	Experiment title:	Experiment number:
ESRF	**X-ray dichroisms in copper metaborate CuB_2O_4 single crystal**	HC-717
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Report

Scientific Background

Systematic understanding of the interplay between a crystallographic and magnetic chirality is an important issue in the field of magnetism. CuB_2O_4 is an example of induction of chirality in the noncentrosymmetric canted antiferromagnet (under T<20 K) by application of a low intensity static magnetic field [1,2]. CuB_2O_4 crystallizes with a noncentrosymmetric but achiral tetragonal space group *I*-42*d*. Magnetic Cu^{2+} ions occupy square planar Cu (A) sites and distorted octahedral Cu (B) sites. Because four Cu(A) sites in a unit cell have different z coordination, the Cu(A) sites form an equal number of left- and right-handed screws propagating along the c axis with a periodicity of the crystallographic unit cell. CuB_2O_4 undergoes successive magnetic transitions at 10 and 21 K [3,4]. Between 10 and 21 K, the magnetic moments at the Cu(A) sites show commensurate easy-plane antiferromagnetism with a canted ferromagnetic component along the [110] axis due to the Dzyialoshinskii-Moriya interaction while the Cu(B) spins are disordered [3,4]. According to [1] the crystal chirality is reversed by a 90^o rotation of the direction of the magnetic field due to the deformation of hole clouds by the spin-orbit coupling at Cu(A) sites making inequivalent the right- and left-handed screws. Above the Neel temperature CuB_2O_4 exhibits the paramagnetic behavior ascribing to the Cu(A) spins. To explain the difference of two Cu sites properties it is necessary to study their electronic states in details.

XNCD and XMCD are the most appropriate techniques to study the electronic states, including the hybridization of electronic states of opposite parity, which are responsible for the optical activity and to give a useful insight into electronic structure of the compounds [5]. X-ray technique also allows to avoid the problem of strong absorption by boron typical for neutrons scattering.

Experimental details

XNCD and XMCD spectra in CuB_2O_4 were measured at the Cu K-edge (8979 eV). The sample of a very good quality cut along appropriate direction and polished was used for the experiment. The absorption coefficients of right-handed and left-handed circularly polarised X-rays with wave vector along the a-axis were measured in the applied magnetic field equal to 17 T with two opposite orientations. We have used the second harmonic of an APPLE-II helical undulator. The circular polarization rate for these photon energies was in excess of 90 %. X-ray absorption spectra were recorded at room temperature using total X-ray fluorescence yield detection mode. The XNCD spectra were obtained as the direct difference of two x-ray absorption spectra recorded with right- and left circularly polarized X-rays summarized over two opposite

magnetic field directions ($I_+(H+)$-$I_-(H+)$+ $I_+(H-)$-$I_-(H-)$)/2. The XMCD spectra was defined as ($I_+(H+)$-$I_-(H+)$- $I_+(H-)$+$I_-(H-)$)/2. The available sample was not suitably cut to measure XMCD signal.

Results

The point symmetry -42m of a crystal is compatible with existence of XNCD with k along a- or b-axes due to the electric dipoleï electric quadrupole (E1E2) interference terms corresponding to the mixing of electronic states with opposite parity [5]. The experimentally measured XMCD and XNCD spectra CuB_2O_4 are represented in figure 1. The measurements were made at the room temperature with the applied strong magnetic field. The existence of the XMCD signal confirms the paramagnetic behavior of the sample. It is important that the XMCD signal exists in the pre-edge region usually associated with the quadrupole resonant transition. The electronic configuration of Cu $3d^{10}4s^1$ contains completely filled d-shell and no atomic magnetic moment while the electronic configuration of Cu^{2+} ions $3d^9$ corresponds to not completely filled d-shell. Correspondingly, the observed XMCD signal in the pre-edge region confirms the existence of the holes in 3d-states while the XNCD signal observed both in the pre-edge region and above means that the Cu 3d-4p hybridization exists in the sample. First calculations made using the FDMNES code [6] are in consistence with the observed XNCD spectra, which are the sum of the signals providing by Cu(b) and Cu(d) sites (see figure 2).

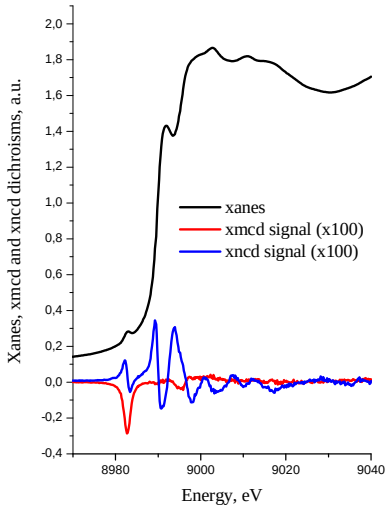

Fig. 1. Experimentally measured XANES, XNCD and XMCD spectra in CuB_2O_4.

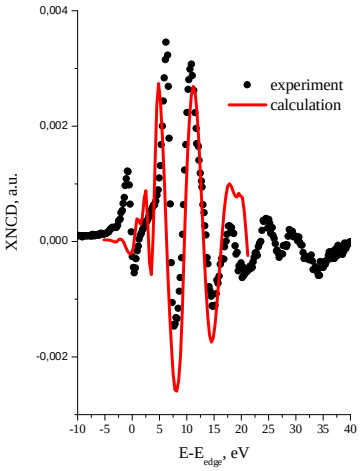

Fig. 2. The measured and simulated XNCD spectra in CuB_2O_4.

Clearly more sophisticated calculations are needed to separate the contribution of nonequivalent Cu sites to XMCD signal and they are in progress. To make this separation more reliable we propose in future to use the scattering geometry, which makes the spectra of circular dichroism sensitive to energy and azimuthal angle due to interference of X-ray scattered by Cu in two inequivalent sites.

References

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Report Summary

XNCD and XMCD signals in CuB_2O_4 were measured at the Cu K-edge along the **a** axis in the applied magnetic field with two opposite directions. The XMCD signal was observed in the pre-edge region while the XNCD exists both in the pre-edge and above. The calculations made using the multiple scattering method have shown the satisfactory agreement with experimental results and have allowed to separate the XNCD signal provided at the Cu K-edge by Cu atoms in two different crystallographic positions.