

# NMR-Study of the Crystalline and Amorphous $\text{CuB}_2\text{O}_4$

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<sup>11</sup>B nuclear magnetic resonance (NMR) spectroscopy was applied to study the crystalline, amorphous and crystallizing from an amorphous states of copper metaborate. The occurrence of trigonal  $\text{BO}_3$  units at the expense of converting tetragonal  $\text{BO}_4$  units was observed in amorphous  $\text{CuB}_2\text{O}_4$ . This fact explains the essential change of  $\text{CuB}_2\text{O}_4$  magnetic properties under amorphization.

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## 1. INTRODUCTION

Copper oxides have attracted growing attention from many researchers in recent years due to a wide variety of their low-temperature magnetic properties. The copper metaborate  $\text{CuB}_2\text{O}_4$  crystallizes in the tetragonal system, space group  $I4_2d$  [1], with twelve formula units in a cell. There are two nonequivalent positions of copper ions: four  $\text{Cu}^{2+}$  ions in square planar coordination and eight  $\text{Cu}^{2+}$  ions in a very distorted octahedron from oxygen ions (Fig. 1). The  $\text{Cu}^{2+}$  ions form two magnetic subsystems with distinct magnetic dimension and order. The magnetic state of  $\text{CuB}_2\text{O}_4$  is determined by the interaction between two subsystems of  $\text{Cu}^{2+}$  ions. It was found that in temperature range from 10 K to the Neel temperature  $T_N = 20$  K this compound is a weak ferromagnetic, in which the magnetic moments of sublattices and the spontaneous magnetic moment lie in the tetragonal crystal plane [1].

The congruent character of a melting of  $\text{CuB}_2\text{O}_4$  and presence in chemical composition classical glass-former  $\text{B}_2\text{O}_3$  afford a unique possibility to transfer this compound in an amorphous state and to study influence of amorphization on magnetic properties of  $\text{CuB}_2\text{O}_4$  by comparison of properties of substance in an amorphous state and its crystalline analog.

The magnetic and resonance properties of crystalline and amorphous  $\text{CuB}_2\text{O}_4$  was reported in paper [2]. The magnetic properties of copper metaborate were changed significantly under amorphization. The amplification of antiferromagnetic interaction, deviation from the Curie–Weiss law lower 40 K and occurrence of anormal in behaviors of a magnetization and resonance properties at temperature  $T \sim 8$  K were observed.

The exchange interactions between ions  $\text{Cu}^{2+}$  ( $S = \frac{1}{2}$ ) in crystalline  $\text{CuB}_2\text{O}_4$  are carried out through the  $\text{Cu}-\text{O}-\text{B}-\text{O}-\text{Cu}$  chains [2]. There are two types of the tetrahedral coordinated boron atoms with different distances  $\text{B}-\text{O}$  in  $\text{CuB}_2\text{O}_4$  (Fig. 1). These  $\text{BO}_4$ -groups are linked by common oxygen atoms to a three-dimensional network of ring type  $(\text{B}_3\text{O}_6)^{3-}$  units [3]. All boron and oxygen atoms take part in numerous indirect interactions with the numerous neighbors. Thus, boron–oxygen skeleton participates in an exchange interaction in  $\text{CuB}_2\text{O}_4$ .

The transformation of boron–oxygen groups under amorphization of  $\text{CuB}_2\text{O}_4$  leads to the transformation of the exchange bridges, and, therefore, the pattern of the exchange interactions. In order to receive the immediate information about a structure of boron anions, coordination of boron and their change under amorphization, we carried out <sup>11</sup>B NMR experiment.

The <sup>11</sup>B NMR experiment was performed in the powder samples of crystalline and amorphous  $\text{CuB}_2\text{O}_4$  at room temperature. It is well known, the

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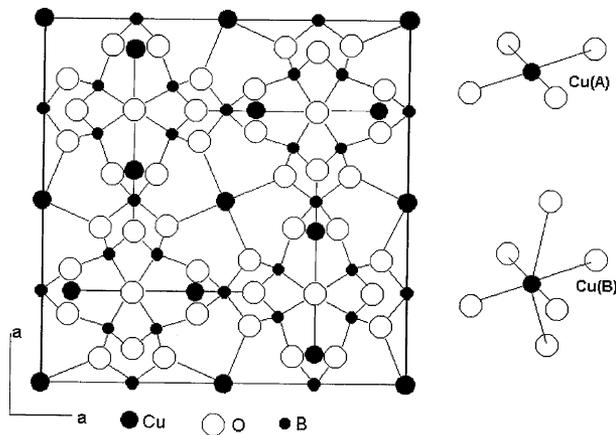


Fig. 1. Crystal structure of  $\text{CuB}_2\text{O}_4$ .

quadrupolar perturbed  $^{11}\text{B}$  NMR experiments is a very appropriate method to investigate small structure distortions of solids. In this paper we report the results of our NMR investigation.

## 2. EXPERIMENT

A growing procedure of copper metaborate single crystals was described in [4]. The amorphous  $\text{CuB}_2\text{O}_4$  was prepared by the rapidly pouring of the melt on a metal substratum. The X-ray diffraction pattern of powdered as-quenched samples showed the wide amorphous halos. The amorphous state of  $\text{CuB}_2\text{O}_4$  was supported by differential thermal analysis (DTA) also [2]. The X-ray analysis of a powder, which was exposed heat treatment at 950 K, revealed all most typical lines of crystalline  $\text{CuB}_2\text{O}_4$ .

The NMR solid echo spectra of  $^{11}\text{B}$  were measured at room temperature with operating frequency 96.3 MHz using a BRUKER AVANCE 300 NMR spectrometer. An excitation of the complete spectra was achieved with pulse durations of  $3 \mu\text{s}$ . To avoid the influence of the dead time a quadrupole spin echo sequence with a pulse distance of  $\tau = 20 \mu\text{s}$  was used.

In this work, the microscopic characteristics of copper metaborate are determined from the  $^{11}\text{B}$  NMR spectra.  $^{11}\text{B}$  nuclei possess a quadrupole moment. Nuclear magnetic resonance at quadrupole nuclei provides valuable information on the magnitude and symmetry of crystal-electric-field gradients at the

studied nucleus. For a strong external magnetic field  $\mathbf{B}_0$ , when the Zeeman interaction energy substantially exceeds the energy of interaction between the nuclear quadrupole moment and the crystal field, the crystal field brings about a perturbation of equidistant Zeeman levels and a splitting of the NMR line into  $2I$  components ( $I$  is the nuclear spin), which are symmetrically located with respect to the Larmor precession frequency  $\nu_0$  in the magnetic field  $\mathbf{B}_0$ . Consequently, the NMR spectrum of boron ( $I = \frac{3}{2}$ ) consists of triplets (with relation of intensities 2:3:2 [5]) whose number for a single-crystal sample in the general case is equal to the number of magnetically non-equivalent boron nuclei. The position of the central NMR line (transition  $\frac{1}{2} \leftrightarrow -\frac{1}{2}$ ) coincides with Larmor precession frequency  $\nu_0$ , whereas quadrupole splitting between side band NMR lines (transitions  $\pm\frac{1}{2} \leftrightarrow \pm\frac{3}{2}$  respectively)  $\nu_2 - \nu_1$  is given by [5]

$$\nu_2 - \nu_1 = 6eQV_{zz}/2h \quad (1)$$

where  $Q$  is the quadrupole moment of nucleus,  $e$  is the electron charge,  $h$  is Planck's constant, and  $V_{zz}$ , is the  $z$  component of the electric field gradient (EFG) tensor at the nuclear site (field  $\mathbf{B}_0$  is directed along the  $z$  axis). The intensities of side-band component of powder NMR spectrum decrease sharply with increasing, quadrupole interaction due to the orientation dependences of quadrupole splittings (1). Only the central NMR line can be observed in powder samples very often. In these cases the shape of NMR spectra are described by the second-order quadrupole effects that take into account the dipole-dipole interactions between the magnetic nuclei.

The  $^{11}\text{B}$  NMR spectrum for crystalline  $\text{CuB}_2\text{O}_4$  is displayed in Fig. 2(a). The Fig. 2a shows that there are two components in spectrum. A narrow symmetric line can be assigned to the symmetric  $\text{BO}_4$  groups. A wide asymmetric component is characteristic of the axial-symmetric electric field gradient (EFG) tensor and this line can be assigned to the distorted  $\text{BO}_4$  groups. It can be seen from relative intensity of components that boron nucleus in one structurally nonequivalent position are twice as little than in another. This result corresponds to  $\text{CuB}_2\text{O}_4$  structural data [3,6].

The NMR spectrum for amorphous  $\text{CuB}_2\text{O}_4$  is shown in Fig. 2(c). A NMR central peak of amorphous sample arises from a highly symmetric electronic environment of boron atoms in  $\text{BO}_4$  tetrahedra, while  $\text{BO}_3$  triangles yield a wide peak

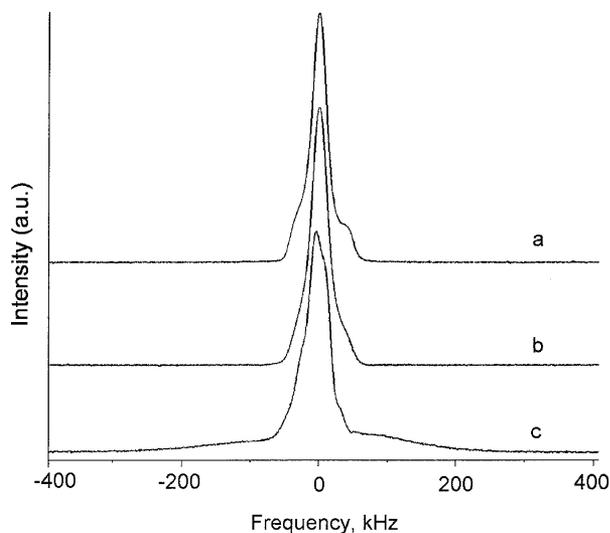


Fig. 2.  $^{11}\text{B}$  NMR spectra of  $\text{CuB}_2\text{O}_4$ : (a) crystalline sample; (b) crystallized from amorphous sample; (c) amorphous sample.

due to large interaction between the  $^{11}\text{B}$  nuclear quadrupole moment and EFG present at the boron site of amorphous  $\text{CuB}_2\text{O}_4$ . The calculation by area method proves that one-third of tetragonal  $\text{BO}_4$  units are converted in triangular  $\text{BO}_3$  units with formation of non-bridging oxygen under amorphization. Thus, our data provide evidence of the essential changes of boron-oxygen network in the amorphous  $\text{CuB}_2\text{O}_4$ .

The NMR spectrum  $^{11}\text{B}$  of the crystallized from amorphous  $\text{CuB}_2\text{O}_4$  sample is shown in Fig. 2(b). This spectrum coincides with a crystalline sample spectrum (Fig. 2(a)) practically completely. The light differences are caused by presence of a small amorphous  $\text{CuB}_2\text{O}_4$  impurity in the sample.

### 3. DISCUSSION

The paramagnetic Curie temperature increasing ( $\theta_{\perp} = -23\text{ K}$ ,  $\theta_{\parallel} = -17\text{ K}$  for crystalline and  $\theta = -56\text{ K}$  for amorphous  $\text{CuB}_2\text{O}_4$ ) and occurrence of anomalies in temperature dependence of susceptibility and of the resonance parameters [2] are the main effects of  $\text{CuB}_2\text{O}_4$  amorphization.

In letter [2] it was assumed that change of exchange chain  $\text{Cu}-\text{O}-\text{B}-\text{O}-\text{Cu}$  under amorphization  $\text{CuB}_2\text{O}_4$  takes place. In the present work we have shown by NMR method, that above-mentioned change takes place in actuality.

Figure 2 shows the  $^{11}\text{B}$  NMR spectra of crystalline  $\text{CuB}_2\text{O}_4$  (a) and amorphous (c), respectively. An NMR spectrum of crystalline  $\text{CuB}_2\text{O}_4$  and an NMR central peak of amorphous sample can be assigned to boron atoms of tetrahedral  $\text{BO}_4$  groups. From the comparison of line shape of these NMR spectra it follows that there are no marked distortions of the part of  $\text{BO}_4$  groups under amorphization. This fact also justifies the maintenance of structure of metaborate ring-type groups in the amorphous  $\text{CuB}_2\text{O}_4$ . The wide component of NMR spectrum (Fig. 2(c)) is characteristic of the trigonal  $\text{BO}_3$  units [7,8]. The integral intensity of a wide component is twice as little than central component. Hence, only bond of ring-type  $(\text{B}_3\text{O}_6)^{3-}$  units is broken with formation of one nonbridging oxygen atom and only  $\text{BO}_4$  tetrahedron of those units is converted to a trigonal  $\text{BO}_3$  unit.

Also, IR spectra show, that the parts of  $\text{BO}_4$  units are converted in trigonal  $\text{BO}_3$  units at amorphization of  $\text{CuB}_2\text{O}_4$  [9]. The IR absorption spectra of powders crystalline and amorphous  $\text{CuB}_2\text{O}_4$  have been measured. The absorption in  $800\text{--}1200\text{ cm}^{-1}$  range is assigned to B—O asymmetric stretching vibration of tetragonal  $\text{BO}_4$  units, and  $600\text{--}800\text{ cm}^{-1}$  range to the vibrations of the ring-type metaborate groups. New broad region of absorption in  $1200\text{--}1600\text{ cm}^{-1}$  range is appears in amorphous  $\text{CuB}_2\text{O}_4$ . It is proves about appearance of trigonal  $\text{BO}_3$  units in boron-oxygen network.

From structural analysis of  $\text{CuB}_2\text{O}_4$  it follows that the longest B—O bond ( $1.48\text{ \AA}$ ) belongs to one of three tetrahedrons of metaborate ring type group and this bond is broken under amorphization more probably. As mentioned above, the exchange interactions between ions  $\text{Cu}^{2+}$  ( $S = \frac{1}{2}$ ) in crystalline  $\text{CuB}_2\text{O}_4$  are carried out through the  $\text{Cu}-\text{O}-\text{B}-\text{O}-\text{Cu}$  chains. The distortions of ring type  $(\text{B}_3\text{O}_6)^{3-}$  units change the strength of exchange interaction in amorphous  $\text{CuB}_2\text{O}_4$ . Furthermore, the appearance of the non-bridging oxygen atoms makes possible formation of more short exchange chains  $\text{Cu}-\text{O}-\text{Cu}$  in which case the effective strength of exchange interaction is increased under amorphization of  $\text{CuB}_2\text{O}_4$ .

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