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## Structure of single selenium chains confined in nanochannels of zeolites: a polarized X-ray absorption study

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Local structure of selenium confined in single crystal zeolites with one-dimensional nanochannels of  $\sim 7\text{\AA}$  in diameter (cancrinite, mordenite, ALPO-5) has been studied by polarized EXAFS and XANES. In cancrinite, selenium is found to form dimers strongly oriented along the channel axis and with the bond lengths of 2.40  $\text{\AA}$ . XANES spectra exhibit two bound-state-like peaks one of which is strongly polarized parallel to the channel whilst the other one is isotropic. Peak positions and their dependence on the sample orientation indicate negative charge on the dimers. In mordenite and ALPO, no strong polarization dependence is observed suggesting that selenium forms continuous helical chains.

**Key words:** selenium, zeolites, polarized EXAFS, XANES

### 1. Introduction

Recent years have witnessed continuous growth in interest in one-dimensional systems. One of the promising ways to fabricate such novel objects consists in stabilization of individual molecules and nanosize clusters in a matrix of microporous materials (e.g. Stucky et al., 1990, Ozin, 1992). Selenium, whose most stable bulk form consists of helical chains held together by weak Van-der-Waals interaction is one of candidate materials. It was shown to be effectively confined in various zeolites. See a recent review by Poborchii (1997) for more details.

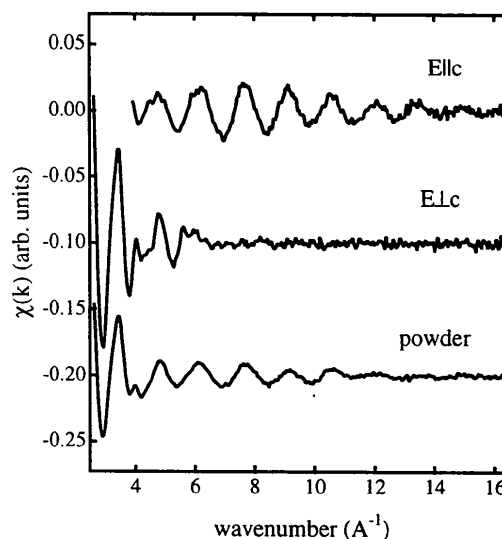
Local structure of Se species confined in various zeolites has been previously studied by EXAFS (Tamura et al., 1986, Paris et al., 1988) but those measurements were done on powder samples and could not provide any information on one-dimensionality of such systems. In this paper we present the results of polarized EXAFS and XANES studies of Se confined in *single crystals* of three different zeolites: cancrinite, mordenite and ALPO-5. Strong anisotropy of selenium confined in nanochannels of cancrinite has been observed.

### 2. Experimental

Selenium was introduced into zeolites from the vapour phase at a typical temperature of 500  $^{\circ}\text{C}$ . More details are given elsewhere (Poborchii, 1997). Measurements were performed in a fluorescence mode at BL13B of the Photon Factory using a 27-pole wiggler. An array of 19-element pure Ge solid-state detectors was used to detect the fluorescence signal. Other details of the experimental equipment are described in detail elsewhere (Kolobov et al., 1997).

### 3. Results and discussion

Figure 1 shows EXAFS spectra for two orthogonal orientations of selenium confined in single crystal cancrinite (Can-Se), namely Ellc and E $\perp$ lc as well as the spectrum taken for the powder of the same material. While the spectrum for the powder is isotropic, the spectra for the single crystal exhibit strong anisotropy.



**Figure 1**

Raw EXAFS oscillations  $k\chi(k)$  as a function of wavenumber  $k$  for Can-Se. Top - single crystal (Ellc and E $\perp$ lc), bottom - powder.

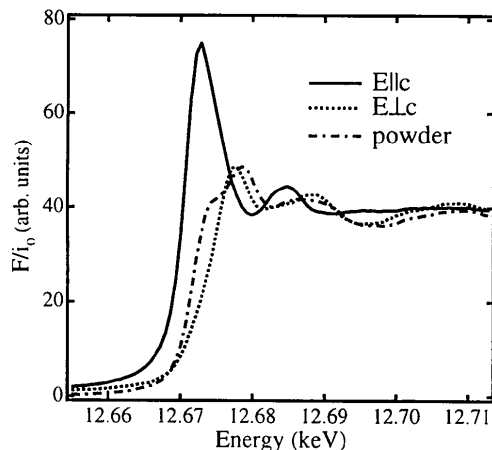
The curve fitting analysis based on the single-scattering theory (more details are given in the electronic archive of XAFS-X, 1998) yields the coordination number of  $1.4 \pm 0.2$  for the powder which is direct evidence for the formation of dimers. For the single crystal the efficient coordination number is  $3.1 \pm 0.5$  assuming isotropic orientation of selenium species. The Se-Se bond length is found to be  $2.40 \pm 0.01\text{\AA}$  which is much longer than in bulk selenium (2.34  $\text{\AA}$ ).

XANES spectra for single crystal and powder and shown in Fig. 2. The near-edge peak at 12,667 eV decreases as the angle between E and c-axis of cancrinite increases and disappears for E $\perp$ lc. Analysis of the polarization dependence based on the procedure described by Stohr and Jaeger (1982) indicates that Se-Se bonds are oriented parallel to the c-axis of cancrinite. This results allows one to obtain the "real" coordination number as  $3.1/3 = \sim 1$  making the results for single crystal and powder consistent.

The position of the white-line peak in Can-Se (Ellc) is lower in energy than that in bulk Se by about 2 eV indicating

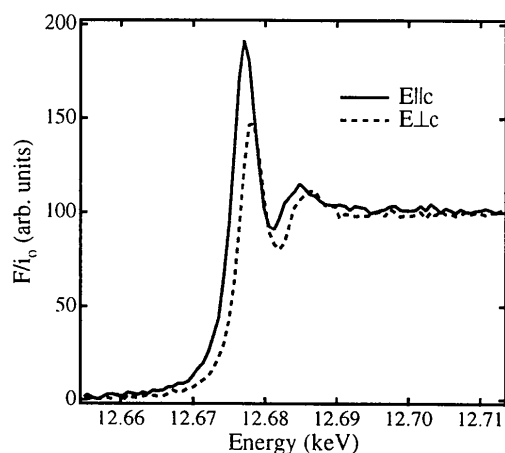
negative charge on Se species, which can also explain the elongated Se-Se bond in the ( $\text{Se}_2^{-2}$ ) dimers.

No noticeable change in EXAFS has been detected with temperature (20K to 300K) despite strong temperature dependence of the Raman scattering, which indicated that the basic structure of dimers is unchanged in the whole temperature range. Further details of this study will be published elsewhere (Kolobov et al., 1998)



**Figure 2**  
XANES spectra for Can-Se, single crystal (Ellc - solid line, ELc - dotted line) and powder (dash-dotted line).

Different from Can-Se, single crystals of mordenite and ALPO-5 (M-Se and ALPO-Se) do not exhibit strong anisotropy in EXAFS or XANES except for a change in the white-line intensity. Figure 3 shows typical XANES spectra



**Figure 3**  
XANES spectra for two orthogonal orientations of M-Se single crystal

for M-Se. We believe that the difference in the white-line intensity is due to one-dimensional nature of selenium chains while the overall similarity of the two spectra indicates that Se-Se bonds are on the average almost randomly oriented. A small difference in the edge positions is within the experimental accuracy.

The coordination number obtained from EXAFS data analysis equals 2 (within the experimental accuracy:  $1.9 \pm 0.3$ ) and the bond length is 2.33 Å in agreement with the results obtained for powder samples. Absence of strong anisotropy, and the coordination number and the bond length being the same as in amorphous selenium suggest that Se forms continuous helical chains in the two latter cases. This is further evidenced by Raman scattering experiments performed by Poborchii et al. (1997a,b).

We would like to stress here that while for the case of helical chains with more or less isotropic orientation of individual bonds both the powder and single crystal yield similar results, for strongly anisotropic samples use of powder samples may lead to erroneous conclusions. Whenever possible, single crystals should be used.

#### 4. Conclusion

To conclude, we have found that Se forms strongly oriented doubly negatively charged dimers ( $\text{Se}_2^{-2}$ ) when confined in nanochannels of cancrinite. We believe that this results from strong interaction with Na cations in the cancrinite matrix. In other types of one-dimensional channels (mordenite and ALPO-5) Se forms continuous helical chains.

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