

## 1. Introduction

Zeolites are known for their properties to stabilise a few atoms metal clusters inside their cages. Silver loaded zeolites of different types (sodalites, LTA, rho) have been studied in INCT for many years using EPR spectroscopy. Extensive studies of cationic silver clusters in zeolites reduced by  $\gamma$ -irradiation or  $H_2$  had been performed. Paramagnetic silver clusters of different nuclearity in  $\gamma$ -irradiated zeolite matrices have been identified. [1-4] and conditions of their stability have been determined. However, EPR method is inherently limited to paramagnetic species only. So it would be interesting to extend studies on clusters structure using a typical structural method such as EXAFS. The comparison of EXAFS results with EPR studies would be particularly helpful in answering the question, whether diamagnetic clusters are also stabilised in zeolites and what is their structure. In order to get preferred extraframework cations distribution inside the zeolites cavities high resolution X-ray synchrotron powder diffraction measurements has been conducted.

## 2. Experimental

Room temperature EXAFS studies have been conducted on silver K-edge for different zeolites – fully silver exchanged Linde type zeolite A and zeolite rho, partially silver exchanged zeolite A and zeolite rho (one silver atom per structural unit), different types of sodalites. Measurements have been performed in step scan mode on Spanish beamline BM25A on ESRF synchrotron facility at room temperature. Typical time of scan amounts to about 45 minutes. HRPD spectra on two wavelengths (below and above silver K-edge) have been measured for samples mentioned above. The samples have been placed in rotating capillaries. Additionally, HRPD spectra on ZK4 zeolite samples annealed for one hour at different temperatures (100, 180 250, 300 °C) have been measured. after cooling to room temperature

Elemental content of selected samples have been determined by EDS microanalysis.

## 3. Results

Fourier transformed EXAFS spectra for fully and partially silver exchanged zeolite A and sodalites are shown in Fig.1. and in Fig.2.

Two different shells around silver atom are clearly seen. In order to clarify whether silver-silver contacts are represented in those spectra Fourier transformed spectra weighted by  $k$ ,  $k^2$  and  $k^3$  have been compared after normalisation of first shell peaks to the same value. Results are presented in Fig.3. It is clearly seen that peaks belonging to first and second shell atoms scale in the same manner. So it implies the presence of light atoms only in those two shells. The different behaviour is observed for higher shell atoms so silver-silver contacts at distances higher than 3 Å are possible.

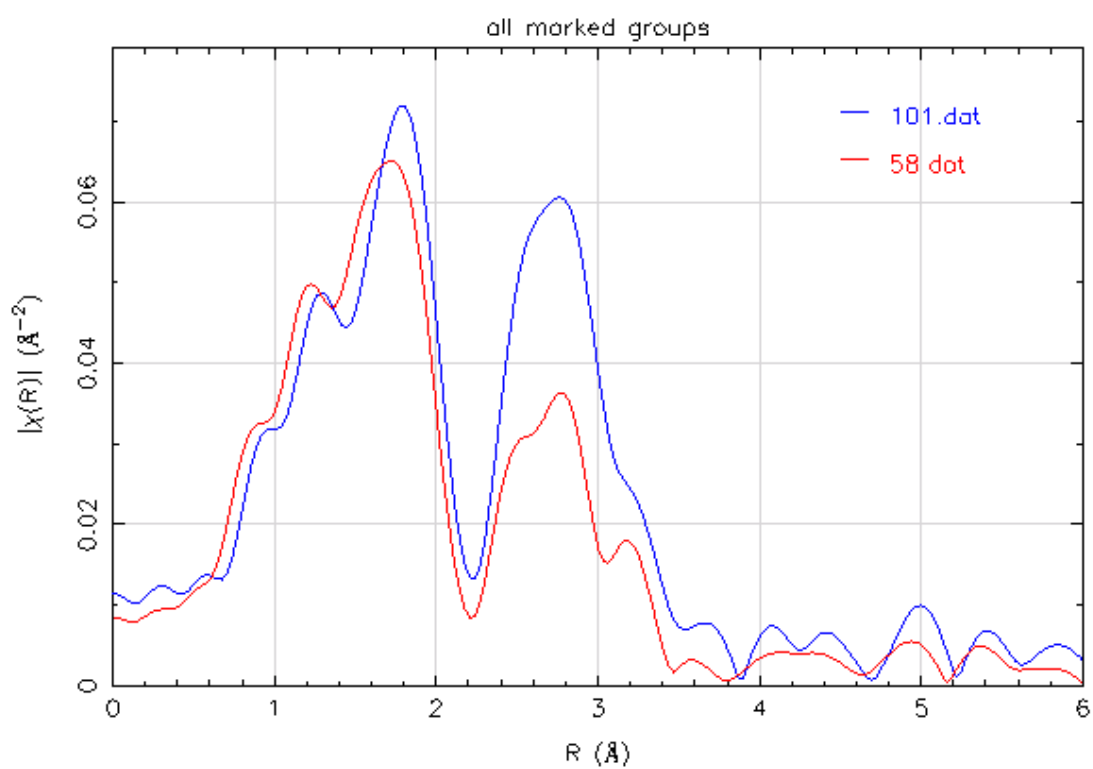


Fig.1. Fourier transformed EXAFS spectra of Ag12\_A (58.dat) and Ag1\_A (101.dat) zeolites.

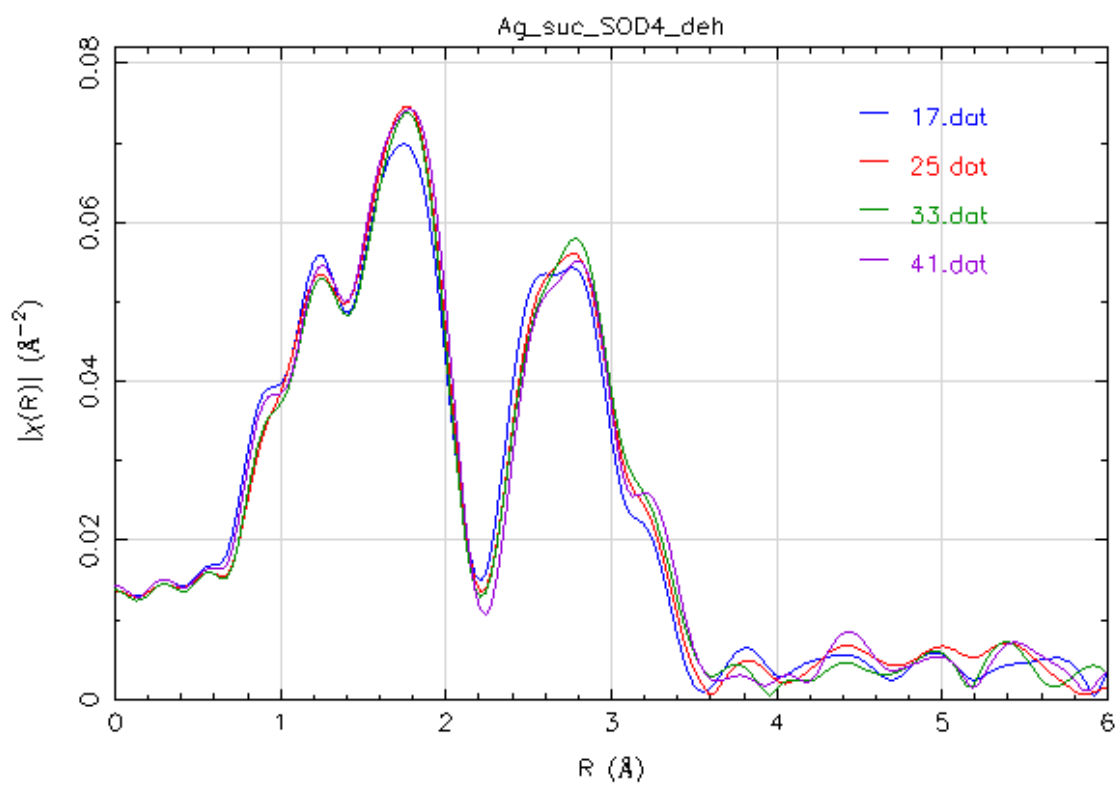


Fig.2. Fourier transformed EXAFS spectra for initially dehydrated sodalite (with succinic acid ligand) for three different runs. Small changes between first and successive samples are seen (probably as the results of water uptake).

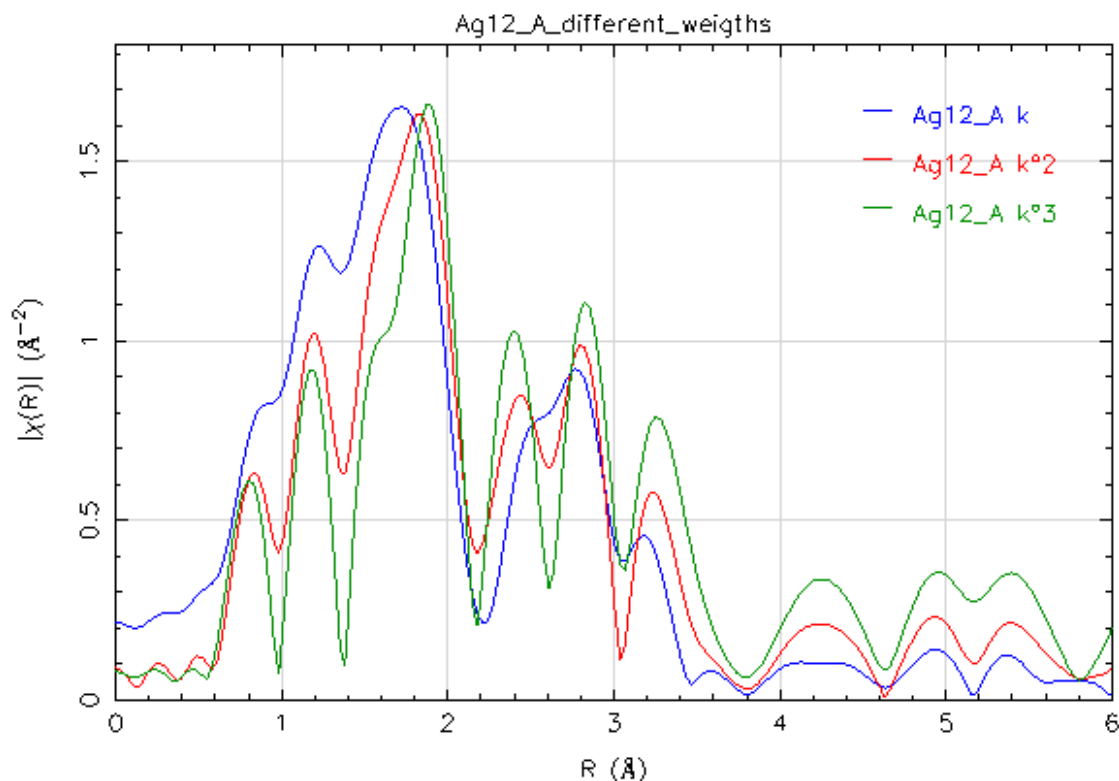


Fig 3. Fourier transformed EXAFS spectra of Ag12\_A zeolite for three different weighting factors.

Due to complex character of EXAFS spectra we concentrated at first on developing the proper physical model. Crystal structure of fully exchanged dehydrated zeolite A has been determined in [5] on the basis of single crystal diffraction on zeolite A monocrystal. The structure solved in Pm3m space group shows that preferred positions for Ag atom are near the hexagonal window, inside the octagonal window and near four member ring prism. The clusters of atoms corresponding to that position have been generated using Artemis software and theoretical spectra corresponding to those clusters has been calculated. Additionally, silver-oxygen contact simulating silver-water contact has been modelled on the basis of Ag<sub>2</sub>O crystal structure (corresponding silver-oxygen distance amounts to 2.06 Å). All calculated spectra treated as standards have been input to Athena software and linear combination fit of experimental spectra to those theoretical standards has been performed. The main results of this analysis are as follows:

- in the case of fully silver exchanged hydrated zeolite A (Ag12\_A) experimental EXAFS spectra shows similarity to silver near hexagonal window standard (0.222) silver at octagonal window standard (0.573) and silver – water oxygen standard (0.205);
- in the case of hydrated, partially silver exchanged zeolite A (Ag1\_A) experimental EXAFS shows similarity to silver near hexagonal window standard (0.157) and silver –water oxygen standard (0.843)

Using this information an attempt to fit experimental spectra to the models mentioned above has been undertaken. However, the fully satisfactory fit has not been obtained with

those data. Probably, due to the simplicity of models not accounting for more complex, distribution of silver environments.

Standard approach for finding silver preferred positions in the case of crystalline materials is X-ray diffraction on single crystal. Recently, the attempts to solve zeolite structure on the basis of high quality powder diffraction spectra have been reported more often. Alternatively, in the case of purely crystalline materials PDF (Pair Distribution Function) approach of analysis of X-ray diffraction data can be helpful.

We have tried different methods of solving silver exchanged zeolite A structure from HRPD data e.g Rietveld method, Le Bail intensity extraction followed by direct methods of solving crystal structure, superflip method, Maximum Entropy Method as implemented in RIETAN package as well as simulated annealing method as implemented in Fullprof. The main difficulty in obtaining meaningful solution is large degree of reflections overlapping in HRPD spectrum. In fig.4 the result of simulated annealing of Ag1\_A zeolite spectrum is shown and in Table I refined position of atoms included in the fit are presented.

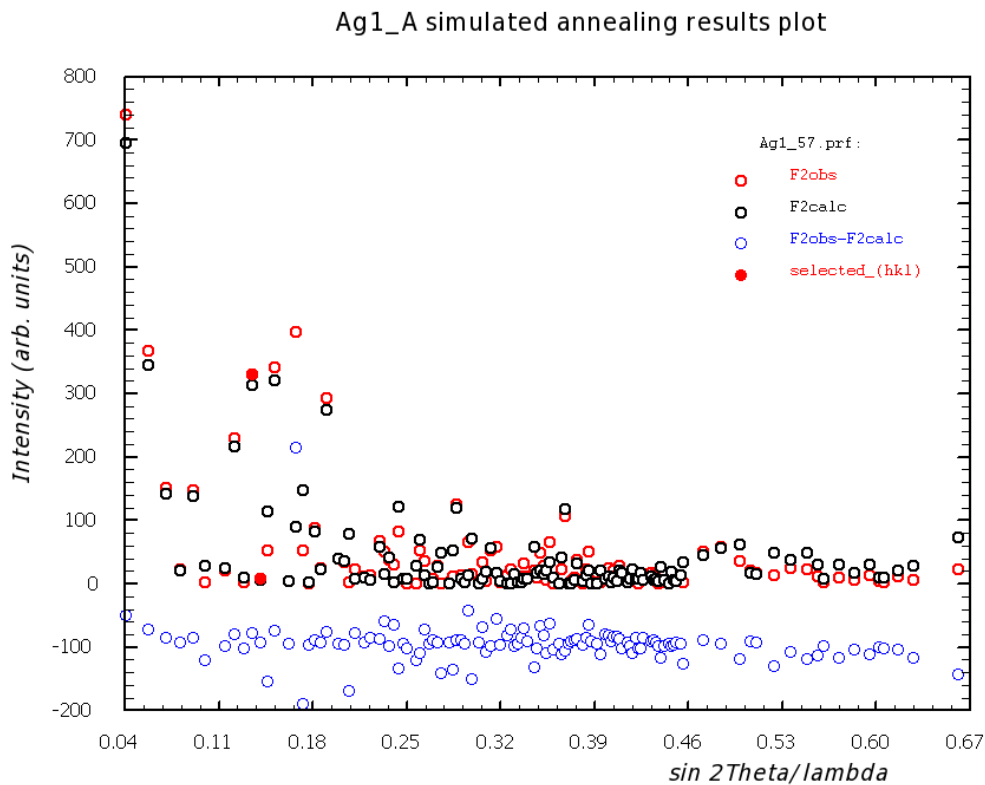


Fig.4. Plot of intensities - experimental and refined by simulated annealing for Ag1\_A zeolite sample.

Table I. Fractional atomic coordinates and occupancies for Ag1-A zeolite sample obtained by SA. method using Fullprof package. Ag1\_A structure has been refined as Pm3m with cell parameter  $a = 12.29582 \text{ \AA}$ .

Atom	x	y	z	occupancy
Si	0.37152	0.18903	0.00000	1.0000
O1	0.33310	0.10655	0.10655	1.0000
O2	0.50000	0.21479	0.00000	0.5000
O3	0.30431	0.30431	0.00000	0.5000
Ag1	0.03748	0.03748	0.03748	0.0533
Ag2	0.50000	0.45501	0.00000	0.0600
Ag3	0.50000	0.00000	0.00000	0.0010
Ag4	0.00000	0.00000	0.22000	0.0500
Na1	0.33304	0.33304	0.33304	0.81174
Na2	0.38000	0.38000	0.38000	0.10000
Ow1	0.45382	0.45382	0.45382	0.37231
Ow2	0.18467	0.18467	0.18467	0.64583
Ow3	0.06498	0.24703	0.06498	0.63836

The simulated intensities follow quite closely the experimental ones. However, it is difficult to predict on the basis of these data the configuration of extraframework atoms and molecules inside zeolite cavities, necessary to solve EXAFS spectra. It seems however, that such preferred arrangements of atomic and molecular species inside zeolite cages should exist as HRPD spectra show good crystal properties. It is possible to find this arrangement using quantum chemistry modelling of extraframework species. Such works are now in progress.

#### 4. Conclusions

1. Combination of HRPD and EXAFS seems still promising for determination of extraframework cations configuration in zeolites.
2. In future experiments more precisely defined sample environment would be necessary e.g. placing the samples in well defined conditions (inert atmosphere and at low temperature). It results from the fact that some of the measurements do not show good repeatability between successive scans e.g. for zeolite rho but good repeatability is obtained for zeolite A. The possible reasons are: water uptake from environment, reduction of silver cations by irradiation introduced by synchrotron radiation beam or both those factors together. Water uptake is possible as EXAFS spectra of sodalite samples dehydrated in laboratory conditions and opened on place do not differ significantly from those of hydrated samples.

Literature

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