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MAGNETISM AND FERROELECTRICITY

Effect of Thermal Instability on the Magnetic Properties of $Cu_{1-x}Zn_xCr_2Se_4$ Solid Solutions

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Abstract—Annealing in vacuum is found to affect magnetic order in polycrystalline $Cu_{1-x}Zn_xCr_2Se_4$ samples (x = 0.88, 0.90). Samples subjected to heat treatment exhibit a temperature dependence of dynamic magnetic susceptibility characteristic of a non-single-phase magnetic state. The annealing-induced magnetic order is assigned to the zinc off-stoichiometry formed in the process. *© 2002 MAIK "Nauka/Interperiodica".*

1. INTRODUCTION

The $Cu_{1-x}Zn_xCr_2Se_4$ solid solutions have been attracting interest due to the rich variety of magnetic states these solutions feature upon different substitutions x [1–3]. This diversity is due to the strong difference in magnetic properties between the extreme compounds in the series, namely, $CuCr_2Se_4$ (ferromagnetic semimetal with T_C ~ 420 K) and $ZnCr_2Se_4$ (helicoidal antiferromagnet with T_N ~ 20 K). The competition between the exchange interactions in the solid solutions gives rise to nontrivial magnetic properties. Of particular interest is the alternation of magnetic phases in the concentration interval from 1.0 to 0.8, where gradual substitution of copper for zinc offers a possibility of observing the following magnetic states successively: simple spin spiral, ferromagnetic spiral, spin glass, ferromagnetic spiral, and collinear ferromagnetism [4].

In our earlier comprehensive investigation [5] of the concentration-driven phase transition in $Cu_{1-x}Zn_xCr_2Se_4$, we measured the magnetic properties of this solid solution in the 0.8–0.9 concentration interval with a small step of 0.02. Polycrystals were prepared by the authors of [6] using solid-phase technology, which is described in considerable detail in [6]. The substituent concentration x_c = 0.88 was established to be critical. Indeed, all compounds with $x < x_c$ are ferromagnets with a Curie temperature of 370–420 K, a sample with x = 0.88 possesses a weak room-temperature magnetic moment, and an x = 0.9 sample undergoes only an antiferromagnetic transition at the same temperature as the extreme compound $ZnCr_2Se_4$.

The magnetic transition from a helicoidal structure in $ZnCr_2Se_4$ to a ferromagnetic structure in $CuCr_2Se_4$ in this series of compounds is accompanied by a change over from semiconducting to semimetallic conduction. Thus, to fully understand the nature of the concentration-driven phase transitions in $Cu_{1-x}Zn_xCr_2Se_4$, one has to make a comprehensive investigation of both the magnetic and electrical properties. This raises the problem of thermal stability of these solid solutions, as electrical measurements on polycrystals are made on pressed and sintered powder samples. This problem was discussed earlier in [6], where studies of the thermal stability of $Cu_{1-x}Zn_xCr_2Se_4$ compositions in air were carried out at temperatures ranging from 500 to 920 K. It was found that up to temperatures of about 650 K, selenium is detached and a selenium-deficient spinel forms [6]. Above 650 K, oxide compounds were observed to form. This study was aimed at establishing whether the heat treatment used in sintering a powder sample results in a noticeable change in its physical properties, primarily in its magnetic properties, and, hence, at estimating the possible effect of the off-stoichiometry caused by the heat treatment.

2. EXPERIMENTAL TECHNIQUE

The samples, pressed into rectangular parallelepipeds measuring 2 × 2 × 4 mm, were placed in quartz ampules evacuated to 10^{-3} mm Hg. One sample lot was annealed at T_1 = 850 K (anneal *1*); the other, at T_2 = 1150 K (anneal *2*). The samples were annealed for two hours, and the operating temperature was reached in three hours of uniform heating. After this, the samples were allowed to cool in the furnace.

The temperature-dependent real part of magnetic susceptibility χ' of the samples subjected to heat treatment was measured using the dynamic ac bridge technique. The sample temperature was varied by blowing it with a stream of heated air in a cylindrical flow-through cryostat with measuring coils mounted on its outer wall. The bridge unbalance was measured with a UNIPAN 232B phase-sensitive nanovoltmeter.

The electrical resistance $R(T)$ was measured using the dc four-probe method. The contacts, made of indium paste, were arranged along a straight line on the larger face of the sample. The current was supplied over thin copper wires 0.06 mm in diameter. The measurements in the cooling runs were also carried out in a flow-through cryostat, and the samples were heated in an unsealed quartz ampoule in a muffle furnace.

3. RESULTS

The magnetic measurements carried out after the annealing revealed that all the samples of the lot under study exhibit spontaneous magnetism with a clearly pronounced ferromagnetic component. This is also valid for compositions with a high zinc concentration, $x = 0.88$ and 0.90, of which the former had an extremely low magnetization before the annealing and the latter was fully paramagnetic at room temperature. Magnetic ordering occurred during both anneals *1* and *2*. The samples of these two compositions demonstrated similar temperature dependences of the dynamic magnetic susceptibility χ'. The measurements made on the sample with $x = 0.88$ are displayed in Fig. 1, which shows, for comparison, χ'(T) curves for compositionally similar samples $Cu_{0.14}Zn_{0.86}Cr_2Se_4$ and $Cu_{0.16}Zn_{0.84}Cr_2Se_4$ measured before the heat treatment. We readily see from Fig. 1 that the magnetic susceptibility of the annealed sample (curve *1*), as well as χ'(T) of the $Cu_{0.14}Zn_{0.86}Cr_2Se_4$ stoichiometric composition, vanishes at a temperature close to T_C of the original compound $CuCr_2Se_4$. Note that curve *1* follows a pattern characteristic of a non-single-phase magnetic state of a sample and lies between curves *2* and *3* for the samples with $x = 0.86$ and 0.84, respectively.

The measurements of the temperature dependence of electrical resistance showed that the samples can be divided into two groups. With increasing temperature, the electrical resistance decreases in samples with $x \geq 0.88$ and increases in the other samples. Figures 2a and 2b display the $R(T)$ relations measured for two similar compositions, $x = 0.88$ and 0.86, respectively, featuring different types of conduction.

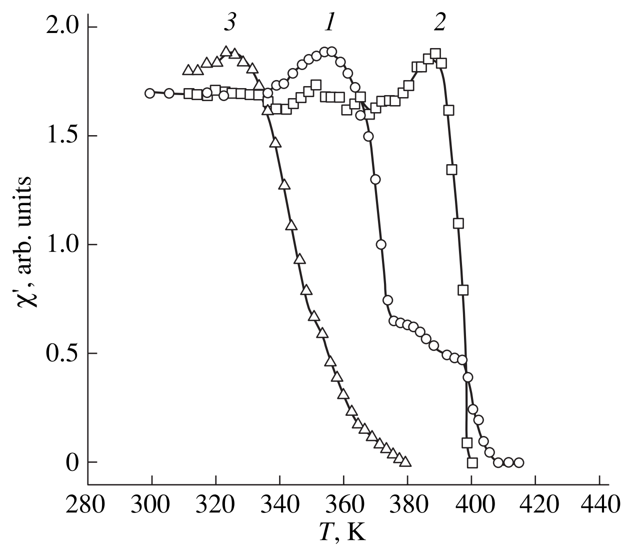

Fig. 1. Temperature dependences of the magnetic susceptibility for (*1*) annealed $Cu_{0.12}Zn_{0.88}Cr_2Se_4$ and (*2*, *3*) the original $Cu_{0.14}Zn_{0.86}Cr_2Se_4$ and $Cu_{0.16}Zn_{0.84}Cr_2Se_4$ samples, respectively.

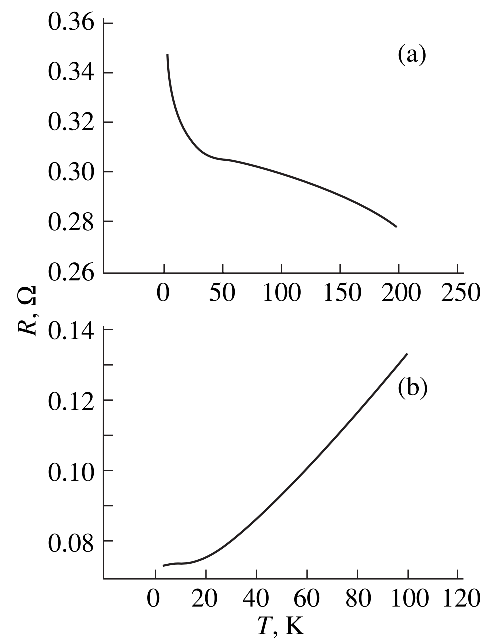

Fig. 2. Temperature dependences of the electrical resistance of annealed samples (a) $Cu_{0.12}Zn_{0.88}Cr_2Se_4$ and (b) $Cu_{0.14}Zn_{0.86}Cr_2Se_4$.

4. DISCUSSION

As already mentioned, it was shown in [6] that annealing $Cu_{1-x}Zn_xCr_2Se_4$ solid solution samples in air up to temperatures of 750–900 K brings about only detachment of selenium, without any visible indications of chemical activity of the Cu and Zn ions. Compositions with a high zinc content were observed to have the highest thermal stability. For instance, the oxidation of $Cu_{0.2}Zn_{0.8}Cr_2Se_4$ started at 920 K. Thus, one might expect that a short annealing in vacuum at a lower temperature (anneal *1*) would not produce a noticeable off-stoichiometry in copper or zinc. However, susceptibility measurements showed that the annealed samples (after either of anneals *1* or *2*) approached, in magnetic properties, the compositions with a lower zinc content, which suggests that the composition shifted toward the zinc-deficient spinel as a result of annealing. Note that the expected selenium deficiency cannot apparently initiate the onset of ferromagnetism, because the ferromagnetism of $CuCr_2Se_4$ is due to the high hole concentration in the valence band.

The additional electrons appearing as a result of selenium deficiency entail partial compensation and, hence, weakening rather than enhancement of the magnetic properties.

One more important result of this study consists in supporting the assumption made in [5] that the concentration-driven magnetic transition within the critical concentration region in $Cu_{1-x}Zn_xCr_2Se_4$ occurs through separation of the compound into two magnetic phases, namely, a ferromagnetic phase with a high T_C and an antiferromagnetic phase. This is argued for by the observation that the Curie temperature for the heat-treated samples, as well as for the untreated $x = 0.86$ sample, is close to T_C of the extreme compound in the series, $CuCr_2Se_4$, although the content of copper in them is considerably lower than that of zinc. Also, the heat-treated samples with $x = 0.88$ and 0.90 behave as semiconductors. It is this combination of properties, according to [7], that is characteristic of a magnet with highly conducting ferromagnetic particles embedded in a weakly conducting antiferromagnetic matrix.

Thus, our heat treatment of $Cu_{1-x}Zn_xCr_2Se_4$ samples apparently resulted in a compositional shift toward a spinel which is deficient not only in selenium but also in zinc. The reason for this probably lies in the high volatility of zinc subjected to annealing in vacuum. Indeed, the boiling point of pure zinc drops from 1210 K at a pressure of 10^3 mm Hg to 565 K at 10^{-3} mm Hg, which is substantially below the anneal temperature used in the study. Because the study was carried out in the critical concentration region, a slight change in the composition apparently produced a substantial change in the physical properties. One can thus conclude that even short anneals, such as those needed to sinter $Cu_{1-x}Zn_xCr_2Se_4$ samples for resistance measurements, should be performed under an intentionally produced excess zinc-vapor pressure.

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REFERENCES

1. S. Jusczyk, J. Krok, I. Okonska-Kozlowska, *et al.*, Phase Transitions **2**, 67 (1981).
2. J. Krok, J. Spalek, S. Juszczuk, and J. Warczewski, Phys. Rev. B **28** (11), 6499 (1983).
3. J. Krok, S. Jusczuk, J. Warczewski, *et al.*, Phase Transitions **4**, 1 (1983).
4. T. Gron, H. Duda, and J. Warczewski, Phys. Rev. B **41** (18), 12424 (1990).
5. A. D. Balaev, É. G. Zhukov, N. B. Ivanova, *et al.*, Fiz. Tverd. Tela (St. Petersburg) **43** (6), 1053 (2001) [Phys. Solid State **43**, 1089 (2001)].
6. É. G. Zhukov, E. S. Populyak, G. S. Varnakova, and V. A. Fedorov, Zh. Neorg. Khim. **38**, 167 (1993).
7. É. L. Nagaev, *Physics of Magnetic Semiconductors* (Nauka, Moscow, 1979).

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