ESRF	**Experiment title:** **Charge Ordering in Mixed Valence Rare Earth Sr-doped Cobaltates**	**Experiment number**: HE-1716
Beamline: ID31	**Date of experiment**: from: 7/4/2004 to: 13/4/2004	**Date of report**: 4/3/2005
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Report:

Synchrotron X-ray diffraction patterns for a range of rare-earth perovskites materials were collected (at λ = 0.5001(1) Å) on the high-resolution powder diffraction beam line ID31. These data should contribute to 3 research publications.

These experiments may be summaries as follows:

(i) Structural variation in the $Y_{1-x}Sr_xCoO_{3-\delta}$ family of compounds.

The $Y_{1-x}Sr_xCoO_{3-\delta}$ family of compounds forms single phase samples for compositions x> 0.6. Our previous studies have shown that oxygen-deficient superstructures of the basic perovskite are formed at room temperature.[1,2] For $0.6 < x \leq 0.9$, a 2×2×4 tetragonal (*I4/mmm*) superstructure is formed; while the x = 0.95 composition crystallises with a 1×1×2 tetragonal (*P4/mmm*) superstructure at 295 K.

We collected diffraction patterns for $Y_{1-x}Sr_xCoO_{3-\delta}$ for x = 0.7, 0.8, 0.9 and 0.95 at temperatures ranging from 80 K to 700 K.

Samples of $Y_{0.3}Sr_{0.7}CoO_{3-\delta}$ showed a clear structural transition as a function of temperature, with a different structure types being observed below 250 K compared to the previously observed tetragonal superstructure above 350 K. Figure 1 shows an expanded region of the diffraction profiles of this material as a function of temperature, which reveals the collapse in the tetragonal splitting below 250 K.

Samples of $Y_{0.2}Sr_{0.8}CoO_{3-\delta}$ also showed a clear structural transition as a function of temperature. Below 500 K additional superstructure peaks appear indicating a decrease in symmetry along with a collapse in the tetragonal splitting for the low temperature structures.

Samples of $Y_{0.1}Sr_{0.9}CoO_{3-\delta}$ and $Y_{0.05}Sr_{0.95}CoO_{3-\delta}$ revealed only the effects of thermal expansion on their structures.

(ii) Structural variation in the $Eu_{1-x}Sr_xCoO_{3-\delta}$ family of compounds.

The $Eu_{1-x}Sr_xCoO_{3-\delta}$ family of compounds has a far more extended solid solution than the Y analogues, ranging from x = 0 to x=0.95. With increased Sr-doping across this series the structure was found to vary from orthorhombic (*Pbnm*) (x = 0.1 – 0.2) through a two-phase region to a tetragonal form (*I4/mmm*) (x = 0.7 – 0.9) – analogous to that observed for the above $Y_{1-x}Sr_xCoO_{3-\delta}$ phases. Data was collected for all compositions on ID31 at 295 K and 80 K. Analysis of these structural variations as a function of doping and temperature are continuing.

(iii) Structural variation in the $Sr(Sc_{1-x}Co_x)O_{3-\delta}$ family of compounds.

The $Sr(Sc_{1-x}Co_x)O_{3-\delta}$ family of compounds shows a limited solid solution range of B-site doping for x ≥ 0.7. At first glance these data appear be based on a simple-cubic (*Pm-3m*; ~3.88 Å) perovskite structures. However, the very high signal-to-noise afforded by these ID31 data reveal very weak, broad superstructure peaks indicative of short-range order based on a 2×2×4 tetragonal (*I4/mmm*) superstructure (lower peak markers in Figure 3).
These data and structural analysis have contributed a manuscript that has been submitted to Solid State Sciences.[3]

References

1. M. James, D. Cassidy, D. J. Goossens and R. L. Withers, "The Phase Diagram and Tetragonal Superstructures of the Rare Earth Cobaltate Phases $Ln_{1-x}Sr_xCoO_{3-\delta}$?(*Ln* = La^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Gd^{3+}, Y^{3+}, Ho^{3+}, Dy^{3+}, Er^{3+}, Tm^{3+} and Yb^{3+})", *J. Solid State Chem.*, **177**, 1886-1895 (2004).

2. M. James, D. Cassidy, K. F. Wilson, J. Horvat and R. L. Withers, "Oxygen Vacancy Ordering and Magnetism in the Rare Earth Stabilised Perovskite Form of "$SrCoO_{3-\delta}$".", *Solid State Sciences*, **6(7)**, 655-662 (2004).

3. M. James, K. S. Wallwork, R. L. Withers, P. J. Smythe, X. L. Wang and D. Cassidy, "The Crystal Chemistry and Magnetic Properties of the Oxygen-Deficient Perovskite $SrSc_{1-x}Co_xO_{3-\delta}$ (x ≥ 0.7).", *Solid State Sciences*, Submitted (2004).

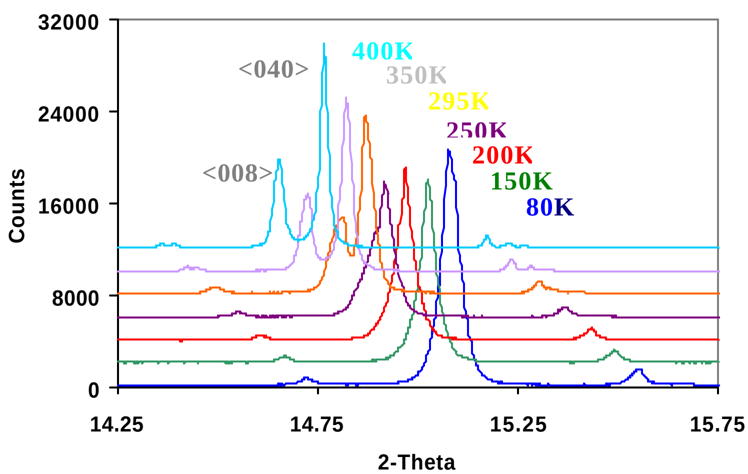

Figure 1. Structural evolution of $Y_{0.3}Sr_{0.7}CoO_{3-\delta}$ versus temperature

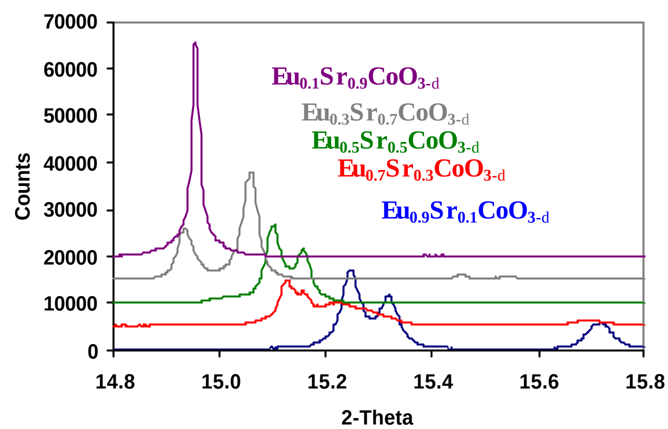

Figure 2. Structural evolution of $Eu_{1-x}Sr_xCoO_{3-\delta}$ with Sr-doping

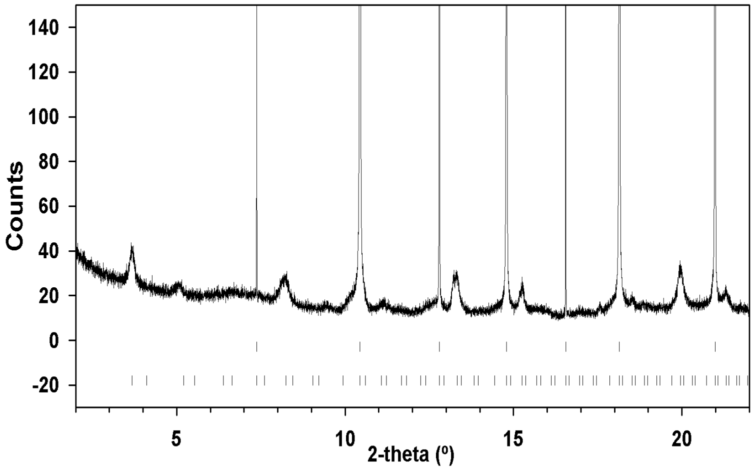

Figure 3. Short-range ordered 2×2×4 tetragonal superstructure reflections in $Sr(Sc_{0.2}Co_{0.8})O_{3-\delta}$