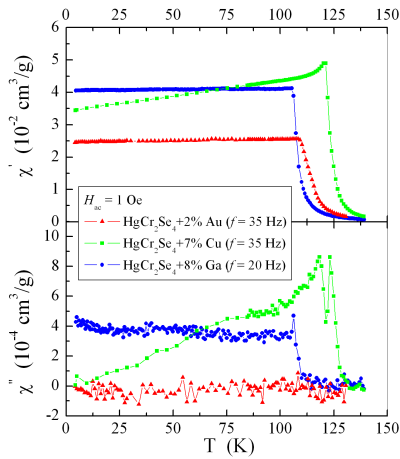the dynamic magnetic susceptibility are relatively higher and reveal anisotropic behavior.

Fig. 4. The real χ' and imaginary χ'' parts of ac magnetic susceptibility vs. temperature T at $H_{ac} = 1$ Oe for: $HgCr_2Se_4+2\%$ Au, $HgCr_2Se_4+7\%$ Cu and $HgCr_2Se_4+8\%$ Ga.
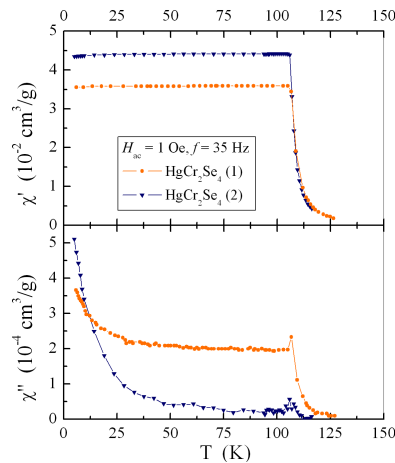

Fig. 5. Comparison of the temperature dependences of the ac magnetic susceptibilities for $HgCr_2Se_4$ (1) and $HgCr_2Se_4$ (2) with deficiency and excess of Hg, respectively.

Figure 5 gives the comparison of the ac magnetic susceptibility for the single crystals of $HgCr_2Se_4$ contain-

ing both deficiency and excess of Hg. In general, the technological processes do not influence on the ordering temperature (see Table), remaining the unchanged long-range magnetic interactions. Only in case of the excess of Hg a small weakness of the short-range interactions, evidenced by the reduction of the Curie–Weiss temperature, is observed.

The most important magnetic parameters are presented in Table. Taking into account the experimental results described above and the values of the magnetic parameters one can say that: (i) dopant substitution of Au, Cu and Ga ions in place of Hg^{2+} ones causes the increase of T_C in comparison with T_C of pure $HgCr_2Se_4$ while the values of θ_{CW} remain almost constant, (ii) with an increase of dopant content the Curie constant decreases, entailing a decrease of the effective magnetic moment according to the formulae $\mu_{eff} = 2.83\sqrt{MC_\sigma}$ (where M is the molar mass), (iii) the external magnetic field strongly influences on T_C, shifts it to higher temperatures, and (iv) small ZFC and FC splitting of the magnetic susceptibility suggest an occurrence of the weak frustration of magnetic interactions below the ordering temperature, probably caused by the structural and spin defects.

4. Conclusions

In all single crystals under study one deals with the randomness of introducing either dopants or defects into a $HgCr_2Se_4$ matrix. This randomness is guaranteed for a system below the percolation threshold. Generally, dopants substitution of Au, Cu and Ga influences mainly on the long range interactions in the compounds under study.

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