

## Polarised X-ray Absorption Study of Selenium Chains Confined in Channels of Cancrinite

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Polarised Extended X-ray Absorption Fine Structure (EXAFS) and X-ray Absorption Near Edge Structure (XANES) have been applied to investigation of selenium chains confined in channels of cancrinite. Direct evidence is obtained for creation of strongly oriented selenium dimers. Possible mechanisms for stabilisation of dimers are discussed

### 1. INTRODUCTION

Confinement of nanosize clusters in microporous materials such as zeolites is a promising technique for creating materials with novel properties. See refs 1 and 2 for recent reviews. A variety of potential applications has been predicted for this kind of systems. A number of semiconductor clusters has been successfully confined in various zeolites [1,2]. Of particular interest are clusters of selenium, which can form different structures depending on the topology of the zeolite framework [3-11]. Selenium confined in zeolites was shown to exhibit photo-induced structural changes [12] similar to those in amorphous selenium [13] from which it was concluded that the structural change is localised within a few Ångströms.

Recently, confinement of selenium in cancrinite single crystals (Can-Se) which have a system of parallel channels formed by 12-membered rings made of (Si, Al)O<sub>4</sub> tetraedra was reported [14 - 17] and from the results of optical and Raman studies it was concluded that selenium in cancrinite formed *linear* (as opposed to helical) dimerised chains.

In this paper we report the results of polarised Extended X-ray Absorption Fine Structure (EXAFS) and X-ray Absorption Near

Edge Structure (XANES) and present first experimental evidence for the formation of strongly oriented Se dimers.

### 2. EXPERIMENTAL

Se was introduced into the cancrinite matrix from the vapour phase at a temperature of about 500 °C. Details of the experimental procedure are given elsewhere [16]. EXAFS measurements were performed in the fluorescence mode at BL13B station at the Photon Factory using a 27-pole wiggler. An array of 19-element pure Ge solid-state detectors was used to detect the signal.

Se K-edge EXAFS and XANES spectra were measured in the temperature range from 20 to 300K. In order to study anisotropy of Can-Se we have also investigated angular dependence of the XANES spectra when the angle between the *c*-axis of the cancrinite and the electric vector *E* of the incident X-ray beam was varied from 0 to 90 degrees.

A film of crystallized selenium (*c*-Se) with trigonal phase was used as a standard to obtain experimental phase-shift function for the Se-Se pair.

The EXAFS oscillations  $\chi(k)k$  were Fourier transformed into a real space using the region extending from 4.5 to 15 Å<sup>-1</sup>. To obtain structural information, a least-squares curve-fitting analysis, based on a single scattering

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theory [18] and FEFF amplitudes [19] was performed.

### 3. RESULTS

Fig. 1 shows Se K-EXAFS oscillations taken at 30K for Can-Se oriented with  $c$ -axis respectively parallel and perpendicular to the electric vector of the X-ray beam. The back-

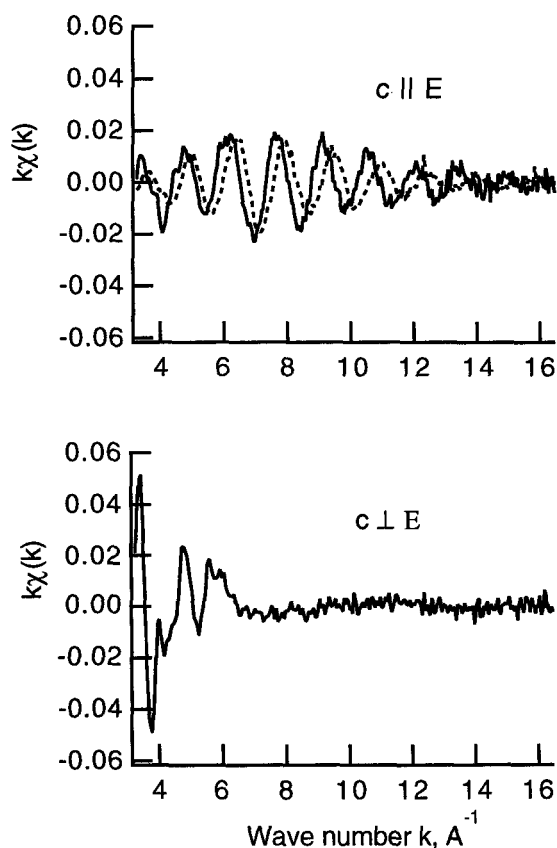


Fig. 1. Se K-EXAFS for Can-Se oriented parallel (top) and perpendicular (bottom) to the  $\mathbf{E}$ -vector of X-rays. The spectrum for  $a$ -Se is shown by dashed line for comparison

ground function was normalized to the edge jump and subtracted from the fluorescence yield spectrum. Se K-EXAFS oscillations for amorphous selenium ( $a$ -Se) measured under similar experimental condition are also shown for comparison. One can see that in the  $k$ -range from 5 to 16  $\text{\AA}^{-1}$  the envelope functions of Can-Se ( $c \parallel \mathbf{E}$ ) and  $a$ -Se agree very well. However, at smaller  $k$  there are pronounced peaks in the case of Can-Se implying interaction with a light

element. In the spectrum of Can-Se ( $c \perp \mathbf{E}$ ), no oscillations are observed in the region characteristic of Se-Se interaction. Instead, EXAFS oscillations are observed at much smaller  $k$ -values, their amplitude decreasing rapidly.

The Fourier-transformed spectra for the two sample orientations are shown in Fig. 2. For the orientation  $c \parallel \mathbf{E}$  there is one strongly pronounced peak representing Se-Se interaction with no second or third peak observed. The other spectrum ( $c \perp \mathbf{E}$ ) has several broad peaks at distances different from that of Se-Se bond length.

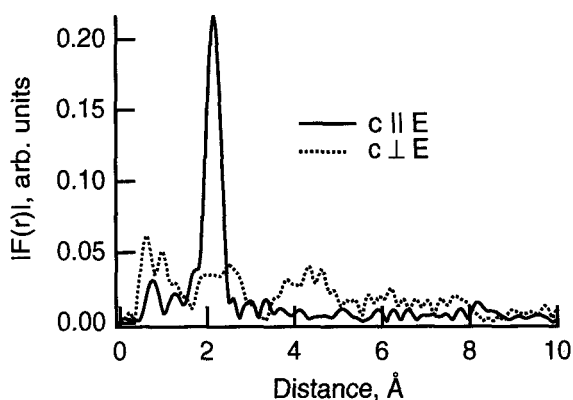


Fig. 2. Fourier-transformed spectra for the two orientation.

The data analysis gave the efficient coordination number of  $N^* = 2.7 \pm 0.5$ , assuming isotropic orientation of selenium chains, and the bond length of 2.40  $\text{\AA}$ . The mean-square relative displacement was similar to that in amorphous selenium.

Fig. 3 shows XANES spectra for two perpendicular orientations for Can-Se and for  $a$ -Se. One can see that the spectrum for  $c \parallel \mathbf{E}$  resembles that for amorphous selenium while the spectrum for  $c \perp \mathbf{E}$  looks very much different. The white line (the peak in absorption at energies slightly exceeding the absorption edge) characteristic of semiconductors disappears for the sample oriented  $c \perp \mathbf{E}$ . The spectrum for this orientation has an appearance characteristic of metals.

Fig. 4 shows the X-ray photoemission spectrum for selenium confined in cancrinite single crystal. Deconvolution of the spectrum clearly shows the presence of two components with comparable peak intensities. The energy

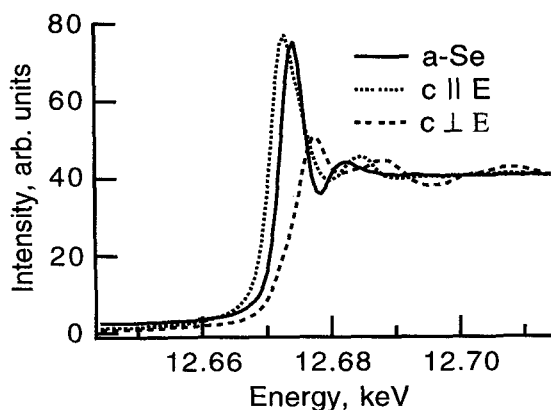


Fig. 3. Angular dependence of XANES.

difference for the two peaks corresponds to the charge difference of two. Calibration of the spectra gave the charged states for the two selenium components to be +1 and -1.

#### 4. DISCUSSION

First we discuss raw EXAFS data for the two orientations. Similarity of the envelope curves for the  $c \parallel E$  orientation and  $a$ -Se demonstrates that the main interaction is between Se-Se atoms. Appearance of more intense oscillations at smaller  $k$  for  $c \perp E$  is caused by interaction between selenium and light elements (Na, OH or O).

The obtained bond length of 2.40 Å is larger than the bond length in amorphous (2.32 Å) or crystalline (2.36 Å) selenium. The increase in the bond length is very unusual since isolated chains in cancrinite do not interact with each other and, as a result, the intrachain interaction becomes stronger which should lead to a decrease in the bond length as observed for selenium in mordenite [6]. The increase in the bond length most likely represents strong interaction between selenium atoms and the cancrinite matrix.

Raw EXAFS for the perpendicular orientation has very strong oscillations at low  $k$  while for larger  $k$  where Se-Se interaction is most strongly pronounced, the oscillatory behaviour disappears. Such a dependence is an evidence for the absence of Se-Se interaction in the direction perpendicular to the  $c$ -axis of cancrinite confirming the conclusion made from the Raman studies [14 - 17] that selenium in cancrinite forms *linear* (and not

helical) chains. Strong anisotropy of Se chains in cancrinite is also evidenced by the XANES spectra.

Fourier-transformed spectrum also shows that there is no peak at a distance characteristic of Se-Se bond length. The presence of rather intense peak at larger  $r$  shows a large degree of ordering of selenium with respect to the host matrix.

Strong anisotropy of selenium chains allows one to understand the seemingly large efficient coordination number. Taking the strong orientation of selenium chain into account the actual coordination number is approximately  $N^*/3 \sim 1.0$  which means that each selenium atom has only one nearest neighbour, i.e. *selenium chains are dimerised* in agreement with the conclusion made earlier [14 - 17] from the Raman studies.

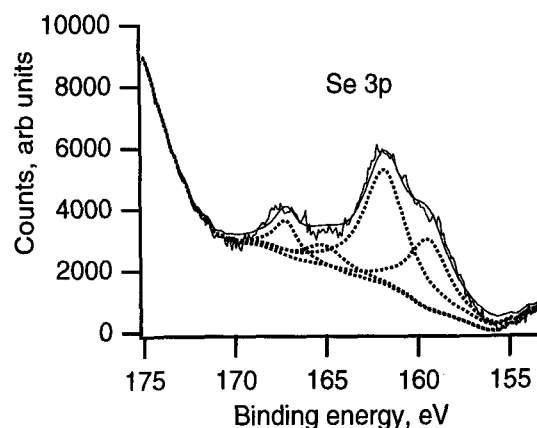


Fig. 4. XPS absorption spectrum for Can-Se.

We shall discuss now possible mechanisms for selenium dimerisation. The formation of conventional free dimers is excluded because of very large differences in the bond length for a free dimer and selenium in cancrinite. Another possibility is the presence of dangling bonds with unpaired electrons on each of them. Such dimers should have metal-like band structure and the disappearance of the white line for the  $c \perp E$  orientation in the XANES spectrum is in favour of such a possibility.

On the other hand, the observed two peaks with equal intensities in the XPS spectrum indicate that one of the atoms in a dimer is positively charged while the other one is charged negatively. In such a case a resonating bond would explain the selenium dimerisation. It should be noted, however, that similar

measurements made for an as-crushed powder sample show only one peak [20] with a binding energy corresponding to the charged state of -2 which was interpreted as resulting from the interaction between selenium and the neighbouring sodium with a charge transfer from the latter to the former.

The observed inconsistency for the data regarding the charged state of selenium in cancrinite could be an indication that various possibilities may coexist with either one or the other being dominant which would account for the observed phase transitions in this system [15,16]. Further studies are needed in order to resolve this inconsistency and verify the type of interaction of dimers with each other and with the host matrix.

## 5. CONCLUSION

Se atoms confined in channels of cancrinite are shown to form strongly oriented dimers which are well ordered with respect to the host matrix. The dimers may either have unpaired electrons at each end or be stabilised by resonating bonds or by making bonds with the host material.

## 6. ACKNOWLEDGEMENT

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