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Structural study of magnetic metal chalcogenide nanoclusters incorporated in zeolite LTA

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Introduction

Magnetic metal chalcogenaides show very interesting properties. For example, magnetism of $Ni(S_xSe_{1-x})_2$ alloy changes from Pauli para- to antiferromagnetic with decreasing the *x* value at low temperature. These features may be caused by interaction between 3d electrons of magnetic atoms and the lone pair electrons of chalcogens. So we expect that the nanoclusters of these alloys exhibit new interesting properties different from that of their bulk materials because of the change of the interaction.

Zeolite LTA has large cages with the inside diameter ~11 Å. In a previous study, we have succeeded to produce magnetic metal chalcogenaides nanoclusters in the cage of zeolite LTA. In order to investigate the structure of these nanoclusters and its temperature dependence, we have performed EXAFS measurements for Ni-Se nanoclusters at various temperatures.

Experimental

Cations of zeolite LTA were exchanged with Ni^{2+} ions by soaking zeolite powder in the aqueous $Ni(NO_3)_2$ solution. We describe the number of Ni^{2+} ions per cage as *x*. The dehydrated Ni type zeolite powder was heated up to 450 °C with the weighed Se in order to confine Se clusters in the cages. Then, it was heated in H_2 gas up to 350 °C for two hours to make Ni-Se clusters. The obtained Ni-Se clusters are denoted as Se_y-A(Ni_x)(red.), where *y* represents the number of Se atoms per zeolite cage.

The EXAFS spectra around Ni and Se K edge were mesured by using BL10B beam line. The measurements were carried out from 20 K to room temperature (r.t.) by using the cryo-cooler equipped at the beam line.

Results and discussion

Fig. 1 shows EXAFS oscillations $\chi(k)$ of $Se_{7.6}$-A($Ni_{3.8}$)(red.) around Ni K-edge obtained over the temperature range from 20 K to r.t. These spectra oscillate clearly in wide *k* region which indicates that Ni-Se nanoclusters are formed in LTA cages. Amplitudes of $\chi(k)$ become gradually larger and spectra oscillate higher *k* region with decreasing temperature. This is due to restraint of thermal vibration of atoms at low temperature.

Fig. 2 shows the Fourier transform of $k\chi(k)$ over the *k* range $4.0 < k < 12.0$ Å^{-1} for the data shown in Fig. 1. The first peak strongly appear around 2 Å which is attributable to the first-nearest Ni-Se bond. It is clear that the peak shifts toward larger distance below 150 K. This indicates that the structure of Ni-Se nanocluster incorporated in LTA varies obviously at the temperature between 150 and 100 K.

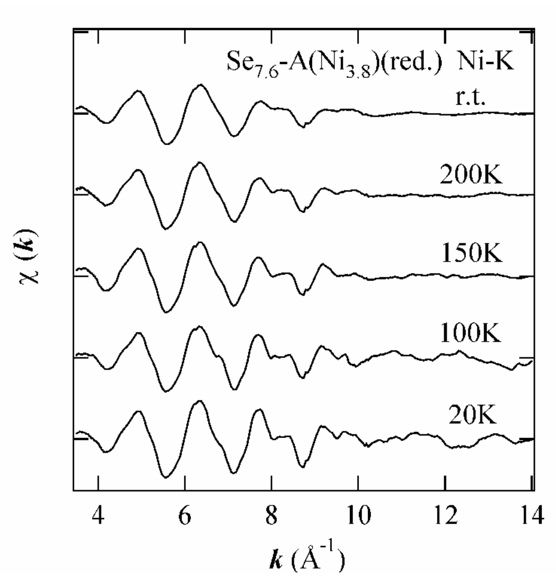

Fig. 1. EXAFS oscillations $\chi(k)$ of $Se_{7.6}$-A($Ni_{3.8}$)(red.) obtained around Ni K-edge at various temperatures.

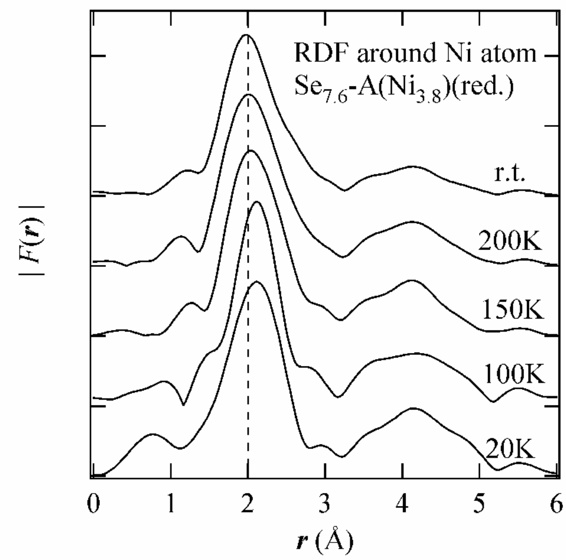

Fig. 2. Fourier transform of $k\chi(k)$, $|F(r)|$, for the data in Fig. 1. A vertical broken line is drawn at $r = 2$ Å.

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