Neutron diffraction and magnetic studies of the $Hg_{1-x}Zn_xCr_2Se_4$ system

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Neutron diffraction and magnetic studies of polycrystalline samples of the $Hg_{1-x}Zn_xCr_2Se_4$ $(0 \leqslant x \leqslant 1)$ system in weak magnetic fields were performed for the first time. It was established that the sample with $x = 0.3$ has a spin-glass-type magnetic structure. A correlation is found between the magnetic and neutron diffraction data.

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Compounds of the $Hg_{1-x}Zn_xCr_2Se_4$ system are magnetic semiconductors with a normal spinel structure, whose lattice parameter depends linearly on the concentration of zinc ions in accordance with the Vegard law.[1] An interest in this system has arisen because a transition from the ferromagnetic state[2] ($HgCr_2Se_4$, $T_c = 120$ K) to the antiferromagnetic with a spiral structure[3] ($ZnCr_2Se_4$, $T = 20$ K) occurs in it as a result of substituting zinc ions for mercury ions. It was reported in Ref. 2 that in an external field $H = 9$ kOe this transition occurs abruptly when the zinc content is $x = 0.5$.

We have synthesized and studied polycrystalline samples of this system. The x-ray and neutron diffraction analyses, performed at $T = 293$ K, confirmed the composition and the presence of only the spinel phase (Hg^{2+} and Zn^{2+} in the tetrahedral A-positions, Cr^{3+} in the octahedral B-positions).

We investigated for the first time the magnetic properties of the system in a weak magnetic field ($H = 30$ Oe). Figure 1 shows the temperature dependence of the magnetization σ that was measured by using a vibrating magnetometer. At $x = 0.2$ the curves have a shape characteristic of ferromagnets and at $x = 0.4$ they have a shape characteristic of antiferromagnets. The temperature dependence of magnetization for $x = 0.3$ has features characteristic of spin glasses. Figure 2 shows the temperature dependence of σ in different external magnetic fields for compositions with $x = 0.3$ and $x = 0.4$. We can see in the figure that an increase in the field leads to a displacement of the maximum toward the lower temperatures, and fields of 1.71 and 6.4 kOe, respectively, transform the samples with $x = 0.3$ and 0.4 into the ferromagnetic state, i.e., the magnetic field influences the magnetic ordering.

To determine the magnetic structure as a function of composition, we performed a neutron diffraction analysis of the samples without applying external magnetic field. The studies were conducted at IRT Moscow Engineering-Physics Institute. The neutron diffraction patterns (at $T = 4.2$ K) of the compounds with $x = 1.0$–0.4 showed the presence of superlattice reflections (satellites) corresponding to spiral magnetic order-

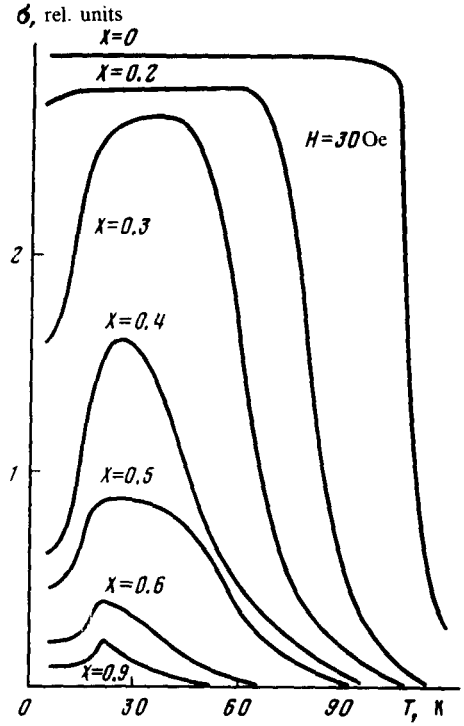

FIG. 1. Temperature dependence of the magnetization σ.

ing. It was established that a decrease of the zinc content produces satellite broadening and asymmetry which increase with decreasing x.

The $Hg_{0.7}Zn_{0.3}Cr_2Se_4$ sample turned out to have a broad, diffuse maximum in-

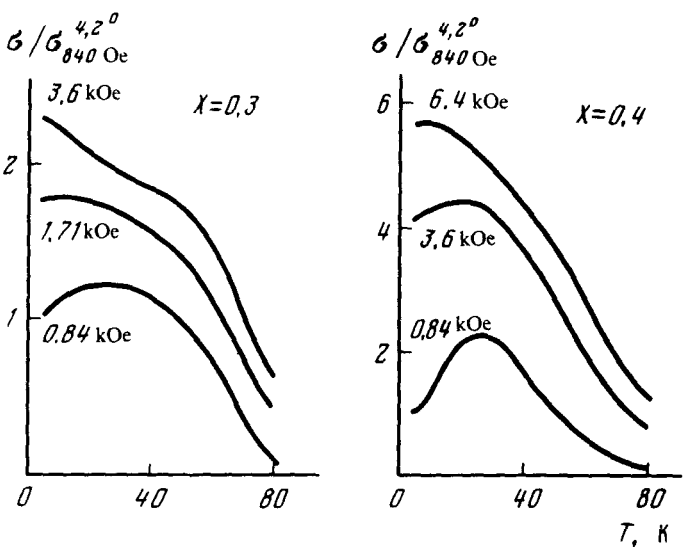

FIG. 2. Temperature dependence of σ in different magnetic fields for $x = 0.3$ and $x = 0.4$.

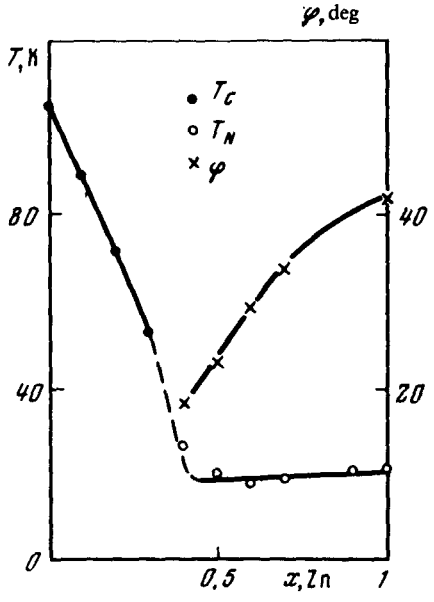

FIG. 3. Dependence of the angle of the magnetic spiral and of the phase transition temperature on the composition.

stead of the 111^- and 111^+ satellites, which indicates the presence of a short-range magnetic order. An analysis of the neutron diffraction patterns showed that the short-range order is equal to ~ 60 Å.

Figure 3 shows the dependence of the angle of the magnetic spiral and of the phase transition temperature T on the composition.

We can draw from the obtained data the following conclusions concerning the magnetic structure and its behavior as a function of the external magnetic field for the samples of the given chalcospinel system.

At zero external magnetic field the magnetic structure breaks up in the region with different spiral periods in the samples of the $Hg_{1-x}Zn_xCr_2Se_4$ system as the mercury concentration increases; this is indicated by a broadening of the satellites in the neutron diffraction patterns. These regions apparently appear because the Hg^{2+} ions, surround the Cr^{3+} ions nonequivalently and their size and number depend on their concentration. The $Hg_{0.7}Zn_{0.3}Cr_2Se_4$ sample has a spin-glass-type magnetic structure, since only a short-range magnetic order appears in the neutron diffraction pattern, and the temperature dependence of the magnetization has a shape characteristic of spin glasses. At concentrations $x = 0.3$ the exchange interactions responsible for ferromagnetism are dominant, and only the ferromagnetic ordering peaks are present in the neutron diffraction patterns of these compositions.

An application of external magnetic field, which influences the ordering and temperature-dependent behavior of the sample, can convert the sample from the antiferromagnetic state to the ferromagnetic. The difference between the critical concentration determined by us, at which the ferro-antiferromagnetic transition occurs, and that

determined in Ref. 2 is probably attributable to the fact that the measurements in Ref. 2 were performed in comparatively high magnetic fields ($H = 9$ kOe).

In conclusion, we note that both in the $Hg_{1-x}Zn_xCr_2Se_4$ system and the $Cd_{1-x}Zn_xCr_2Se_4$ system, previously investigated by us,[4] the variation of the magnetic structure of the composition occurs in a similar ("flowing") manner; however, the critical zinc concentration in these systems is different. For the mercury system this concentration is equal to 0.3, and for the cadmium system, it is 0.4. The lattice parameters in these systems are the same and the cation in the tetrahedral A-position of the chalcospinel apparently plays the major role in this difference.

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