ESRF	Experiment title: Electron density studies and accurate High Energy diffraction experiment in zeolite A and X type : Electron density and electrostatic potential	Experiment number: CH-324
Beamline: ID 11	Date of experiment: from: 05-Nov-98 7h00 to:10-Nov-98 7h00	Date of report:
Shifts: 15	Local contact(s): H. Graafsma	*Received at ESRF:* 06 SEP. 1999

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Report:

This project was a part of the "Doctorat de l'Université H. Poincaré" of F. Porcher (defended in December 1998).

Accurate structures of zeolites are required for understanding their selective sorption capacities and their catalytic properties. In peculiar, the positions of the exchangeable cations and their interactions within the framework are of great interest. The CH-324 experiment dealt with the accurate crystal structure of a fully exchanged and fully dehydrated CaA zeolite ($Ca_{48}Al_{96}Si_{96}O_{384}$). This zeolite possesses a framework formed by SiO_4 and AlO_4 corner sharing tetrahedra whose regular alternation in the structure is responsible [1] for a doubling of the unit cell (from $a \cong 12$Å, $Pm\bar{3}m$ to $a \cong 24$Å, $Fm\bar{3}c$) and for the existence of weak substructure reflections ((h k l), h, k, l = 2n+1). Despite numerous studies [2,3] during the last 20 years, the location of Ca^{2+} cations in CaA's voids were still uncertain. Moreover, in all structures described before this experiment, thermal displacement ellipsoids of oxygen atom

O2 were very elongated suggesting a positional disorder that cannot be resolved with low resolution data.

Data were collected at room temperature on ID11 beamline ($\lambda = 0.248$ Å). All possible space groups were checked on the base of systematic extinctions and intensities of symmetry equivalent reflections. The two possible remaining space groups, $F\bar{4}3c$ and $Fm\bar{3}c$, were tested during the structure refinements.

The crystal structure was redetermined in $Fm\bar{3}c$ by direct methods (NRCVAX [4]); Ca^{2+} cations are disordered on three different 'sites I', on and around the threefold axis near a hexagonal window of a sodalite cage.

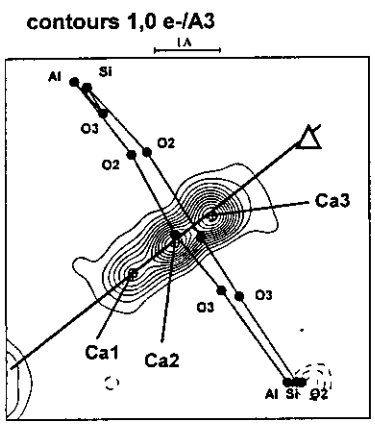

Figure 1

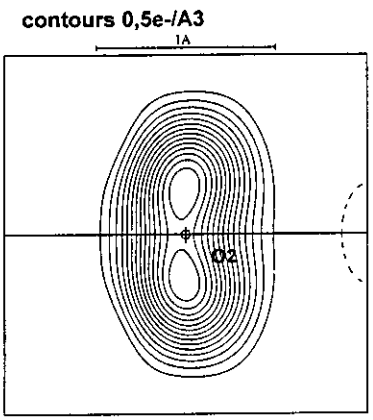

Figure 2

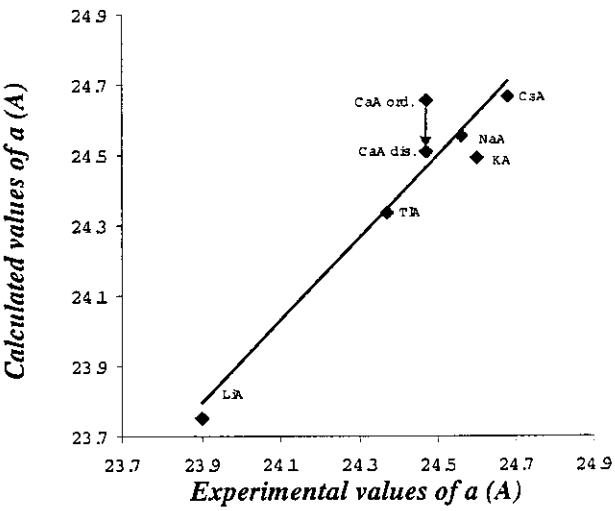

Figure 3

Fourier synthesis showing cation sites I (Figure 1) and disorder at O2 position (Figure 2) Calculated values of cell parameter in A type zeolites as a function of Si-O-Al angles (Figure 3)

Refined relative occupancies of those sites agree with their mean coordination : hence site Ia which exhibits longer average coordination distances is less occupied than sites Ib and Ic .The cations location on sites I is also in agreement with the previous crystal structures of LiA [5,6], NaA [7], KA [8], SrA [9] and TlA [10] in which the 96 monovalent cations occupy preferably site I which is energetically more favorable than site II in the eight membered ring. When the charge compensating cations are divalent (CaA [2] and SrA [9]), site I has a multiplicity high enough to accommodate all 48 cations and site II is not occupied.

This study has also explained why thermal displacement parameters for O2 oxygen atom were abnormally large : our high resolution synchrotron data clearly show that this latter oxygen atom is disordered, lying ~0.3 Å out of the mirror plane (Figure 2). This feature

is related to the Ca^{2+} cations disorder. Resolution of the structure in $F\bar{4}3c$ space-group lead to the same conclusion. However, in the latter refinement, no significant departure from $^{[1\,0\,0]}$m mirror symmetry was found, indicating that space group $Fm\bar{3}c$ is statistically more significant than $F\bar{4}3c$.

Comparison with other A-type zeolite structures also confirms that cation exchange distorts severely the skeleton, especially around oxygen atoms and affects therefore the cell parameter. The distortion is the result of a conformational adaptation of the non rigid framework in order to optimize the coordination of cations with various charge and ionic radii. In the case of zeolites A, the geometry of the structure is simple enough to give an estimate of the cell parameter as a function of silicon to aluminum distance and Si-O-Al angles [6]. The plot of calculated cell parameter values for dehydrated LiA, NaA, KA, CsA and CaA as a function of experimental values shows that taking into account the disorder at O2 position in CaA allows to calculate more precisely the CaA cell parameter. The displacement of O2 out of the (1, 0, 0) plane insures a relaxation of CaA framework, with a diminution of Si-O2-Al angle from 179.0°(1) to 158.0°(2)) and a preservation of the geometry of SiO_4 and AlO_4 tetrahedra.

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