On the Two-Phase Magnetic State in a $Cu_xZn_{1-x}Cr_2Se_4$ Cation-Substituted Chalcogenide Spinel

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Abstract—The region of the concentration magnetic phase transition in a $Cu_xZn_{1-x}Cr_2Se_4$ chalcogenide spinel in which the substituted ion concentration x smoothly varies from 0.1 to 0.2 with a step of 0.02 is thoroughly investigated. An anomalous behavior of the Curie temperature is observed. This anomaly is associated with the nucleation of ferromagnetically ordered microregions in the vicinity of Cr ions with an intermediate valence and subsequent long-range magnetic ordering at a critical Cu concentration in the range $0.12 < x_c < 0.14$. The possible coexistence of ferro- and antiferromagnetism in the same temperature range is revealed. © *2001 MAIK "Nauka/Interperiodica".*

1. INTRODUCTION

Investigation of cation-substituted chalcogenide spinels $Cu_xZn_{1-x}Cr_2Se_4$ has been attracting attention for a long time due to the existence of various types of magnetic ordering in pure samples of $ZnCr_2Se_4$ (helicoidal antiferromagnetism with $T_N \sim 20$ K) and $CuCr_2Se_4$ (ferromagnetism with $T_C \sim 400$ K). This permits one to observe the consequences of competitive exchange interactions in solid solutions with different degrees of substitution [1–4]. Moreover, since the ionic radii of Zn and Cu are very close in magnitude, it is possible to obtain a continuous series of single-phase samples for all x values. Apart from the magnetic properties, the electrical properties are also of interest because the conductivity changes from the semiconductor to the metallic type as Zn atoms are replaced by Cu atoms. Earlier [4], it was shown that ferromagnetism manifests itself in the studied compound at $x \sim 0.2$ and T_C smoothly increases as the copper concentration increases. It was also found that the compounds with $x < 0.1$ are antiferromagnets. However, the mechanism of the transition from noncollinear antiferromagnetism (NCAF) to ferromagnetism (FM) remained unclear. The objective of the present work was to thoroughly investigate the region of the concentration magnetic phase transition. For this purpose, we measured and analyzed the temperature and magnetic-field dependences of the magnetization and magnetic susceptibility of $Cu_xZn_{1-x}Cr_2Se_4$ polycrystalline samples in the concentration range 0.1–0.2 with a step of 0.02.

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

The samples of $Cu_xZn_{1-x}Cr_2Se_4$ solid solutions used were powder polycrystals prepared by solid-phase synthesis in evacuated silica tubes. The synthesis procedure was described in detail in [5]. Samples 1–6 had concentrations in the range $x = 0.1–0.2$ with a step of 0.02. Then, the samples were pressed for resistive measurements.

Measurements of the magnetization M were carried out on a vibrating-coil magnetometer with a superconducting solenoid in the temperature range 4.2–150 K. The real component of the magnetic susceptibility χ' was measured with a phase-sensitive detector by the inductance technique. In the latter case, the sample temperature was maintained and controlled using a flow-type glass cryostat with measuring coils fastened to its outer wall. The coils were exposed to air flow with the aim of reducing spurious temperature drift. Gaseous nitrogen or heated air flow over the sample allowed measurements in the temperature range 80–600 K.

The x-ray diffraction spectra of samples 2 and 3 revealed that these samples have single-phase spinel structures with the same lattice parameter within the limits of experimental error.

3. EXPERIMENTAL RESULTS

The measurements of the temperature dependence of the magnetic susceptibility showed that it is weak for samples 1 and 2 at $T > 80$ K. This is most likely due to

T_C, T_N, K
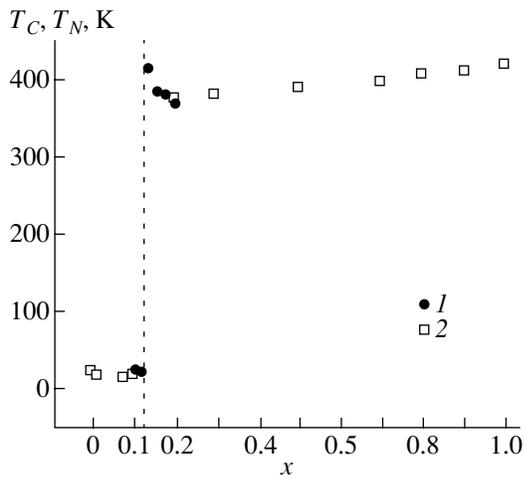
Fig. 1. Concentration dependence of the Curie temperature and Néel temperature: (*1*) our data and (*2*) the data taken from [4].

$M,$ emu/g
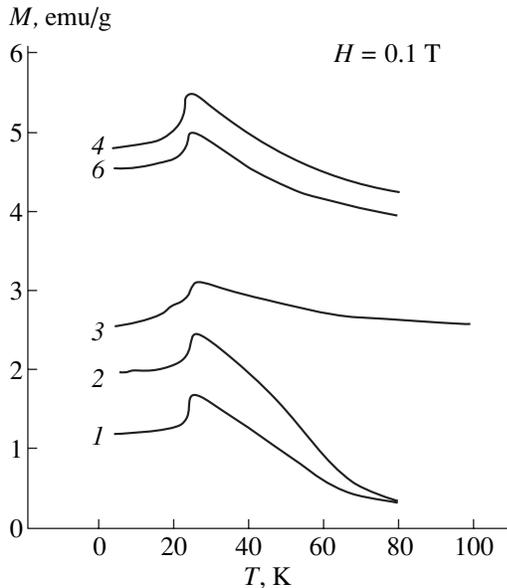
Fig. 2. Temperature dependences of the magnetization. The numerals at the curves correspond to the sample numbers.

the paramagnetic state. However, the measurements of $\chi'(T)$ for samples 3–6 yielded an unexpected result. In contrast to the linear decrease in T_C with a decrease in the copper concentration in the composition range covered, which was observed in [4], it was found that T_C rises nonlinearly and reaches a value of 415 K at $x = 0.14$ (Fig. 1), which is characteristic of pure $CuCr_2Se_4$.

The low-temperature behavior of the magnetization also exhibits salient features. The measurements of temperature dependences showed that the $M(T)$ curve has a peak at $T_N \sim 22$ K for all the samples, both with

and without magnetic transition at T_C. The essential difference between the $M(T)$ curves for ferromagnetic and nonferromagnetic samples is the following. As is seen from Fig. 2, the magnetization above T_N tends to zero for samples 1 and 2 and to a constant value of M_0 (different for all the samples) for the remaining samples.

Figures 3a–3c display magnetization curves for different temperatures. The character of the $M(H)$ curves at $T = 4.2$ K is the same for all samples. Only the saturation magnetization is different. For this reason, only the dependence for sample 3 ($x = 0.14$) is shown. It can be seen from this figure that the $M(H)$ curve has two pronounced features at $H \sim 1$ T and ~ 7 T, which correspond to the spin-reorientation transitions. The latter feature was also observed in [4].

Figures 3b and 3c present the magnetization curves for samples 2 and 3, which are similar in composition but drastically differ in their properties. It is seen that, well above T_N, the behavior of sample 2 at 150 K is purely paramagnetic, whereas the curve for sample 3 is of a ferromagnetic character. The shape of the dependences $M(H)$ is intermediate at $T = 50$ K (Fig. 3b).

4. DISCUSSION

In [2, 4], the magnetic properties of $Cu_xZn_{1-x}Cr_2Se_4$ were interpreted in terms of competitive exchange interactions. The effects observed were explained by the authors of [2, 4] with the use of a complex chain of concentration magnetic phase transformations: simple spiral–FM spiral–spin glass–FM spiral–collinear ferromagnet. The existence of the collinear spin ordering in the pure and cation-substituted $ZnCr_2Se_4$ compounds at certain concentrations and temperatures was confirmed by neutron diffraction data. However, neutron scattering spectra cannot always be interpreted unambiguously [6] and the satellite lines can be attributed not only to the noncollinear magnetic structure of the sample but also to the two-phase state of the sample when it represents a mixture of ferromagnetic and antiferromagnetic regions. Moreover, Nagaev [7] theoretically proved that the NCAF system is less stable than the collinear systems, specifically at high temperatures and low concentrations. In this connection, we cannot say with certainty that it is these noncollinear magnetic structures that are realized in $Cu_xZn_{1-x}Cr_2Se_4$ over a wide range of concentrations and temperatures.

The majority of previously obtained experimental data, as well as that in this work, can easily be explained within the model of the two-phase magnetic state [8]. In this model, the ordered ferromagnetic state coexists with the antiferromagnetic state.

For example, a part of the Cr ions in the state 3+ transforms into the state 4+ as copper atoms are incorporated into pure $ZnCr_2Se_4$. The state with a variable valence is realized. As was shown in [7], individual ferromagnetic microregions can be formed about impurity atoms in this process. This should lead to an increase in

the paramagnetic Curie temperature with small variations in T_N, as was actually observed in [4]. As the impurity concentration x increases, the ferromagnetic region becomes simply connected at a certain critical value x_c and the macroscopic ferromagnetic order with the Curie temperature T_C is established. From this point on, the antiferromagnetic regions are present as inclusions in the ferromagnetic matrix. It is presumably this mechanism that is observed in our case when samples 3–6 exhibit T_N and T_C simultaneously, and the antiferromagnetic peak at T_N is seen against the background of the ferromagnetic contribution M_0, whereas the Cr^{4+} concentration in samples 1 and 2 is insufficient for ferromagnetic ordering. According to our data, the critical value x_c for $Cu_xZn_{1-x}Cr_2Se_4$ lies in the concentration range 0.12–0.14.

The two-phase model can also explain the unexpected decrease in T_C in the series of samples 3–6. It is reasonable to assume that, for x close to the critical value, the ferromagnetic "network" which has already been formed should predominantly capture impurity ions; i.e., for the most part, the regions containing copper ions and neighboring chromium atoms should be ferromagnetic. The magnitude and sign of the exchange interaction will be characteristic of pure $CuCr_2Se_4$ with the corresponding T_C value. As the ferromagnetic region increases, a larger number of Zn ions will be captured and the competition between the exchange interactions can lead to a decrease in the T_C temperature, which will then rise again as more and more Zn atoms are replaced with Cu.

The two-phase model is also supported by resistive measurements. Warczewski *et al.* [2] noted a concentration transition from a well-conducting to semiconductor state, which accompanies the disappearance of macroscopic ferromagnetism. Our preliminary measurements of the resistance of pressed samples also showed that samples 1 and 2 have a higher resistance than the others. This also agrees with the predictions of the two-phase model, according to which the samples containing a singly connected ferromagnetic region with an increased carrier concentration should possess a higher conductivity. Thus, almost the whole totality of experimental data for the region of the concentration transition can be described within a unified approach in the model of the two-phase magnetic state, which was proposed in [6–8].

However, a certain part of our data can be interpreted in favor of NCAF ordering. This mainly concerns the indications of two spin-flop transitions in the $M(H)$ dependence at 4.2 K. The first transition presumably takes place when the helicoidally ordered magnetic moment leaves the plane, and the second transition can be attributed to the collinear ferromagnetic ordering. Surprisingly, the former transition was not noted by Krok *et al.* [4], who conducted similar measurements on compositions partly coinciding with
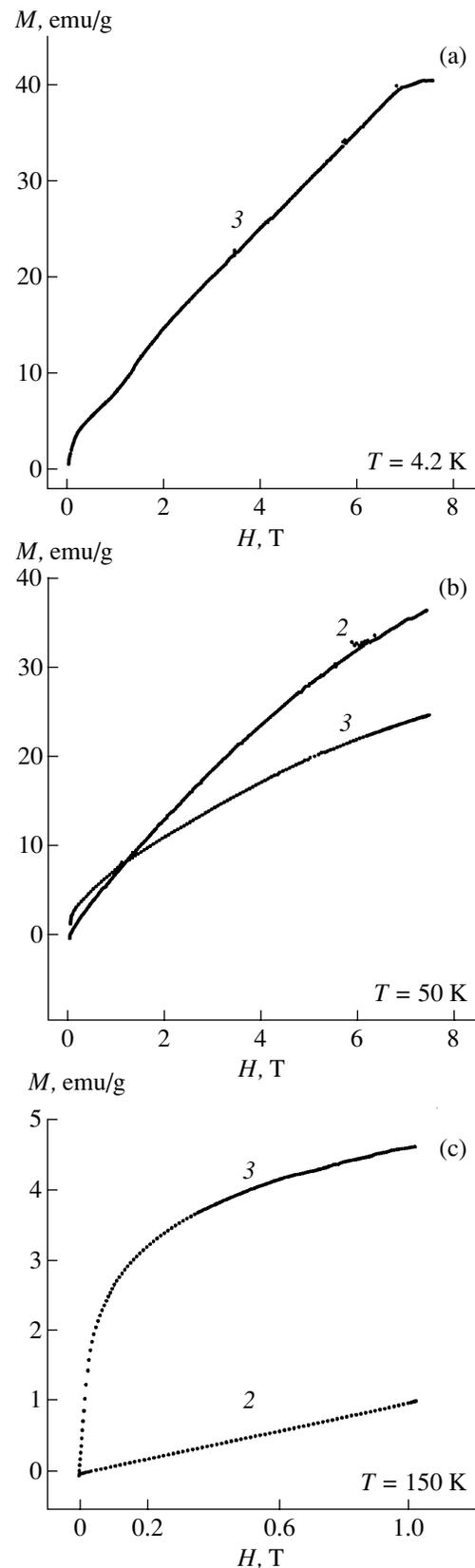
Fig. 3. Magnetization curves at different temperatures T, K: (a) 4.2, (b) 50, and (c) 150. The numerals at the curves correspond to the sample numbers.

those used in our work. On the other hand, a similar curve can be obtained by the simple superposition of the ferromagnetic and antiferromagnetic contributions to $M(H)$. In addition, the seemingly "chaotic" jumps of the saturation magnetic moment from sample to sample, which also showed up to some extent in [4], remain unclear.

Thus, it is quite possible that the noncollinear antiferromagnetic ordering is more energetically favorable at low temperatures. Nevertheless, the success of the two-phase model in describing a set of experimental data opens up a field for scientific discussion concerning the boundaries of applicability of one or another model and the ultimate clearing up of the nature of the magnetic phase transition in the cation-substituted chalcogenide spinel $Cu_xZn_{1-x}Cr_2Se_4$.

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