- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.
- bear in mind that the report will be reduced to 71% of its original size. A type-face such as "Times", 14 points, with a 1.5 line spacing between lines for the text, produces a report which can be read easily.

ESRF	**Experiment title: Electron density studies and Accurate High Energy Diffraction experiment in zeolite LiX**	**Experiment number:** CH-416
Beamline: ID11	**Date of experiment:** from: **2/04/1998** to: **8/04/1998**	**Date of report:**
Shifts: 15	**Local contact(s):** Å. Kvick	*Received at ESRF:* 0 6 SEP. 1999

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Report:

This project on " High resolution X ray diffraction studies on dehydrated synthetic NaX zeolite" was part of the "Doctorat de l'Université H. Poincaré" [1] of F. Porcher (defended in December 1998).

The synthetic X type zeolites, used as selective sorbants in gas separation process, exhibits a 3 dimensional framework with large (12,5 Å in diameter) supercages linked together through zigzag channels where sorbed molecules can diffuse. Their chemical composition is $M^{q+}_{x/q}(AlO_2)^-_x(SiO_2)_{192-x}\cdot mH_2O$ with an Si/Al ratio ranging from 1 to ~1.5.

When this ratio is greater than 1.18, the structure is disordered and the space group is $Fd\bar{3}m$. When this ratio is close to 1, the SiO_4 and AlO_4^- tetrahedra alternate regularly in the structure and the space group can be either $Fd\bar{3}$ (total ordering of Si and Al on the tetrahedral sites) or $Fd\bar{3}m$. Si/Al influences the global negative charge of the skeleton and the location of the charge compensating cations sparse throughout the structure [2]. Despite numerous studies, the properties of zeolites M-X, which are related to the nature of the exchangeable cations and their location within the pores, are not fully understood. Since this system is too large (~700 atoms per unit cell) for precise *ab initio* calculations, high resolution X ray diffraction is the only tool to study electron density and derive the electrostatic properties [3, 4] that govern the sorption mechanisms in the zeolite.

In this goal, we have measured high resolution X ray diffraction data sets on dehydrated NaX, ($Fd\bar{3}$ symmetry) on beamline ID11. Data collection and reduction parameters are summarized in Table 1.

Tableau 1 : Data collection parameters

Dehydrated NaX Zeolite $Fd\bar{3}$	
Chemical formula (Z=96)	$Na_{93}Al_{93}Si_{99}O_{384}$
Space group	$Fd\bar{3}$
Cell parameter	25,102(2)Å
Volume ; Density	15817(3)Å^3, 1,425
Temperature	293 K
Radiation	λ = 0,248 Å
Crystal habitus	Octahedron 230 µm along [1, 0, 0]
Reflections measured	72031
$(\sin\theta/\lambda)_{max}$	1.4 Å^{-1}
Unique reflections	6010
Reflections observed (I > 3σ)	11709
R^i	6.96%
R^iw	5.06%

The deformation of electron density due to chemical bonding and charge transfer between atoms is modeled using Hansen-Copens model [5] :

$$\rho_{at}(\vec{r}) = \rho_{coeur}(\vec{r}) + P_{val}\kappa^3\rho_{val}(\kappa.r) + \underbrace{\sum_l\sum_m \kappa'^3 R_{nl}(\kappa' r) P_{lm} Y_{lm}(\theta,\phi)}_{\delta\rho_{at}(\vec{r})}$$

with : $R_{nl}(r) = N_{nl}.r^n.e^{-\xi r}$ κ' : contraction – dilatation coefficient

P_{lm} : multipolar populations $Y_{lm}(\theta, \phi)$: Real spherical harmonics.

This modeling shows (Figures 1, 2) that the maximum of the electron density is centered on the Si-O and Al-O bonds, with a slight polarisation toward neighbouring Na^+ cations. In the hexagonal prism (Figure 1), the lone pairs of 3 oxygen atoms O2 point toward the cation Na1 they coordinate (Na1-O2 = 2.32 Å). This polarisation (Figure 2) is even more prononced for cation Na4 which is strongly coordinated to oxygen atom O4 (Na4-O4 = 2.14 Å, Figure 3).

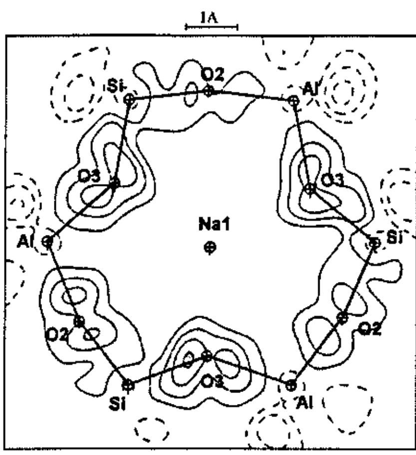

Figure 1

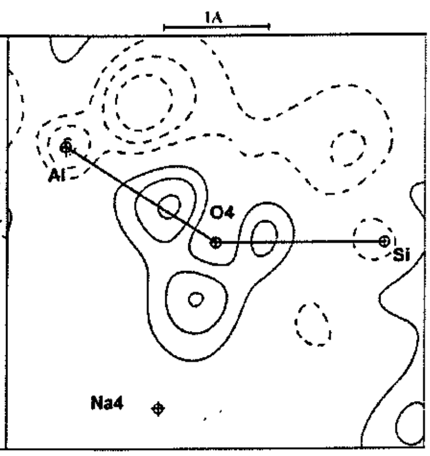

Figure 2

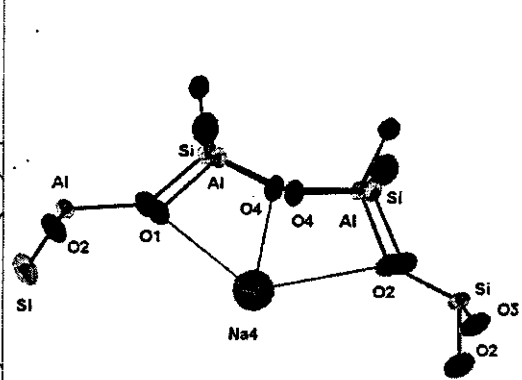

Figure 3

Dynamic deformation density in hexagonal prism (Figure 1) and Si-O4-Al plane (Figure 2) of NaX (contours : 0.1 $e^-/Å^3$) and coordination polyhedron of Na4(Figure 3)

The total electron density has been studied afterwards by the means of topological analysis (Bader (1991)[6]). The interactions between atoms are characterized by the topology of the electron density at its critical points, *i. e.* the points where the gradient of $\rho(\bar{r})$ vanishes:

$$\bar{\nabla}\rho(\bar{r})=\frac{\partial\rho(\bar{r})}{\partial x_1}\bar{i}+\frac{\partial\rho(\bar{r})}{\partial x_2}\bar{j}+\frac{\partial\rho(\bar{r})}{\partial x_3}\bar{k}=\bar{0}$$

Topological analysis shows that, in the case of framework atoms, the position of the bond critical point is similar after either a spherical model or a multipolar model refinement : the critical points of Si-O and Al-O bonds sit on the bonds, as expected, and are closer to Si or Al atoms because they are more electropositive than O.

Table 2 shows that the method to position and quantify the electron density at critical point is robust in the two types of bonds (Si-O and Al-O). Electron density at critical point is higher in Si-O bonds than in Al-O ones.