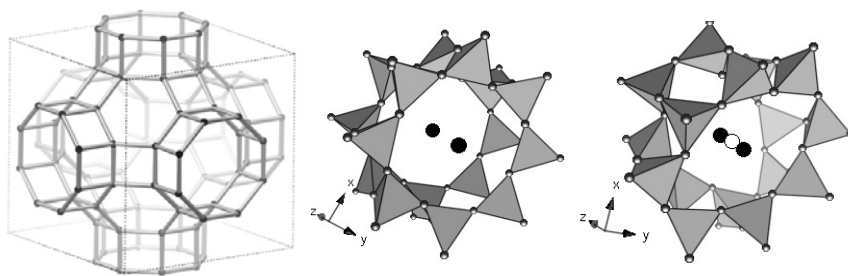




Beamline: ID-09	Experiment title: On the pressure response of zeolite Cd-Rho ($\text{Cd}_{6.1}\text{Cs}_{0.3}\text{Al}_{12.5}\text{Si}_{35.5}\text{O}_{48}\text{nH}_2\text{O}$ ($n \approx 60$)) Date of experiment: from: 05 February 2003 to: 09 February 2003	Experiment number: HS-1900 Date of report: 2/12/04
Shifts:	Local contact(s): Michael Hanfland	<i>Received at ESRF:</i>
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Introduction

Zeolites are naturally occurring aluminosilicate materials crystallizing in a variety of low-density framework structures constructed from corner-connected (Al,SiO₄)-tetrahedra (T), which define pores and channels (Fig. 1) within the framework that are approximately of molecular dimensions. The flexibility of the T-O-T angle connecting the tetrahedral units compared to the rigidity of the internal O-T-O angle, allows these structures to contract and



expand without significant distortion of the TO₄ unit. Depending on the unit cell composition, P and T, zeolite RHO (Fig. 1) adopts centric (*Im* $\bar{3}$ *m*) or acentric (*I* $\bar{4}$ *3m I**23*, *R**3*) symmetry and cations in pores can change position. Pressure is a means to vary unit cell volume, and to potentially alter cation position [1].

(a)
Fig.1 (a). Framework RHO in space group *Im* $\bar{3}$ *m* and $a \approx 15.03 \text{ \AA}$. In this representation the T-sites (Al, Si) are at the nodes and oxygen atoms, removed for clarity, lie at the centers of the lines. The large cage (α -cage) is accessed through double 8-rings (D8R) of tetrahedra (TO₄, T=Si, Al) shown right in (b). Within these structural units two types of sites, in the center of the single 8-rings (S8R) and D8R shown as black and white circles respectively,

Experimental

Pressure was generated by loading a methanol-ethanol liquid and RHO powder [$\text{Cd}_{6.1}\text{Cs}_{0.3}\text{Al}_{12.5}\text{Si}_{35.5}\text{O}_{48}\text{nH}_2\text{O}$ ($n \approx 60$)], in a DAC and data collected on a MAR IP. These data were integrated using fit2D and then used for Rietveld structure refinements. Distinct

changes in relative intensities above 2.3 GPa are consistent with a transition from centric $Im\bar{3}m$ to acentric $I\bar{4}3m$ asymmetry [1-3].

Results and Discussion

Models derived from Distance Least Squares Refinement (DLS) [4], used to determine positions for the TO_2 -framework positions consistent with the unit cell volume, provide excellent starting points to phase Fourier difference maps and thereby locate possible sites for Cd and water in the pores. Refinement of occupation factors for these sites, while constraining the framework positions to the very reasonable values provided by DLS, allows us to quickly test models. For the final refinements all constraints were released and the refinements converged quickly.

The occupancy of the sites in the D8R are summarized in Fig. 2 (right hand vertical axis).

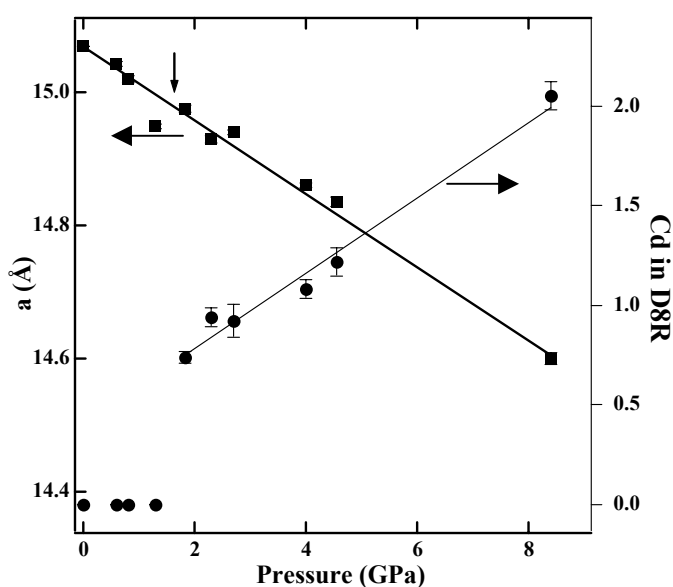


Fig. 2. Variation in the cubic lattice parameter with pressure (right axis) for Cd-AlSi-Rho. The vertical arrow designates the approximate pressure at which the symmetry changes from $Im\bar{3}m$ to $I\bar{4}3m$. The right-vertical axis refers to the contents of the double 8-ring site (the unfilled circles in Fig. 1b)

The centric (C-) phase with circular D8-rings persists up 2 GPa where upon it transforms to the acentric (A-) phase with elliptical 8-rings (Fig. 1). Within the C-phase the cadmium occupies the site close to the plane of the S8R (the black sites in Fig. 1b) and in the A-phase this site depopulates and the site at the D8R becomes occupied as pressure increases.

In the acentric phase the water content varies unsystematically from 55(2) to 65(3) H_2O . This is a pleasing result since it suggests that indeed the extra-framework cation redistribution is purely pressure (volume) driven and not also depend on water content. This was ambiguous in the high temperature measurements where both temperature and water content were changing simultaneously [1]. Furthermore, population of the S8R site occurs more slowly and over a greater range of cell volumes.

Acknowledgements

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