



Experiment title: X-ray circular dichroism in resonant scattering by metaborate CuB₂O₄ single crystal		Experiment number: HC-1229
Beamline: ID 12	Date of experiment: from: 16-22 July 2014	Date of report: 30.03.2015
Shifts: 18	Local contact(s): Andrei Rogalev	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Dr. Pavel Prosekov, A.V.Shubnikov Institute of Crystallography, Moscow, Russia Dr. Elena N. Ovchinnikova, Moscow State University, Moscow, Russia Dr. Vladimir E. Dmitrienko, A.V.Shubnikov Institute of Crystallography, Moscow, Russia		

Report

Scientific Background

Copper metaborate CuB₂O₄ crystallizes with a noncentrosymmetric but achiral tetragonal space group *I*-42*d*. Magnetic Cu²⁺ ions occupy square planar Cu (A) sites and distorted octahedral Cu (B) sites. Below 20 K CuB₂O₄ exhibits chiral magnetic structure, which has attracted much attention because of its novel behavior of magnetization. Above the Neel temperature copper metaborate demonstrates paramagnetic behavior, which is usually associated with one of the Cu sites. Recently measured at the beamline ID12 XMCD and XNCD in copper metaborate exhibiting the crystal and magnetic chirality confirms the existence of the holes in 3d-states and 3d-4p hybridization of Cu electronic states (report HC-717). Both methods give information averaged over two Cu sites. The contributions from two Cu sites can be separated using the geometry of scattering with circularly polarized incident radiation. In the experiment HC-1229 carried out at the beamline ID12 the energy and azimuthal dependences of the difference $I(E) = I_+(hkl) - I_-(hkl)$ were measured for two forbidden reflections 330 and 110 with right and left circular polarizations in the vicinity of the Cu K-edge. Huge value of I was observed for the reflection 110. The interference of the X-rays scattered by two nonequivalent Cu sites makes the energy spectra of forbidden reflections sensitive to the azimuthal rotation and the usage of circularly polarized beams, which allows to extract the information about the electronic states corresponding to nonequivalent Cu sites.

Experimental details

The energy spectra of the forbidden reflections 330 and 110 were measured reflection with right-handed and left-handed circularly polarised X-rays, in dependence on energy and azimuthal angle at the energies close to the Cu absorption edge (8979 eV). 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 002 reflection declared in the proposal could not be observed because of bad sample quality, but we have studied two hh0 reflections using a good and polished crystal with appropriate surface. The measured energy spectrum of the 330 forbidden reflection and difference $I(E) = I_+(330) - I_-(330)$ (circular dichroism or asymmetry) are shown in figure 1. The energy spectra of the 110 forbidden reflection were measured for the right- and left polarization at two azimuthal angles: 40° and 50°, exhibiting a huge value of $I(E)$. In the last experiment the azimuthal dependence of the 110 reflection in maximum of intensity was measured.

Results

The space symmetry group $I-42d$ does not contain any screw axis, which can provide the chirality (asymmetry) of the dipole-dipole forbidden reflections for two circular polarizations as was predicted in [1]. Such asymmetry was observed in crystals with the screw axes [2,3]. Recently asymmetry of the forbidden reflection was discovered in BiFeO_3 with $R3c$ space symmetry in the pre-edge of Fe, which corresponds to the dipole-quadrupole scattering [4]. In the copper metaborate we have observed the huge asymmetry of the 110 forbidden reflection intensity in a wide energy range from the pre-edge up to the white line. We suppose it is provided by the interference between the $E1E2$ x-ray scattering by copper atoms in Cu (A) sites and the $E1E1 + E1E2$ scattering by Cu (B) sites. Observed azimuthal dependence of the $I(E)$ for the 110 reflection is in a good consistence with calculations (fig.2) and demonstrates higher symmetry than the azimuthal dependence corresponding to each polarization.

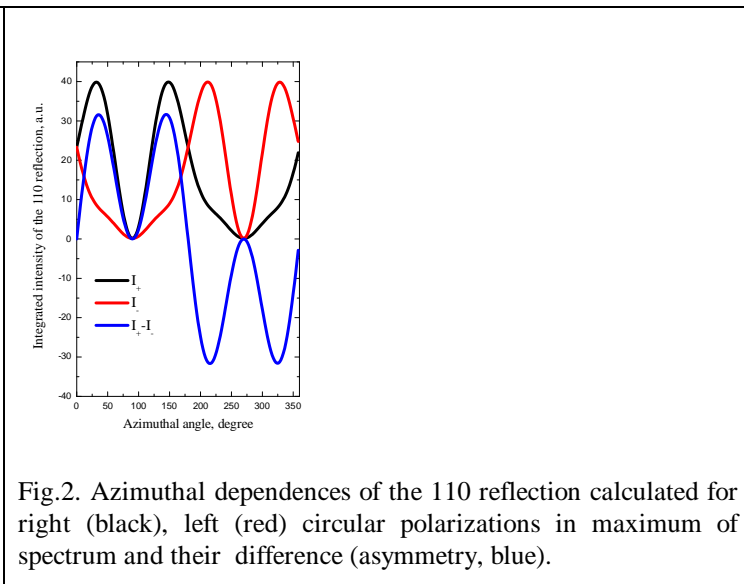
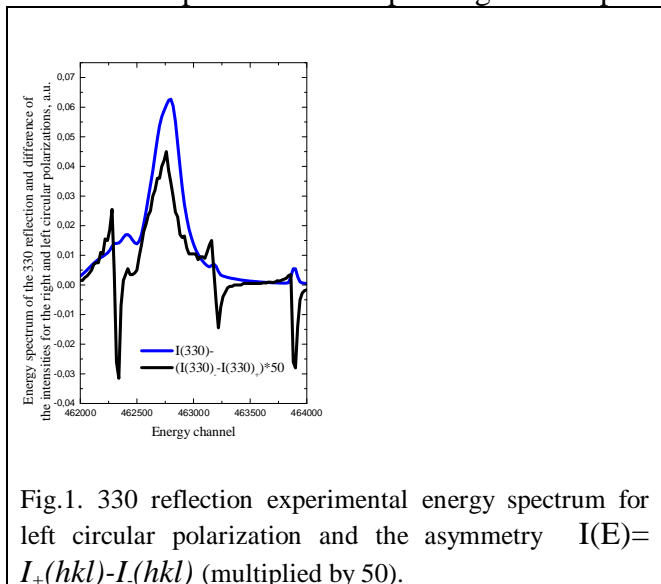


Fig.1. 330 reflection experimental energy spectrum for left circular polarization and the asymmetry $I(E) = I_+(hkl) - I_-(hkl)$ (multiplied by 50).

Fig.2. Azimuthal dependences of the 110 reflection calculated for right (black), left (red) circular polarizations in maximum of spectrum and their difference (asymmetry, blue).

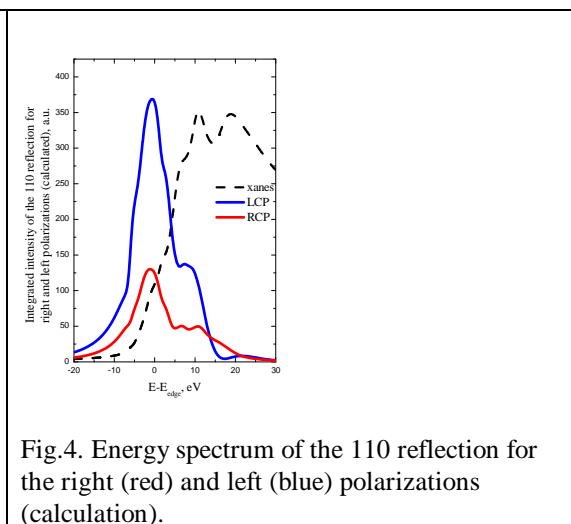
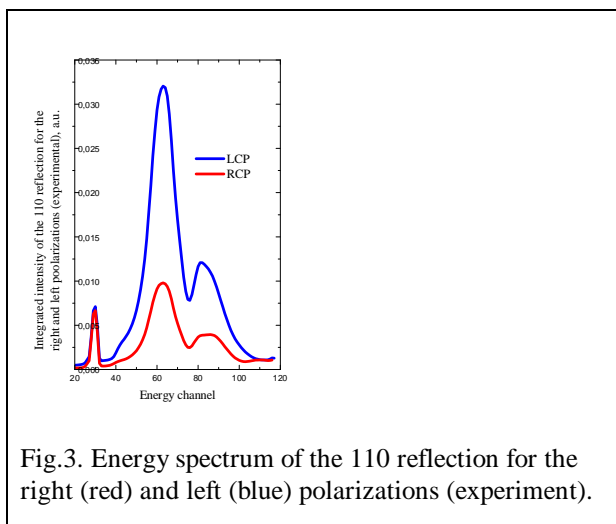


Fig.3. Energy spectrum of the 110 reflection for the right (red) and left (blue) polarizations (experiment).

Fig.4. Energy spectrum of the 110 reflection for the right (red) and left (blue) polarizations (calculation).

First calculations of the 110 and 330 reflections energy spectra made using the FDMNES code [5] have shown a qualitative consistence with the experimental data (fig. 3,4) but clearly more sophisticated calculations are needed to achieve quantitative coincidence, which will allow to separate the contributions of nonequivalent Cu sites to forbidden reflections spectra and they are in progress.

References

- [1] V.A.Belyakov, V.E.Dmitrienko. Sov. Phys. Usp.32, 6976719 (1989).
- [2] Y. Tanaka, S.W. Lovesey. Eur. Phys. J. Special Topics 208, 67674 (2012).
- [3] T. Usui, Y. Tanaka, H. Nakajima, et al. Nature Materials 13, 6116618 (2014).
- [4] A. Rodriguez-Fernandez, S.W.Lovesey, S.P. Collins, G.Nisbet, J. A. Blanco. Journal of Physics: Conference Series **519**, 012012 (2014).
- [5] <http://www.neel.cnrs.fr>

Report Summary

The energy spectra of the forbidden Bragg reflections 330 and 110 in CuB_2O_4 were measured at the Cu K-edge with right and left circular polarizations of incident radiation. It was obtained that the difference between the diffracted intensity corresponding to the right and left circular polarizations (asymmetry) is much more for the 110 reflection than for the 330 reflection and strongly depends on the azimuthal angle. The shape of the energy spectra is determined by interference between the resonant scattering of X-rays by Cu atoms in two different crystallographic positions.