

Structural study of magnetic metal chalcogenide nanoclusters confined in zeolite A

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Introduction

Iron-group metal chalcogenides show very interesting properties. For example, magnetism of $\text{Co}(\text{S}_x\text{Se}_{1-x})_2$ alloy changes from ferro- to antiferromagnetic with decreasing the x value below 100 K. These features may be attributable to the interaction between 3d electrons of iron-group metals and the lone pair electrons of chalcogens. So we expect that the nanoclusters of these alloys exhibit new curious properties different from their bulk materials because of the change of the interaction.

In a previous study, we have succeeded to produce iron-group metal chalcogenides nanoclusters in the α cage of zeolite A ($\sim 11\text{\AA}$ diameter). In order to investigate the structure of these nanoclusters and its temperature dependence, we have performed EXAFS measurements for Co-Se nanoclusters with various compositions.

Experimental

The Na^+ cations of zeolite A were exchanged with Co^{2+} ions by soaking zeolite powder in the aqueous $\text{Co}(\text{NO}_3)_2$ solution. The number of Co^{2+} ions per cage, x , was determined with ICP mass analysis. The dehydrated Co type zeolite powder was heated up to $450\text{ }^\circ\text{C}$ with the weighed Se in order to confine Se clusters in the cages. After that, it was heated in H_2 gas up to $350\text{ }^\circ\text{C}$ for two hours to make Co-Se clusters. The obtained Co-Se clusters are denoted as $\text{Co}_x\text{Se}_y(\text{red.})$, where y represents the number of Se atoms per zeolite cage.

The samples were packed into a Teflon cell in a glovebox to prevent containing water. EXAFS spectra around Co and Se K edge were measured by using BL10B beam line. In order to investigate the temperature dependence of the structure at low temperature, measurements were carried out from 20K to room temperature (r.t.) using equipped cryo-cooler.

Results and discussion

EXAFS oscillations $\chi(k)$ of $\text{Co}_{5.0}\text{Se}_{8.0}(\text{red.})$ around Co K-edge obtained over the range 20K to r.t. are shown in Fig. 1. It is clear that the $\chi(k)$ at 20K has larger amplitude around $k \sim 6\text{\AA}^{-1}$ than those at different temperatures. This fact suggests that the interaction between Co and Se becomes stronger below 100K.

Fig. 2 shows the Fourier transform of $k\chi(k)$ for the data shown in Fig. 1. The first peak around 2\AA are attributed to the first-nearest Co-Se bond. This peak shifts toward larger distance with decreasing temperature. The peak shift is large between the data at 100K and 20K, which means that the structure of Co-Se cluster in zeolite cage has temperature dependence.

It is concluded that the structure of $\text{Co}_{5.0}\text{Se}_{8.0}(\text{red.})$ varies below 100K. To know the temperature dependence in detail, we plan to measure EXAFS with smaller interval of temperatures.

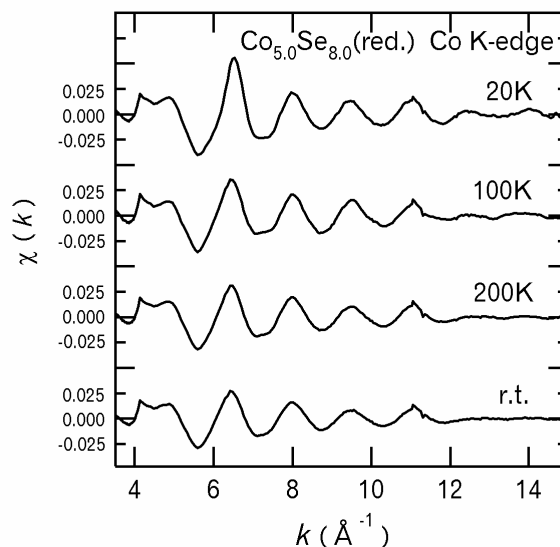


Fig. 1. EXAFS oscillations $\chi(k)$ of $\text{Co}_{5.0}\text{Se}_{8.0}(\text{red.})$ obtained around Co K-edge at various temperatures.

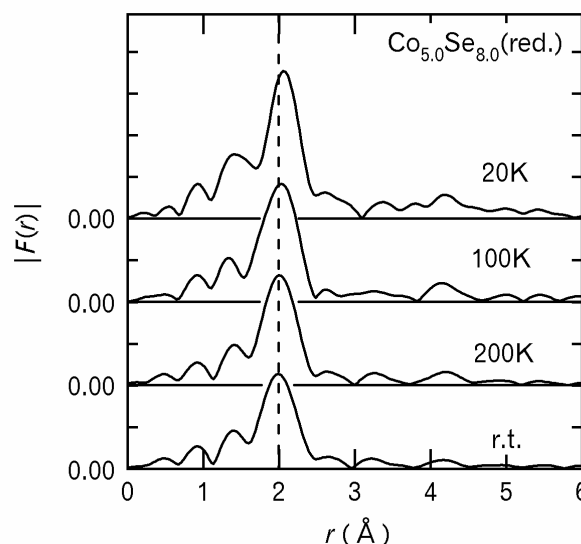


Fig. 2. Fourier transform of $k\chi(k)$, $|F(r)|$, for the data in Fig. 1. Vertical dashed line is drawn at $r = 2\text{\AA}$.

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