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Effect of Ni-substitution on magnetic phase transition in CuB_2O_4

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Abstract

The single crystals $Cu_{1-x}Ni_xB_2O_4$ with $x = 0.002$; 0.005; 0.009; 0.014 were grown by spontaneous crystallization and the magnetic properties of these crystals have been studied. The strong influence of substitution on the value of critical fields $H_{\perp c}$ at which the modulated states transform into a weak ferromagnetic one was observed in the temperature range 9.5–20 K. The essential change of temperature dependence of a paramagnetic susceptibility χ for Ni-doped samples in comparison with pure CuB_2O_4 was revealed. The modulated state was not observed in the temperature range 9.5–20 K for Ni content more than $x = 0.009$.

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Keywords: Modulated magnetic state; Short-range magnetic order; Phase transition

1. Introduction

The intensive investigations of the magnetic state of copper metaborate CuB_2O_4 were carried out by different methods: neutron diffraction [1,2], magnetic measurements [3], heat capacity, μSR [4,5], magnetic resonance [6] and theoretical calculations [7]. It was assumed [8], that the ground state of copper metaborate in the temperature range 9.5–20 K is a long-periodic modulated state. In the weak magnetic field applied in the basal plane this state transforms into the field induced commensurate weak ferromagnetic state. Below 9.5 K the magnetic state is a incommensurate one.

According to X-ray and neutron diffraction studies [1,9], CuB_2O_4 crystallizes in tetragonal space group $I\bar{4}2d$ (D_{2d}^{12}). In the unit cell of copper metaborate Cu^{2+} ions occupy two nonequivalent crystallographic positions-4b and 8d. Four Cu^{2+} ions at the sites 4b form 3-dimensional A subsystem which is antiferromagnetically ordered below $T_N = 20$ K (strong subsystem). Eight Cu^{2+} ions at the sites 8d form weak B subsystem which consists of quasi-one-dimensional zig-zag chains. This subsystem is partially ordered by exchange interaction with A subsystem. It is conceivable that the substitution of Cu^{2+} ions in different sites by diamagnetic and paramagnetic ions with different magnetic moments will influence essentially the magnetic properties and can change the magnetic state of the crystal.

The aim of this work is to study the effect of Ni-substitution on the magnetic properties of CuB_2O_4.

2. Experiment

The single crystals $Cu_{1-x}Ni_xB_2O_4$ with $x = 0.002$; 0.005; 0.009; 0.014 were grown by spontaneous crystallization [10].

The determination of nickel content in doped crystals was carried out on the powder samples by the X-ray spectral fluorescent analysis using SPARK-1 spectrometer. We found that the actual concentration of Ni^{2+} in crystals is less than nominal one in a melt.

The magnetization of pure and Ni-doped CuB_2O_4 have been studied using MPMS-5 SQUID magnetometer at various temperatures in magnetic field up to 500 Oe applied in the basal plane of a crystal and in the field up to 50 kOe applied along a tetragonal axis.

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Fig. 1 shows the field dependence of magnetization of pure CuB_2O_4 at $T = 11\,K$ and $Cu_{1-x}Ni_xB_2O_4$ with $x = 0.002$; 0.009 samples at various temperatures in magnetic field $H_{\perp c}$ up to 500 Oe. The initial part of the field dependence of magnetization is shown in the inset of Fig. 1.

Fig. 2 shows the temperature dependence of reciprocal susceptibility $(1/\chi)$ for $Cu_{1-x}Ni_xB_2O_4$ with $x = 0.002$ sample. The deviation of $1/\chi$ from Curie–Weiss law for CuB_2O_4 begins approximately at 140 K (see inset) whereas for Ni-doped samples this deviation begins at 40 K. The paramagnetic Curie temperature remains negative but reduced from $\theta_\perp = -23\,K$ for pure crystal down to $-4\,K$ for Ni-doped one.

3. Discussion

It is known, that the paramagnetic susceptibility of quasi-low-dimensional magnet is characterized by a deviation from Curie–Weiss law at a temperature at which short-range order correlations begin. This temperature considerably exceeds the temperature of magnetic phase transition. In pure CuB_2O_4 the deviation from Curie–Weiss law begins at $T \sim 140\,K$ and is connected with low-dimensional character of B subsystem. The decreasing of this temperature up to 40 K for Ni-doped crystals can be explained by breaking of homogeneity of chains in the B subsystem caused by the appearance of ions with another spin in chains.

Thus these data allow to assume, that Ni ions occupy mainly B positions. This conclusion was confirmed also by increasing of saturation magnetization of weak B subsystem (Fig. 3) at 2 K.

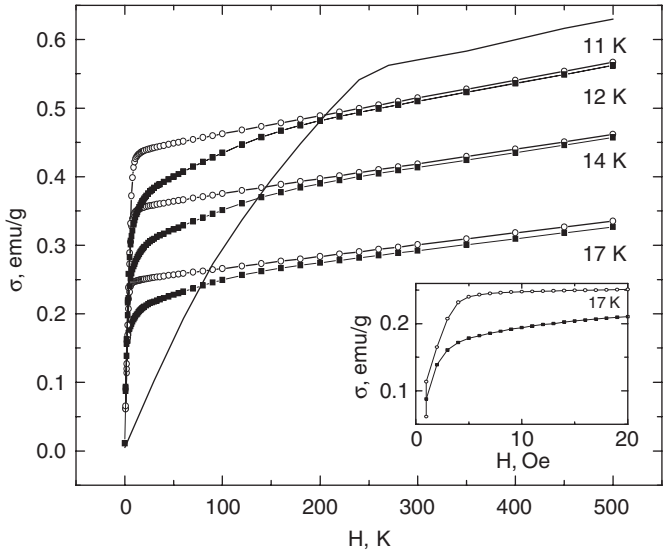

Fig. 1. Field dependences of magnetization of pure CuB_2O_4-solid line and $Cu_{1-x}Ni_xB_2O_4$: $x = 0.002$—light symbol, $x = 0.009$—black symbol. The insert shows the initial part of the field dependences of magnetization $Cu_{1-x}Ni_xB_2O_4$: $x = 0.002$—light symbol, $x = 0.009$—black symbol at $T = 17\,K$.

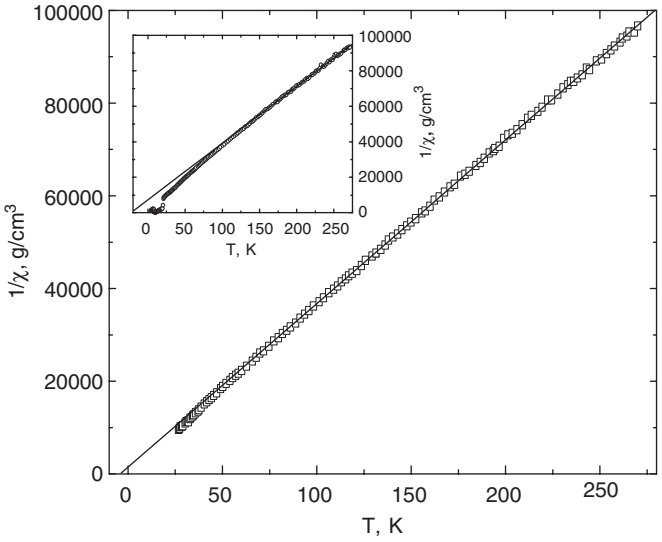

Fig. 2. Temperature dependence of reciprocal susceptibility of $Cu_{1-x}Ni_xB_2O_4$ ($x = 0.002$), $H_{\perp c} = 50$ Oe; inset shows the temperature dependence of reciprocal susceptibility of CuB_2O_4.

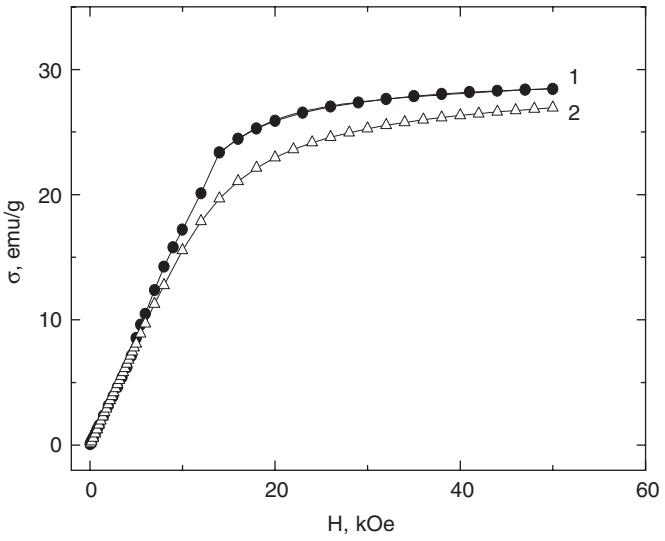

Fig. 3. Field dependences of magnetization of (1) $Cu_{1-x}Ni_xB_2O_4$ ($x = 0.009$), (2) CuB_2O_4 at $T = 2\,K$, $H_{||c}$.

Fig. 1 shows that Ni-substitutions result in reduction of a critical field of transition from modulated state to the field induced commensurate weak ferromagnetic state which corresponds to kink point at magnetization curve. For example, the critical field of this phase transition is $H_{\perp c} = 280$ Oe at $T = 11\,K$ for pure CuB_2O_4 whereas $H_{\perp c} = 9$ Oe at $T = 12\,K$ for Ni-doped ($x = 0.002$) sample. The field dependence of magnetization for $Cu_{1-x}Ni_xB_2O_4$ with $x = 0.009$ has other form without a kink point, i.e. in this sample the magnetic state is weak ferromagnetic one at $H = 0$.

Thus, Ni-substitution in B subsystem suppresses the modulated state in CuB_2O_4, that is an evidence of the

important role of B subsystem in formation of magnetic states in CuB_2O_4.

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