ESRF	**Experiment title: Anomalous Scattering Study to Determine the Ordering in the Double Perovskite System of $Sr_2TbRu_{0.90}Cu_{0.10}O_6$**	**Experiment number**: 01-01-610 Run 4-02
Beamline: BM1B	**Date of experiment**: from: 4/9/02 to: 5/9/02	**Date of report**: February 2004
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Report:

The crystal structures of the double perovskites $Sr_2B'Ru_{1-x}Cu_xO_6$ (B' = Y, Ho or Tb and $x = 0 – 0.15$) have been studied recently [1] because copper doping induces superconductivity in the materials and the level is too low for CuO_2 planes to form [2 - 4]. The superconducting transition temperature is 30 – 40 K and additionally the materials develop long-range magnetic order in this temperature region. In order to fully understand the role of the copper dopant, it is important to know its location in the material so that the effect on the superconductivity and magnetism, which may be closely related, can be investigated. Prior studies of $Sr_2TbRu_{1-x}Cu_xO_6$ had determined that this series was free of crystalline impurities and the best system to conduct this study.

The unit cell of a double perovskite is shown in Figure 1 and for Sr_2TbRuO_6 the 2*c* sites are occupied by terbium and the 2*d* sites by ruthenium. With the introduction of copper, there are three cations, Tb, Ru and Cu, and to determine their distribution over the two fully occupied sites requires two diffraction patterns with different scattering factors. Neutron diffraction is blind to the cation distribution as the neutron scattering lengths of these elements are so similar. However, synchrotron X-ray diffraction, combining anomalous and non-anomalous diffraction, will provide two sets of scattering factors. At wavelengths practical for diffraction, the largest change in the scattering factor was determined to occur at the Ru *K*-edge at ~ 22117 eV, an energy ideally suited for experiments at BM1B

As the precise position of the edge depends on the chemical environment, a fluorescence scan was performed on $Sr_2TbRu_{0.90}Cu_{0.10}O_6$ (Figure 2) and the edge determined to be at 22130 eV. Diffraction patterns were then measured from 2 to ~ 27° at each of the energies indicated in Figure 2, as well as 22050 eV, so different scattering factors of ruthenium could be utilised throughout the edge. Three of the diffraction patterns are compared in Figure 3 for the small angular range of 6.5 – 8.1° and the effect of the change in the ruthenium scattering factor is clear to see on those peaks formed from the sum (7.8° peak) and difference (6.8° peak) of the scattering factors of the 2*c* and 2*d* sites.

The diffraction pattern of $Sr_2TbRu_{0.90}Cu_{0.10}O_6$ measured at 22100 eV is shown in Figure 4 and was refined using the crystal structure determined from an earlier non-anomalous data collection at BM1B, but now allowing *B* cation disorder. The calculated profile accurately replicates the experimental data, particularly the two peaks highlighted in Figure 4, which are formed from the difference of the total scattering factors of the 2*c* and 2*d* sites. The requisite difference in scattering factors on the sites can be achieved by either Tb exchanging site location with 6.8(2) % of Ru, with 5.6(2) % of Cu, or a mixture of the two. Figure 5 shows the disorder diagram for the $Sr_2TbRu_{0.90}Cu_{0.10}O_6$ system and for the 22100 eV measurement these are the intercepts of the axes, with the line between (red) showing all the possible disorder solutions allowed by the one diffraction pattern. Refinement using the data measured at each energy yields a separate line of solutions, the gradient being determined by the scattering factors of the three *B* cations, especially Ru as it varies through the edge. Ideally, they should intersect at a single point, which would indicate the actual distribution of cations in the system. However, the extra absorption of the ruthenium at its *K*-edge, evidenced with the 7.8° peak in Figure 3, was difficult to model precisely and led to this distribution of results. The results of the 22130 eV measurements are significantly different from the rest and unreliable because the scattering factor of ruthenium varies too rapidly with energy (2 electrons per eV) at the edge. This problem is negligible at 20-30 eV away from the edge and suggests future experiments should be performed only at this energy and not at the edge. The other anomalous results are more similar and taken with the non-anomalous results possibly suggest, but do not confirm, that ~ 7 % of the copper is disordered on the 2*c* site.

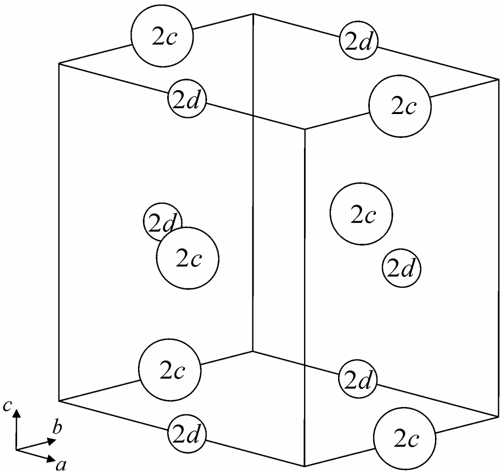

Figure 1. Unit cell of Sr_2TbRuO_6 which has a 1:1 ordered *B* cation arrangement, with Tb on the 2*c* site and Ru on the 2*d* site.

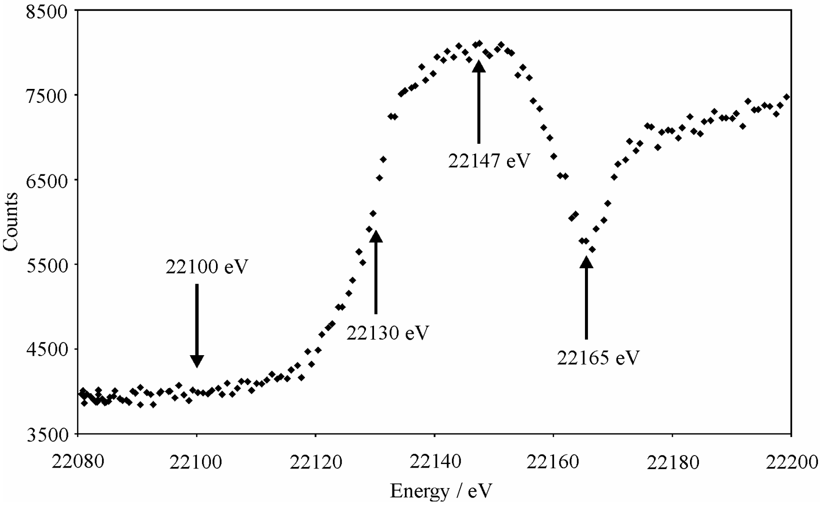

Figure 2. Fluorescence scan of the Ru *K*-edge with arrows marking energies selected for a further diffraction pattern to be measured.

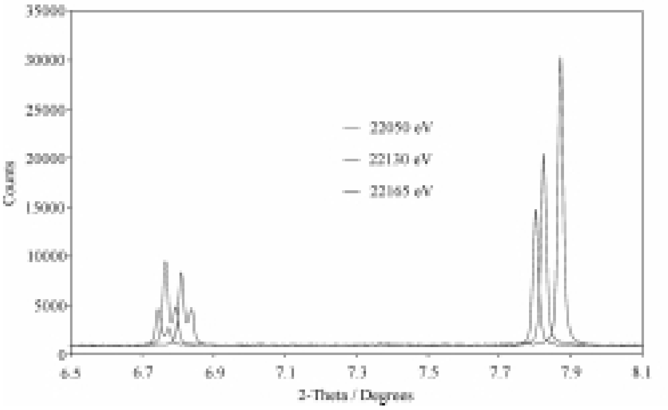

Figure 3. Comparison of same section of diffraction pattern for three different energies, below (22050 eV), at (22130 eV) and above (22165 eV) the edge.

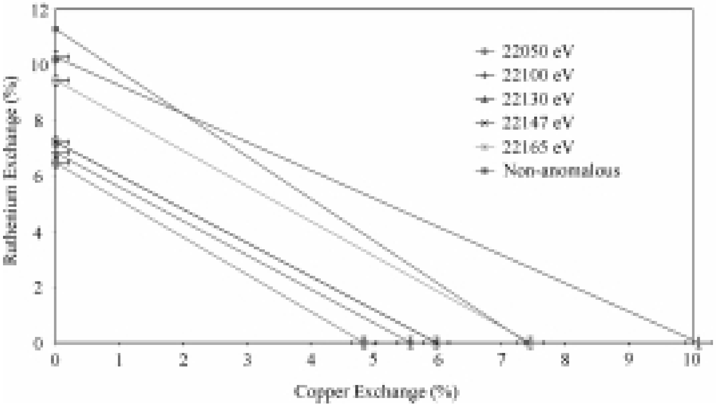

Figure 5. Disorder plot for $Sr_2TbRu_{0.90}Cu_{0.10}O_6$ comparing the results of the anomalous and non-anomalous data collections at BM1B.

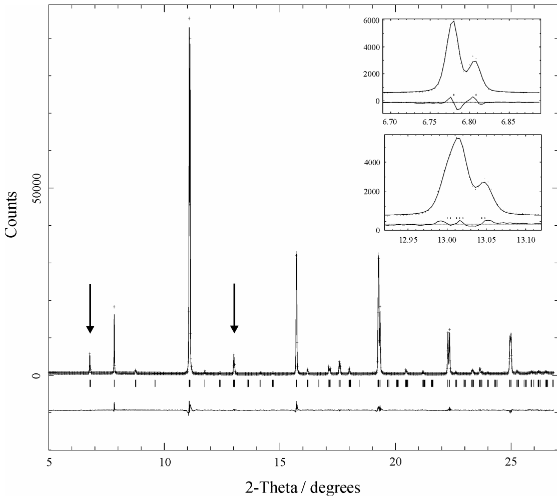

Figure 4. Diffraction pattern measured at 22100 eV. The two most important peaks for determining the cation distribution are arrowed and enlarged in insets. The intrinsic weakness of these difference peaks also benefits from the high intensity of the beamline.

References :

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[3] D.Y. Chen *et al.*, *Physica C* **282**, 73 (1997).
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