

# Concerning one mechanism of the phase transition from the ferromagnetic into the ferrimagnetic state

N. M. Kovtun, V. T. Kalinnikov,<sup>1)</sup> A. A. Shemyakov,  
V. K. Propkopenko, and A. A. Babitsyna

*Physico-technical Institute, Ukrainian Academy of Sciences*

(Submitted December 29, 1976)

*Pis'ma Zh. Eksp. Teor. Fiz.* **25**, No. 3, 162–164 (5 February 1977)

A phase transition from the ferromagnetic to the ferrimagnetic state was observed in CuCr chalcogenide spinels. It is due to electron ordering of the  $\text{Cr}^{3+}$  and  $\text{Cr}^{4+}$  ions with simultaneous redistribution of the electrons among the  $\text{Cu}^+$  and  $\text{Cr}^{4+}$  ions.

PACS numbers: 75.30.Kz, 75.50.Gg, 76.60.—k

It was previously established<sup>[1]</sup> that normal chalcogenide spinels of the type  $\text{MeCr}_2\text{X}_4$ , where  $\text{X} = \text{S}, \text{Se}, \text{Te}$ , are ferromagnetic semiconductors if  $\text{Me} = \text{Fe}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+}$ , and ferromagnetic with metallic conductivity and with magnetic moment  $5\mu_B$  in the case  $\text{Me} = \text{Cu}$  ( $\rho \sim 10^{-4} \Omega\text{—cm}$  at room temperatures). The valence formula of these compounds has not yet been established. Thus, Lotgering<sup>[1]</sup> has proposed that the copper ions are monovalent and have a diamagnetic configuration  $3d^{10}$ , i.e., the cation distribution  $\text{Cu}^+[\text{Cr}^{3+}\text{Cr}^{4+}]\text{S}_4$  is realized. According to Goodenough,<sup>[2]</sup> the copper ions in these ions are divalent:  $\text{Cu}^{2+}[\text{Cr}_2^{3+}]\text{S}_4$ . To reconcile the ferromagnetic ordering, he proposed that the conduction-electron polarization in the delocalized  $t_{2g}$  orbitals of the copper ions decreases the magnetic moment to  $5\mu_B$ . At the same time, neutron diffraction has shown that the copper ions in these compounds have no magnetic moment. As to the chromium ions, their scattering moments are equal.

We present here nuclear-magnetic-resonance data that make it possible to

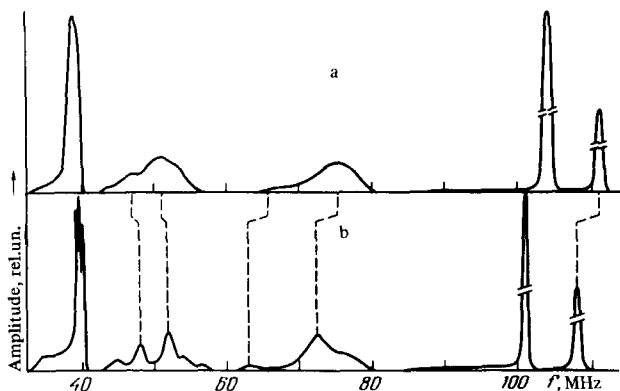


FIG. 1. NMR spectra of  $\text{CuCr}_2\text{S}_4$ : a)  $H_0 = 5$  kOe, b)  $H_0 = 0$ .

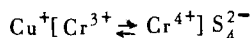
establish not only the valence formula of chalcogenide spinels, but also their magnetic structure.

The NMR measurements were performed on polycrystalline  $\text{CuCr}_2\text{S}_4$  and single-crystal  $\text{CuCr}_2\text{Se}_4$  samples.

The x-ray analysis has revealed no other phase.

The NMR spectrum of the intradomain  $\text{Cr}^{53}$  and  $\text{Cu}^{63,65}$  nuclei of  $\text{CuCr}_2\text{S}_4$  consists at 4.2°K (see Fig. 1) of four groups of lines with different intensities at frequencies 34—40, 42—58, 61—80, and 83—110 MHz. A study of the spectra in an external magnetic field up to 5 kOe has shown (see the figure) that the lines at the frequencies 34—40 and 42—58 MHz are shifted towards lower frequencies with a gyromagnetic ratio  $\sim 240$  kHz/kOe, while the lines at the frequencies 61—80 and 83—110 MHz are shifted towards higher frequencies with gyromagnetic ratio  $\sim 1000$  kHz/kOe. Consequently, the lower two groups of lines corresponded to the chromium ions, and the upper ones to the copper ions. At liquid-nitrogen temperature, the NMR spectrum consists of only two groups of lines at the frequencies 34—40 and 83—110 MHz. The lines at 42—58 and 61—80 MHz are observed up to approximately 60°K. A similar picture is realized also in the compound  $\text{CuCr}_2\text{Se}_4$ . In contrast to these compounds, the NMR spectrum of  $\text{CdCr}_2\text{Se}_4$  reveals no new chromium lines. The NMR spectrum of chromium in the compounds  $\text{CuCr}_2\text{S}_4$  and  $\text{CuCr}_2\text{Se}_4$ , at liquid-nitrogen temperature, just as the additional spectrum produced below 60°K, is analogous to the NMR spectrum of the chromium in the compound  $\text{CdCr}_2\text{Se}_4$ . The complex structure of the spectrum is attributed to the anisotropy of the local field and to quadrupole splitting. We note also that the local field corresponding to the NMR lines in the frequency range 42—58 MHz is equal to the field at the  $\text{Cr}^{3+}$  nuclei in other chalcogenide spinels, while the local field corresponding to the NMR lines in the frequency range 34—40 MHz is smaller by an amount approximately equal to half the field per uncompensated spin.

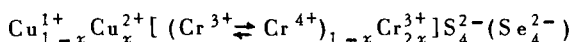
Taking the foregoing into account, we can propose that at temperatures above 60°K the cation distribution



is realized in  $\text{CuCr}_2\text{S}_4$ .

To prove this assumption, we have investigated the fine structure of the x-ray emission spectra of chromium in the compounds  $\text{CuCr}_2\text{S}_4$ ,  $\text{CuCr}_2\text{Se}_4$  and  $\text{CdCr}_2\text{Se}_4$ . We analyzed the energy positions of the  $K_{\beta 1}$  lines of chromium in third-order reflection. The investigations have shown that the  $K_{\beta 1}$  lines of Cr in the compounds  $\text{CuCr}_2\text{S}_4$  and  $\text{CuCr}_2\text{Se}_4$  are shifted relative to the  $K_{\beta 1}$  line of Cr in the compound  $\text{CdCr}_2\text{Se}_4$  by an amount of  $0.12 \pm 0.02$  eV towards the short-wave side. This change of the energy position of the  $K_{\beta 1}$  lines of Cr in the compounds  $\text{CuCr}_2\text{S}_4$  and  $\text{CuCr}_2\text{Se}_4$  relative to  $\text{CdCr}_2\text{Se}_4$  corresponds to a shift of the  $3d$  level of the chromium towards higher energies, i. e., to an increased valence of the chromium. This shift of the  $K_{\beta 1}$  line, according to [4, 5], corresponds to an increase in the valence by 0.4–0.6. It can thus be stated that the  $\text{Cr}^{3+}$  and  $\text{Cr}^{4+}$  in the compounds  $\text{CuCr}_2\text{S}_4$  and  $\text{CuCr}_2\text{Se}_4$  are indistinguishable, i. e., a fast electron exchange takes place between them.

The appearance of additional groups of chromium and copper lines in the NMR spectrum with decreasing temperature can be explained by assuming that electronic ordering of the chromium ions takes place in these compounds. Since the second ionization potential of copper is 20.29 eV, whereas the fourth ionization potential of chromium is approximately 50 eV, it follows according to [2] that a monovalent copper ion cannot be stable in the presence of  $\text{Cr}^{4+}$ , and it gives up one electron to the  $\text{Cr}^{4+}$  ion. The result is the chemical formula  $\text{Cu}^{2+}[\text{Cr}_2^{3+}\text{S}_4]^{2-}$ . However, as follows from the experimental data, the electron ordering is not completed even at 2°K (at 2°K the  $\text{Cu}^{2+}[\text{Cr}_2^{3+}\text{S}_4]^{2-}$  phase amounts to only ~20%). The chemical formula of the compounds  $\text{CuCr}_2\text{S}_4$  and  $\text{CuCr}_2\text{Se}_4$  below 60°K can be represented in the form



The fact that the NMR lines of  $\text{Cu}^{2+}$  and  $\text{Cr}^{3+}$  are shifted in opposite directions in a magnetic field indicates that the copper and chromium ions are antiferromagnetically ordered. As follows from the cation distribution, the magnetic moment per formula unit does not depend on the electronic ordering and is equal to  $5 \mu_B$  at all values of  $x$ ; this agrees with the experimental data. [6]

It can thus be stated that a phase transition from the ferromagnetic to the ferrimagnetic state takes place in  $\text{CuCr}_2\text{X}_4$  compounds and is due to electron ordering of the  $\text{Cr}^{3+}$  and  $\text{Cr}^{4+}$  ions with simultaneous redistribution of the electrons among the  $\text{Cu}^+$  and  $\text{Cr}^{4+}$  ions.

In conclusion, the authors thank Z. A. Samoilenko for measurements of the x-ray emission spectra.

<sup>1</sup>Institute of Inorganic and Organic Chemistry, USSR Academy of Sciences.

<sup>1</sup>F. K. Lotgering, Solid State Commun. 2, 55 (1964).

<sup>2</sup>J. B. Goodenough, Colloque Intern. CNRS 157, Oct. 1965.

<sup>3</sup>C. Colominas, Phys. Rev. 153, 558 (1966).

<sup>4</sup>A. T. Shuvaev and G. M. Kulyabin, Izv. Akad. Nauk SSSR Ser. Fiz. 27, 322 (1963).

<sup>5</sup>A. Z. Men'shikov and S. A. Nemnonov, *ibid.* , 394.

<sup>6</sup>A. A. Samokhvalov, Yu. N. Morozov, B. V. Karpenko, and M. I. Simonova, *Phys. Status Solidi [b]* 73, 455 (1976).