ESRF	**Experiment title: Methodological Study by Anomalous Diffraction of the Precise Location of two Cations In Zeolites Under Working Conditions**	**Experiment number**: CH-1327
Beamline: D2AM	**Date of experiment**: from: 08/10/02 to: 10/10/02	**Date of report**: 01/09/2003
Shifts: 9	**Local contact(s)**: Dr Jean-Louis HODEAU	*Received at ESRF:*

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Introduction

The experiments reported here are part of a PhD thesis (H. Palancher) dedicated to the methodological study by anomalous diffraction of the precise location of cations in zeolites in the presence of multi-component adsorbed phases.

The industrial and scientific background is based on optimisation and development of new molecular sieves (such as X, Y or A zeolites) for high performance processes for separation and purification of hydrocarbon isomers. In such molecular sieves, adsorption properties and, more precisely, selectivity and capacity of adsorption can be correlated with the distribution of charge compensating cations.

Preliminary measurements performed at room temperature, with pre-treated (dehydrated) samples (SrX and SrRbX) sealed in capillary holders have shown the strong sensitivity of AWAXS to the distributions of cations (Sr^{2+} and Sr^{2+} or Rb^{+} respectively) (see ref. [1]). Moreover a dedicated methodology (optimisation of the beam optics, the data collection strategy and the detection system) has been established.

To study *in situ* the variation of the cation distribution in the same samples under a variety of temperature and atmosphere compositions, an experimental set-up (based on ref. [2]) has been especially designed. Its first development has been used to characterise by *in situ* anomalous diffraction SrX at different steps of dehydration [3].

The aim of this experiment was the validation of an improved set-up (including a new heating system) as well as the determination of the cation distribution in highly dehydrated SrRbX. The AWAXS data refinement strategy has been developed on the dehydrated SrX sample data and its efficiency evaluated with the study of dehydrated SrRbX which is a particularly difficult case for X-Ray diffraction: Rb^{+} and Sr^{2+} cations have the same number of electrons [4].

9 shifts on BM2 were allocated by the ESRF Committee.

Experimental set-up

The experimental set-up enables *in situ* diffraction and absorption studies in transmission mode on a sample held in a rotating glass capillary under controlled temperature and flowing gas of controlled composition. This new version consists of the previously used reactor cell, gas admission and extraction system (described in ref. [3]) but also of a new furnace. At 250°C, an extremely low temperature gradient along the sample is obtained (less than 1°C over a 6 mm zone along the capillary). As a consequence, measurement reproducibility is highly

increased. Repeat data collections on a same *in situ* dehydrated sample show only small intensity variations compared to anomalous effect (see figure 1).

Results

SrRbX has been dehydrated *in situ* (dried N_2 used as flushing gas and sample temperature set at 250°C) until a stable state was obtained. Then high quality diffraction patterns were collected at three energies: 10eV below rubidium and strontium K absorption edges (respectively 15.192 and 16.095keV) and far below both edges (14.8keV).

These three datasets were refined simultaneously using the Fullprof software package [5] with non constrained site occupancies. Although the (111) peak was excluded from refinement, the determined structural model was modified to take into account its measured intensity. The quality of the refinement result is illustrated by figure 2. The Rb^{1+} and Sr^{2+} cation distributions detailed in table 1, are consistent with elementary analyses carried out on the same sample. Thus quantitatively correct measurement of Rb^{1+} and Sr^{2+} cation populations on the same crystallographic site (site II) is possible, despite the fact that these two cations produce similar contributions to the electron density [6].

In conclusion, improvement of AWAXS data quality collected on a sample under dynamic conditions as well as the validation of data analysis methodology have been achieved thanks to this experiment.

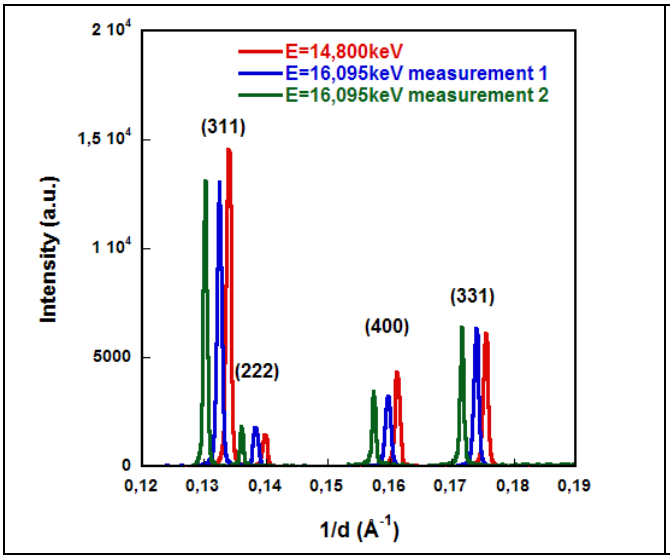

Figure 1: Good reproducibility of measured intensities on dehydrated SrRbX sample (at E=16.095keV) compared to anomalous differences. Patterns are shifted on the 1/d axis for better visualisation.

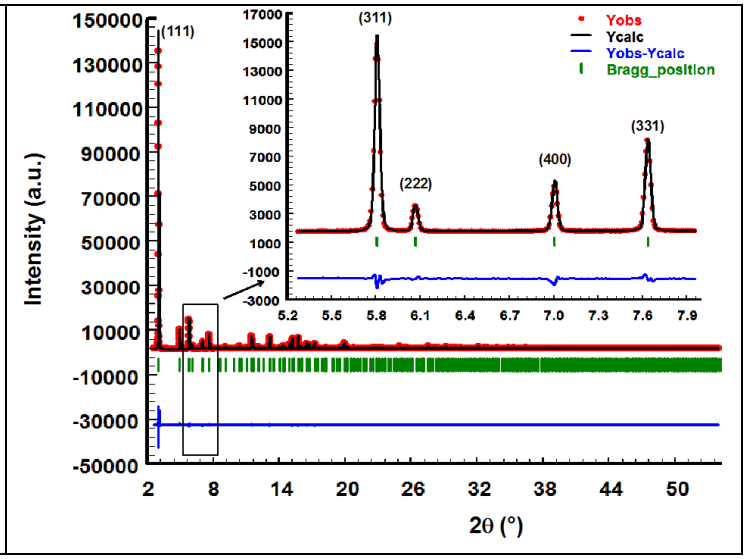

Figure 2: High quality of the multi-energy, multi-cation refinement of the experimental data.

	Site I Sr^{2+}	Site I' Sr^{2+}	Site II' Rb^{+1}	Site II Sr^{2+}	Site II Rb^{+1}
Cations per unit cell	9.8	9.5	0.7	10.7	16.3

Table 1: Rb^{+1} and Sr^{2+} cation distributions in dehydrated SrRbX.

[1]: experimental reports CH1216 and CRG 02-02-188-a, C. Pichon, J.F. Berar, J.L. Hodeau, H. Palancher, J. Lynch, B. Rebours, 2002.

[2]: P. Norby, C. Cahill, C. Koleda and J.B. Parise, *J. Appl. Cryst.* (1998) 31, 481-483.

[3]: experimental report CRG 02-02-188-b, H. Palancher, C. Pichon, J.F. Berar, J.L. Hodeau, J. Lynch, B. Rebours, 2002.

[4]: J.L. Hodeau, V. Nassif, H. Palancher, J.F. Berar, E. Dooryhee, R. Carbonio, Ch. Pichon, B. Rebours, J. Lynch, *ECM (Durban- South Africa)* 2003

[5]: J. Rodriguez-Carvajal, In: *Collected abstracts of Powder Diffraction Meeting*, Toulouse, France, 127 (1990).

[6]: H. Palancher, J.L. Hodeau, C. Pichon, J. Lynch, J.F. Berar, B. Rebours, *manuscript in preparation*.