ESRF	**Experiment title:** Compositional tuning of charge-ordering spin-state transition in $REBaFe_2O_{5+w}$	**Experiment number:** 01-01-249
Beamline: BM01B	**Date of experiment:** from: 28.03.2001 to: 03.04.2001	**Date of report:** 30.07.2001
Shifts: 18	**Local contact(s):** Dr. Vouter van Beek, Mr. Hermann Emmerich	*Received at ESRF:*

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Report:

Synchrotron x-ray powder diffraction data suitable for Rietveld refinements of the double-cell perovskite superstructure were collected for four samples of $EuBaFe_2O_{5+w}$ across the oxygen non-stoichiometry range from $w = 0.010$ to 0.18 and one sample with $w = 0.300$ at temperatures 200 and 320 K. For the sample with the least oxygen non-stoichiometry, super-superstructure (that is, double superstructure) reflections were detected, associated with charge ordering of the two integer valences of iron, *viz.*, Fe^{2+} and Fe^{3+}. Although these extremely weak Bragg lines eventually proved not sufficient for the actual refinement of the super-superstructure, their detection with the four detection channels operating at that time is very promising for the new setup having six chanels with untreated (sharply resolving) Si analyzer crystals. Up to the the non-stoichiometry level of $w = 0.18$, manifestations of the charge ordering are detected in the orthorhombic deformation of the low-temperature phase (two samples at higher oxygen contents could not be measured in the beam-time available). A very subtle orthorhombic distortion, resolvable only in synchrotron x-ray powder diffraction experiments is associated with the premonitory Verwey transition that precedes the main charge ordering and is a novel feature of these mixed-valence oxides.

The Janis cryostat installed at the diffractometer provides an excellent temperature control, and finely scaled isothermal scans could be made across both the main and premonitory Verwey transitions. While sufficient to establish the data relevant to the main transition, the resolution of the short-scan technique with the suspended cryostat is on its limit with respect to establishing the unit-cell evolution at the premonitory transition. A contributing factor is the temperature limit of 340 to 350 K that does not provide so many points above the transition as desirable to establish the temperature dependence versus the occurring random errors. It is possible that the use of the sharp-resolving analyzer crystals in the six-detector arrangement will allow data collection over a weaker in intensity but more robust high-order set of Bragg peaks and improve the stability of the results. Unfortunately, wide-angle data for full Rietveld refinements including systematic treatment of diffractometer constants would require prohibitively long data collection for those at least 30 such patterns necessary to establish the unit-cell evolution. A new beam-time has been applied for and partially granted, to try to finish these experiments.