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Magnetic phase transitions and linear magnetic dichroism in manganese-doped copper metaborate (Cu,Mn)B_2O_4

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Abstract. The work presents a study of manganese-doped copper metaborate (Cu,Mn)B_2O_4 using optical spectroscopy. The temperature of the antiferromagnetic phase transition $T_N = 19$ K has been defined according to the absorption spectra. Polarization studies (Cu,Mn)B_2O_4 in isotropic *ab*-plane show the presence of linear antiferromagnetic dichroism in the magnetically ordered state previously observed in pure copper metaborate CuB_2O_4.This measurement allows to find the magnetic phase transition into an elliptical structure at the temperature $T^* = 7.0$ K.

1. Introduction

Magnetic materials with complicated crystal and magnetic structures attract great attention because of their interesting properties and features. One of the brightest representatives of such compounds is a copper metaborate CuB_2O_4. This compound demonstrates a unique combination of magnetic, magnetoelectric, linear and nonlinear optical properties. CuB_2O_4 has a complex crystal structure (S.G. *I42d*, Z = 12) in which the magnetic ions Cu^{2+} (S = 1/2) occupy two different crystallographic positions, *4b* and *8d* [1], forming two magnetic subsystems. The “strong” magnetic Cu (*4b*) subsystem orders at the Néel temperature T_N= 21 K into an antiferromagnetic commensurate (C) structure with the spins lying in the easy *ab*-plane and then at the temperature $T^* \sim 8$ K into an incommensurate helical (IC) structure while the "weak" quasi-one-dimensional subsystem Cu (*8d*) not completely ordered and fluctuate even at the lowest temperatures [2-6]. Multiple frustrated and nonfrustrated antisymmetric exchange interactions within and between the *4b* and *8d* magnetic sublattices result in a rich complex magnetic phase diagram. The study of electronic absorption spectra of CuB_2O_4 revealed narrow zero-phonon (ZP) lines for all transitions between the crystal-field-split *3d*-states of Cu^{2+} ions [7]. Recently, sublattice-sensitive optical linear dichroism in the crystallographically isotropic *ab*-plane attributed to a magnetic Davydov splitting has been detected below the temperature of an antiferromagnetic ordering [8]. It should be noted that LD was observed only on ZP exciton lines associated with the magnetic subsystem Cu(*4b*). Also, using the LD method a splitting of the phase transition at T^* into two transitions (at $T_1^* = 8.5$ K and $T_2^* = 7.9$ K) not previously registered by other methods has been established.

In a study of the magnetic properties of copper metaborate, a special interest is the investigation of CuB_2O_4 compounds in which the copper Cu^{2+} ion is partially replaced by another magnetic *3d*-ion. For example, a possibility of the weak ferromagnetic moment in Ni-doped CuB_2O_4 rotation up to ±30°by applying an electric field was demonstrated [9]. A recent paper dedicated to the investigation of magnetoelectric properties has also revealed the possibility of induction and control of electric polarization in (Cu, Ni)B_2O_4 under a magnetic field [10]. The authors explain observed phenomenon in the framework of spin-dependent metal-ligand hybridization. These results indicate a strong correlation between magnetic and electric orders and shed light on the mechanism of the magnetoelectric effect in (Cu, Ni)B_2O_4. So it was expected that a doping with another magnetic *3d*-ion could lead to new interesting magnetic and magnetoelectric effects. However, LD studies have not been performed for doped metaborates up to now. Thus, our work is aimed at studying magnetic properties of hybrid metaborates, namely manganese-doped copper metaborate (Cu,Mn)B_2O_4. In this paper, we report results of high-resolution optical spectroscopy investigation of (Cu,Mn)B_2O_4 with linearly polarized light, in the same geometry that was used in the experiments [8].

2. Experimental details

Single crystalline samples of (Cu,Mn)B_2O_4 were grown by the flux method in the system $Bi_2Mo_3O_{12}$ - B_2O_3 - Na_2O - Mn_2O_3 – CuO at spontaneous crystallization. The crystals have dark-blue color and a maximum size of 3x4x5 mm^3. Mn^{2+} concentration was estimated to be 2.0±0.2% by X-ray fluorescence.

Optical absorption measurements were performed with a resolution 1.2 cm^{-1} using a Bruker IFS 125HR Fourier spectrometer and a closed-cycle Cryomech ST403 cryostat at the temperatures between 3.2 and 300 K. The polarization of an incident light was controlled by a Glan-Taylor prism.

3. Results and discussion

Figure 1(b) shows the LD spectra shifted from each other along the *y*-axis in the region of the first Cu (*4b*) ZP line. Figure 1(a) shows the same spectra as an intensity color map with the frequency-temperature axes.

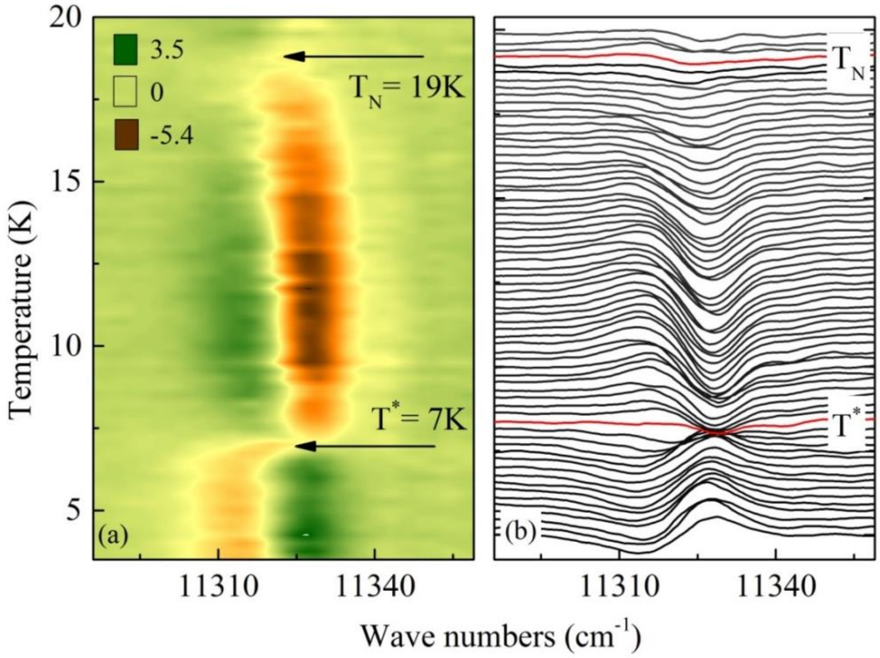

Figure 1.LD spectra in the region of the first *4b* ZP line of (Cu,Mn)B_2O_4 at temperatures below T_N, (for the light polarized along and perpendicular to the [110] direction; **k**||z), presented as (a) intensity color map, (b) shifted spectra.

The emergence of the LD below the temperature $T_N = 19.0$ K indicates a magnetic phase transition into an antiferromagnetic commensurate (C) structure as well as in CuB_2O_4 studies [8]. The reverse of LD has also been observed at the temperature $T^* = 7.0$ K.

As mentioned above, the features of the CuB_2O_4 magnetic structure at $T < T^*$ were considered earlier in [8]. The LD method made possible to clarify the previously proposed model of a simple circular helical magnetic structure. It has been shown that elliptical magnetic structures are realized below T^* with the large axis of the ellipse reorientation by π/2 at T_1^* and T_2^* sequentially. Thus, it can be assumed that $T^*$is the temperature of the $(Cu,Mn)B_2O_4$ magnetic phase transition into a simple helical structure, below which in the temperature interval $T < T^*$ an elliptical helical magnetic structure takes place.

Figure 2 shows a comparison of the pure and manganese-doped copper metaborates LD signals in the temperature region of 3.5 – 21 K.

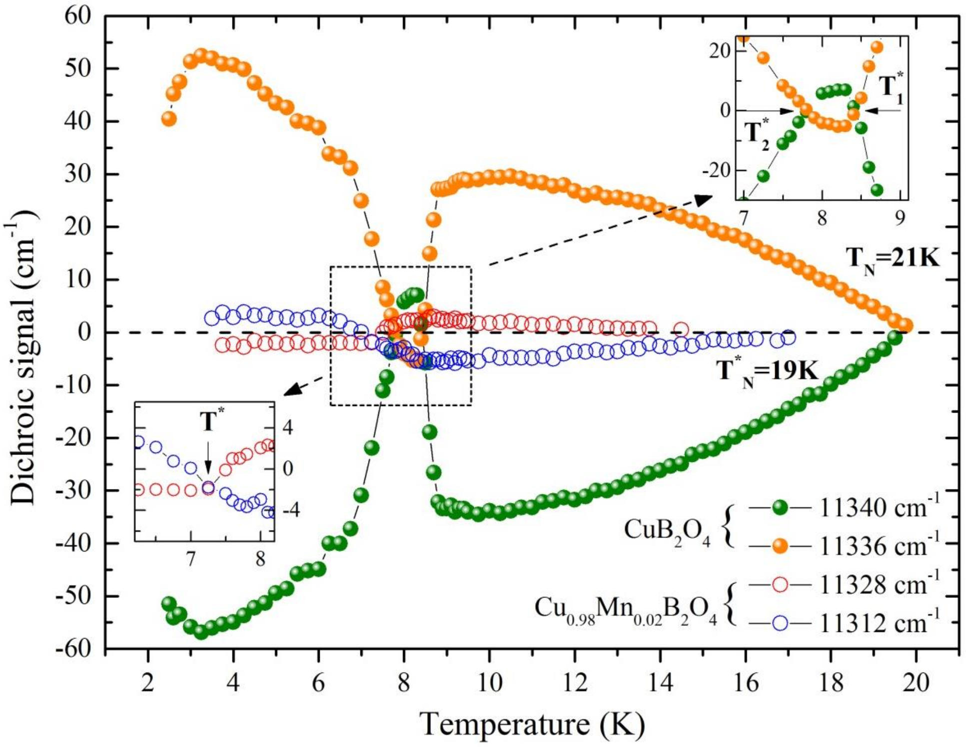

Figure 2. Temperature dependences of $(Cu,Mn)B_2O_4$ and CuB_2O_4 LD signals (for the light polarized along and perpendicular to the [110] direction). The inserts show the close-lying areas of the magnetic phase transitions of $(Cu,Mn)B_2O_4$ (T^*) and CuB_2O_4 (T_1^*, T_2^*) separately.

We can see that the LD signal of $(Cu,Mn)B_2O_4$ is about 10 times less than that in undoped metaborate. Doping with manganese results in a decrease of the CuB_2O_4 magnetic phase transitions temperatures ($T_N = 21$ K and $T^* \sim 8.0$ K for pure metaborate). The LD of $(Cu,Mn)B_2O_4$ undergoes a sign reverse at $T^*$and then does not disappear or change sign at least up to the lowest measured temperature of 3.5 K. In contrast to the pure metaborate, no splitting of T^* transitions are observed.

4. Conclusions

The absorption spectra of manganese-doped copper metaborate $(Cu,Mn)B_2O_4$ has been studied in the region of the first *4b* ZP line at temperatures below T_N. Linear dichroism associated with a magnetic

Davydov splitting has been observed in the magnetically ordered state of (Cu,Mn)B_2O_4, the same as in undoped metaborate CuB_2O_4. According to the LD spectra the temperatures of magnetic phase transitions into an antiferromagnetic commensurate (C) and an incommensurate helical (IC) structures has been established ($T_N = 19.0$ and $T^* = 7.0$ K respectively). The presented results reveal interesting opportunities of studying complicated magnetic structures by sublattice-sensitive optical linear dichroism method.

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