ESRF	**Experiment title:** Structural investigation of Cu-based quantum magnets $(CuBr)LaNb_2O_7$, $(CuCl)LaTa_2O_7$, and $(CuBr)Sr_2Nb_3O_{10}$	**Experiment number**: HE3351
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Shifts: 9	**Local contact(s)**: Caroline Curfs	*Received at ESRF:*

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Report:

The experiment was devoted to an accurate structural study of the $(CuBr)LaNb_2O_7$, $(CuCl)LaTa_2O_7$, and $(CuBr)Sr_2Nb_3O_{10}$ compounds that belong to the enigmatic family of layered Cu^{+2} oxyhalides with non-trivial magnetic behavior [1]. Recently, high-resolution x-ray and neutron diffraction (including our own work performed at ESRF [2]) were very successful in elucidating the correct crystal structure of $(CuCl)LaNb_2O_7$, the parent compound of the family [2–4]. The diffraction experiments amended the previously published tetragonal structural model, and established the orthorhombic symmetry within a four-fold supercell. The revised structural information was essential to clarify the origin of the spin gap in this compound, and to explain the peculiar features of excitation spectra measured by inelastic neutron scattering [2]. Since the interesting magnetic behavior of $(CuBr)LaNb_2O_7$, $(CuCl)LaTa_2O_7$, and $(CuBr)Sr_2Nb_3O_{10}$ still lacks any microscopic interpretation, it is tempting to apply similar methods and reconsider the crystal structures of these compounds that were previously refined within the tetragonal symmetry.

The bulk of this report deals with the first compound, $(CuBr)LaNb_2O_7$. In $(CuBr)Sr_2Nb_3O_{10}$, neither synchrotron x-ray diffraction (XRD) nor neutron powder diffraction revealed any superstructure reflections or reflection splittings that would violate the published tetragonal unit cell. In $(CuCl)LaTa_2O_7$, we were also unable to observe any deviations from the tetragonal symmetry in the ID31 measurements. However, the neutron data clearly showed the superstructure, which is remarkably similar to the scenario of $(CuCl)LaNb_2O_7$. The discrepancy between the x-ray and neutron data might be related to different penetration depth or to a slight difference between the samples. Presently, we try to understand the origin of this discrepancy by additional experimental studies including an electron microscopy investigation.

The x-ray data for $(CuBr)LaNb_2O_7$ are seemingly similar to our previous results on $(CuCl)LaNb_2O_7$ [2]. The weak but clearly visible superstructure reflections, as well as the notable splitting of the 400 and 040 subcell reflections (Fig. 1), indicate the four-fold orthorhombic supercell, which is doubled along both *a* and *b* directions. After analyzing possible distortions and refining the ID31 data together with the neutron data from the D2B and D20 instruments of ILL, we arrive at the unique structure solution in the *Pbam* space group. Although the neutron experiment is more sensitive to the positions of light atoms, a refinement solely based on the neutron data was highly unstable, because the weak orthorhombic splitting is barely visible in the neutron experiment. Therefore, the XRD measurements on $(CuBr)LaNb_2O_7$ are indispensable and essential for the accurate structure refinement.

The refined structure of $(CuBr)LaNb_2O_7$ reveals the $a^0b^-c^0$ tilting distortion of the $LaNb_2O_7$ perovskite block, and the displacements of the Cu and Br atoms in the *ab* plane (Fig. 2). The shorter Cu–Br bonds form zigzag chains running along the *b* direction. The structure is very similar to our model of $(CuCl)LaNb_2O_7$ [2]. One important difference is the partial disorder of the Br atoms that occupy a split position with the nearly 1:1 ratio of the Br1/Br2 occupancies. Based on the arguments of chemical bonding and electronic structure, we conjecture that the occupation of the split Br position is not fully random, i.e., the Br atoms in the vicinity of each Cu atom occupy either Br1 or Br2 positions. In $(CuCl)LaNb_2O_7$, the short Cu–Cl bonds have a clear preference to the *trans*-arrangement (Cl–Cu–Cl angle of about 180 deg), and a similar scenario should be operative in $(CuBr)LaNb_2O_7$.

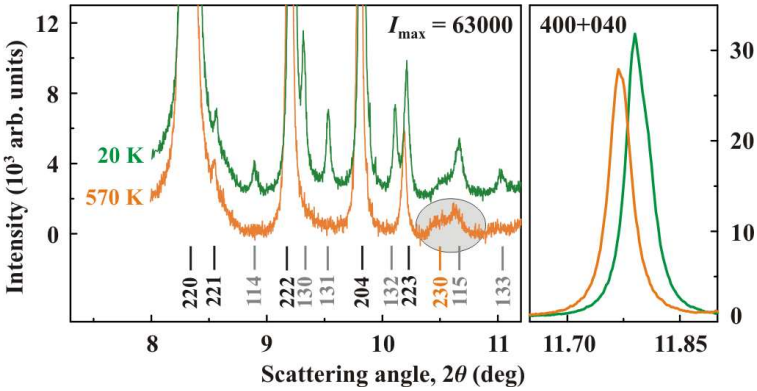

Fig. 1. Left: XRD patterns of $(CuBr)LaNb_2O_7$ measured at 20 K and 500 K. Gray indices denote the superstructure reflections with *h*+*k* even, while the shaded area shows the diffuse scattering at *h*+*k* odd. Right: the splitting of the 400 reflection at 20 K

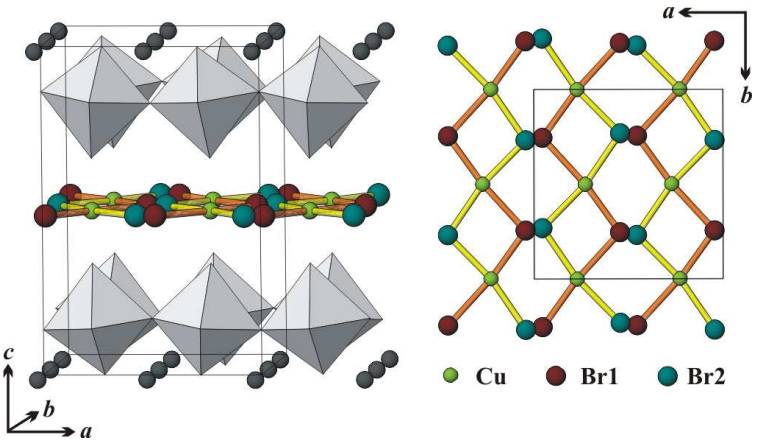

Fig. 2. Overall view of the orthorhombic $(CuBr)LaNb_2O_7$ structure with the $a^0b^-c^0$ tilting pattern of the NbO_6 octahedra, and the projection of the [CuBr] layer featuring the split Br position.

The partial disorder of the Br atoms is reflected in the peculiar shape of the superstructure reflections *hkl* that show a sizable broadening for *h*+*k* odd (Fig. 1). The superstructure reflections with *h*+*k* odd indicate the ordered arrangement of Br atoms. If these reflections are narrow, the structure should be fully ordered, as in $(CuCl)LaNb_2O_7$. The broadening of the superstructure reflections implies that the complete ordering of the Br atoms takes place on the short length scale only. The neighboring domains with the full occupation of either Br1 or Br2 positions are transformed into each other by half of the lattice translation along *b*. This transformation maps Br1 onto Br2, and represents an antiphase boundary. Our scenario is corroborated by an electron-microscopy investigation that reveals a very small size of the fully ordered domains (5–10 nm), which is compatible with the broadening of the superstructure reflections.

At high temperatures, the orthorhombic $(CuBr)LaNb_2O_7$ structure transforms into a tetragonal polymorph with regular $LaNb_2O_7$ blocks and disordered displacements of the Cu and Br atoms in the *ab* plane. This transformation involves a single structural phase transition around 500 K, where the superstructure reflections with *h*+*k* even disappear. The diffuse scattering at *h*+*k* odd is also present above 500 K and gradually diminishes at higher temperatures without an abrupt phase transition.

Based on the combination of XRD and neutron data, we were able to revise the structural model of $(CuBr)LaNb_2O_7$, and study in detail the peculiar atomic arrangement in this compound, which shows both similarities and differences to $(CuCl)LaNb_2O_7$. The main effect is the tendency to disorder because of the larger size of Br compared to Cl. Presently, we are using the structural data for modeling the magnetic behavior. **The results of the present experiment are published in Phys. Rev. B 85, 214427 (2012) [$(CuBr)LaNb_2O_7$] and Phys. Rev. B 86, 064440 (2012) [$(CuCl)LaTa_2O_7$].**

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