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The size dependence of the Einstein temperature of the tellurium nanoparticles

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Abstract. The Debye-Waller factors obtained by EXAFS analysis of the Te nanoparticles are analyzed by a Einstein model. The Einstein temperatures for the intra- and interchain interactions are depend on the size of the Te nanoparticles. With decreasing the size of the Te nanoparticles the Einstein temperature for the intrachain correlations increases, while that for the interchain correlations decreases. The value of the static components of the Debye-Waller factors for both the intra- and interchain correlations increase with decreasing of the size. The reduction of the interchain interactions for the Te nanoparticles would induce the increase of the Einstein temperature for the intrachain correlations and the decrease of the interchain correlations.

1. Introduction
Trigonal tellurium (t-Te) has a highly anisotropic crystal structure consisting of helical chains of covalently bound atoms, which are in turn bound together into a hexagonal lattice [1]. The adjacent chains are situated at distances larger than the covalent bond length but shorter than the van der Waals distance. Overlapping between the antibonding orbitals and the lone-pair orbitals on adjacent chains induces the interchain interactions, which are stronger than the van der Waals interaction. This hierarchic structure is key feature in Te with contrary to other semiconductor elements, such as, Si and Ge, and metal elements. The hierarchic structure would bring about exotic characters to the Te nanoparticles.

Extended x-ray absorption fine structure (EXAFS) is a powerful tool for studying the local structure of disordered and nanoparticles [2][3]. We reported the features of the Te nanoparticles obtained by EXAFS analysis [4]. The Debye-Waller factors ($\sigma^2$) obtained by EXAFS analysis reflect strength of interatomic correlations and static disorder. We have discussed the Debye-Waller factors for one size of the Te nanoparticles [4][5]. In this paper, we report size dependence of the Einstein temperature and static components for the Debye-Waller factors of the Te nanoparticles.

2. Experimental
Tellurium of 99.999% purity and NaCl of 99.99% purity were slowly deposited alternately onto substrates cooled by water. The ratio of the thickness of Te to that of NaCl was 1:20. The formed
Te films were discontinuous with isolated island formation. By these steps, the Te nanoparticles were isolated in NaCl matrix[2]. The thickness was monitored with a quartz oscillator sensor (ULVAC CRTS-4). As mentioned above, the Te nanoparticles were formed in thin films, and, in this Paper, samples are referred to by their average Te thin film thickness. In 5 and 10-nm-thick films the formation of nanoparticles was confirmed by using field emission scanning electron microscopy (JEOL JSM-6700F at the Center for Instrumental Analysis, University of Toyama). It is indisputable that the nanoparticles were formed in the 0.5-nm-thick films.

X-ray absorption measurements were performed using the spectrometer installed at NW10A of the Photon Factory (PF-AR) in the High Energy Accelerator Research Organization (KEK), Tsukuba, Japan. EXAFS data were obtained for the Te K-edge (31.8 keV). The intensities of the incident beam and the transmitted beam were monitored by ionization chambers. The Fourier filtered EXAFS functions, $k^2\chi(k)$, were fitted by a nonlinear least-square method to the theoretical function with the frame of a two-shell model up to $C_3$ according to the method previously reported [4]. The first and second shells correspond to the intra- and the interchain first nearest neighbor (1NN) correlations, respectively. FEFF8.2 code [6] was used for the theoretical EXAFS parameters.

For the analysis of the temperature dependence of the Debye-Waller factor, we apply the Einstein model described as

$$\sigma^2(T) = \sigma_{\text{static}}^2 + \frac{\hbar^2}{Mk_B\Theta_E^2} \coth\left(\frac{\Theta_E}{2T}\right)$$  

where we use the DW factor $\sigma^2(T)$ at temperature $T$, $\Theta_E$ the Einstein temperature, static component $\sigma_{\text{static}}^2$, atomic mass $M$.

3. Results

The Debye-Waller factors for the intra- and the interchain 1NN of t-Te are shown as a function of the measurement temperature in Fig. 1. The lines denote fits obtained with the correlated Einstein models for them. Such thermal behaviors are well approximated by the Einstein model, as clearly shown in the figure. The values of Debye-Waller factors for the interchain correlations are larger than those of the intrachain correlations at whole temperature range. This suggests that the interchain correlations are weaker than the intrachain correlations.

Figure 2 shows the size dependence of the intrachain 1NN Einstein temperature ($\Theta_{E\text{intra}}$). The value for t-Te is plotted at 900 nm for the convenience. The value of $\Theta_{E\text{intra}}$ for the 0.5 nm-thick-films is 20 K larger than that of t-Te, but the size dependence of the other size of nanoparticles is small. The analysis of the Einstein model requires high quality of the Debye-Waller factors, so at this stage it is difficult to discuss the size dependence of $\Theta_{E\text{intra}}$.

The analysis of the Debye-Waller factors with the Einstein model gives the static components of the Debye-Waller factors. Figure 3 gives the size dependence of the static components of the Debye-Waller factors for the intrachain interactions. On the contrary to the case of $\Theta_{E\text{intra}}$ there is clear size dependence. With decreasing the size of the nanoparticles the value of the static components of the Debye-Waller factors for the intrachain interactions increases, and the increase is prominent below 10 nm.

Figure 4 shows the size dependence of the interchain 1NN Einstein temperature ($\Theta_{E\text{inter}}$). The value of $\Theta_{E\text{inter}}$ decreases gradually with decreasing the film thickness. That of the 0.5 nm-thick-films is 10 K smaller than that of t-Te. Trend of the size dependence of $\Theta_{E\text{inter}}$ is opposed to that of $\Theta_{E\text{intra}}$. It might reflect the difference between the intrachain and interchain interactions of tellurium.

Figure 5 gives the size dependence of the static components of the Debye-Waller factors for the interchain interactions. With decreasing the size of the nanoparticles the static components of the Debye-Waller factors for the interchain interactions increases.
Figure 1. The Debye-Waller factors for the intra- and the interchain 1NN of t-Te. The lines denote fits obtained with the correlated Einstein models for them. Red circles: the Debye-Waller factors for the intrachain correlations. Blue triangles: the Debye-Waller factors for the interchain correlations.

Figure 2. Variation of $\Theta_{E_{\text{intra}}}$ for the intrachain 1NN with thickness of Te layer.

Figure 3. Variation of the static components of the Debye-Waller factors for the intrachain 1NN with thickness of Te layer.

4. Discussion

The value of the Einstein temperatures reflects strength of atomic interactions. It is interesting that the value of $\Theta_{E_{\text{intra}}}$ increases with decreasing of the Te film thickness while that of $\Theta_{E_{\text{inter}}}$ decreases. This means that the covalent bonds strengthen while the interchain interactions weakens with decrease of the size for the Te nanoparticles. Overlapping between the antibonding orbitals and the LP orbitals on the neighbor chains elongates the covalent bonds. In the Te nanoparticles the interchain interactions are reduced, which induces the strengthening of the intrachain covalent bonds[4]. Therefore, the size dependencies of $\Theta_{E_{\text{intra}}}$ and $\Theta_{E_{\text{inter}}}$ are reasonable.

Some of the structure parameters obtained by the Einstein model show the size dependence. In the region where the thickness is thicker than 10 nm the values are similar with those of t-Te, and they change around the 10 nm-thick films. Character of the Te nanoparticles appears below
Figure 4. Variation of $\Theta_E$ for the interchain 1NN with thickness of Te layer.

Figure 5. Variation of the static components of the Debye-Waller factors for the interchain 1NN with thickness of Te layer.

10 nm.

5. Conclusion
The Einstein temperatures and the static components obtained by the analysis of the Debye-Waller factors for the Te nanoparticles are depend on the size of the Te nanoparticles. With decreasing the size of the Te nanoparticles the Einstein temperature for the intrachain correlations increases, while that for the interchain correlations decreases. Decreasing the Te nanoparticles size increases the static components of Debye-Waller factors for both the intra- and interchain correlations.

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