

## The EXAFS Debye-Waller Factors of the Tellurium Nanoparticles\*

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The Debye-Waller factors obtained by EXAFS analysis of the trigonal Te (t-Te) and the Te nanoparticles are analyzed by a Debye model. In t-Te the Debye temperature ( $\Theta_D$ ) of the intrachain interactions is about two times higher than that of the interchain atomic interactions. The  $\Theta_D$  for the intrachain interactions of the Te nanoparticles is higher than that of t-Te, but  $\Theta_D$  for the interchain interactions of the Te nanoparticles is lower than that of t-Te. The reduction of the interchain interactions for the Te nanoparticles would induce the change of the Debye temperatures. [DOI: 10.1380/ejssnt.2009.45]

Keywords: Tellurium; Nano-particles; EXAFS; Debye-Waller factors; Debye temperature

### I. INTRODUCTION

In trigonal phase, Te atoms are incorporated into chains, and 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. 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. We reported the features of the Te nanoparticles obtained by extended x-ray absorption fine structure (EXAFS) analysis [1]. The Debye-Waller factors ( $\sigma^2$ ) obtained by EXAFS analysis are due to thermal vibrations and static disorder. The temperature dependence of  $\sigma^2$  is usually analyzed by an Einstein model. But the Te nanoparticles are composed of only one kind of elements, a Debye model would be suitable for the analysis of  $\sigma^2$ . In this paper, we report the result of the analysis by the Debye model for the EXAFS Debye-Waller factors.

### II. EXPERIMENTAL AND DATA ANALYSIS

Tellurium of 99.999% purity and NaCl of 99.99% purity were slowly deposited alternately onto substrates from an alumina crucible. The formed Te films were discontinuous with isolated island formation. By these steps, samples of the Te nanoparticles isolated in a NaCl matrix were obtained. The thickness was monitored with a quartz oscillator, and the ratio of the thickness of Te to that of

NaCl was 1:20. 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-nm-thick films confirmation of formation of nanoparticles was verified by using field emission scanning electron microscopy (FESEM) (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 [1]. The first and second shells correspond to the intra- and the interchain correlations, respectively. FEFF8.2 code [2] was used for the theoretical EXAFS parameters.

For the analysis of the temperature dependence of the Debye-Waller factor, we apply the Debye model described as [3]

$$\sigma^2(T) = \sigma_{\text{static}}^2 + \frac{\hbar}{m} \int \rho(\omega) \coth\left(\frac{\hbar\omega}{2k_B T}\right) \frac{d\omega}{\omega} \quad (1)$$

$$\rho(\omega) = \frac{3\omega^2}{\omega_D^3} \left[1 - \frac{\sin(k_D \omega r / \omega_D)}{k_D \omega r / \omega_D}\right] \quad (2)$$

$$k_D = \sqrt[3]{6\pi^2 n} \quad (3)$$

$$\Theta_D = \frac{\hbar\omega_D}{k_B} \quad (4)$$

where we use the DW factor  $\sigma^2(T)$  at temperature  $T$ , static component  $\sigma_{\text{static}}^2$ , atomic mass  $m$ , the distance to the scatterer  $r$ , and number density  $n$ .

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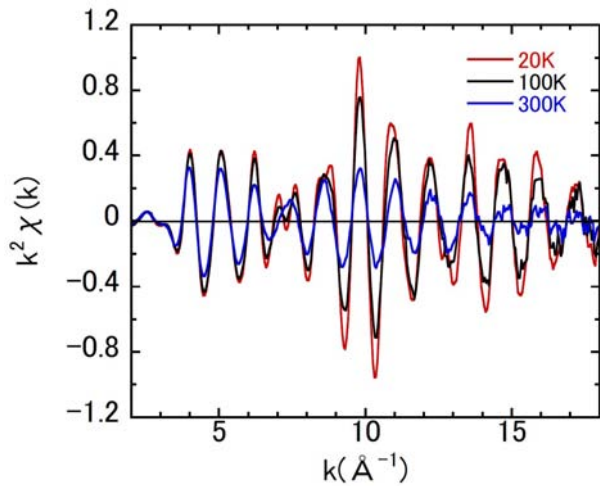


FIG. 1: EXAFS oscillations for t-Te at 20, 100 and 300K.

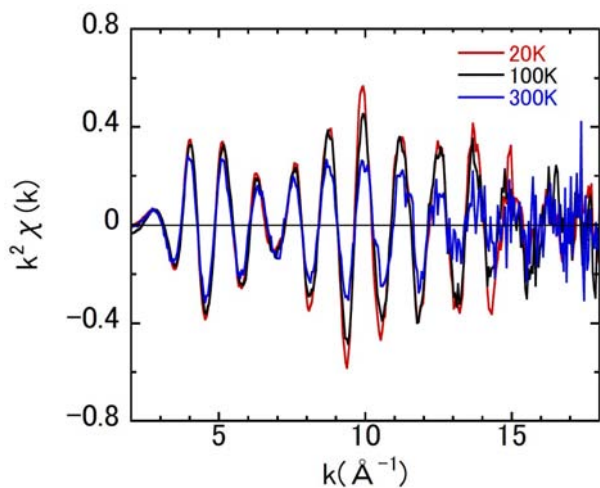
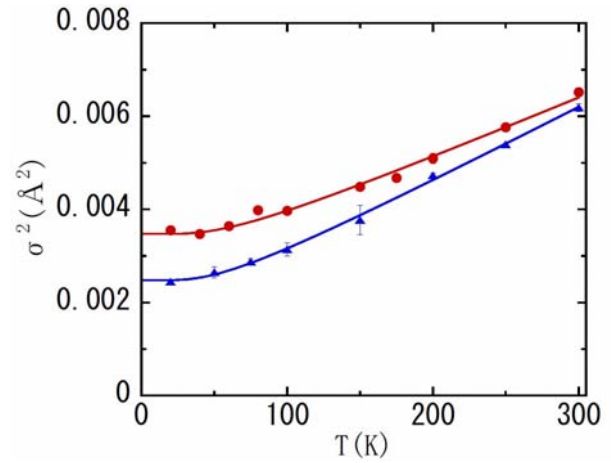
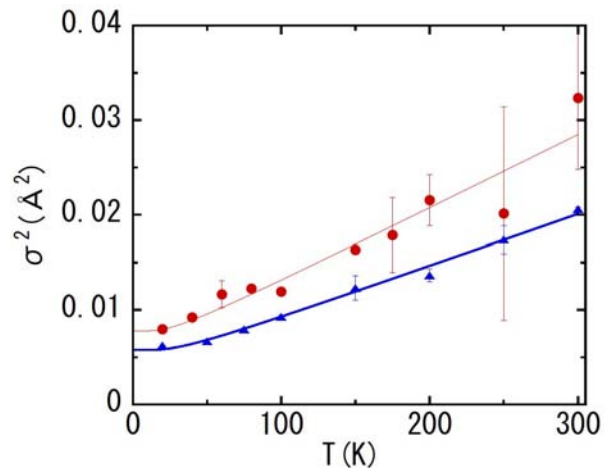


FIG. 2: EXAFS oscillations for 0.5 nm-thick films at 20, 100 and 300K.

### III. RESULTS AND DISCUSSION

Figures 1 and 2 show the EXAFS oscillation functions,  $k^2\chi(k)$ , at various temperature (20K, 100K, 300K) for t-Te and 0.5-nm-thick films, respectively. Data quality is quite satisfactory up to  $k=18 \text{ \AA}^{-1}$ . The amplitude of  $k^2\chi(k)$  function is much enhanced in high wave number,  $k$ , region for lower temperature. For 0.5-nm-thick films particles the thermal reduction of the amplitudes is prominent in comparison with t-Te. We obtained the several structural parameters with the non-linear-least-square-fitting. In this paper, we focus on the discussion about the temperature dependence of the Debye-Waller factors for the nearest intra- and interchain Te-Te atomic correlations.

In Fig. 3, we report the temperature dependence of the EXAFS Debye-Waller factors  $\sigma^2$  of the intrachain interactions for t-Te and the 0.5-nm-thick films. Such thermal behaviors are well approximated by the Debye correlated model as well as the Einstein model, as clearly shown in the figure. The values of  $\sigma^2$  for the 0.5-nm-thick films are larger than those of t-Te in the whole measured temperature range, but temperature gradient of  $\sigma^2$  for the 0.5-nm-thick films is smaller than that of t-Te.

FIG. 3: Debye-Waller factor  $\sigma^2$  of the intrachain nearest neighbor as a function of the measurement temperature, with the respective correlated Debye model (lines). The blue triangles denote  $\sigma^2$  for t-Te; the red circles denote  $\sigma^2$  for the 0.5-nm-thick films.FIG. 4: Debye-Waller factor  $\sigma^2$  of the interchain nearest neighbor as a function of the measurement temperature, with the respective correlated Debye model (lines). The blue triangles denote  $\sigma^2$  for t-Te; the red circles denote  $\sigma^2$  for the 0.5-nm-thick films.

The values of the corresponding Debye temperatures ( $\Theta_D$ ) obtained from the fit with Eq. (1) are presented in Table I. The previously reported Einstein temperatures ( $\Theta_E$ ) [1] are also shown in Table I. The  $\Theta_D$  of the 0.5-nm-thick films is about 10% higher than that of t-Te. The trend is similar with the case of the Einstein temperature. The higher  $\Theta_D$  of the 0.5-nm-thick films suggests that the covalent bonds of the 0.5-nm-thick films are stronger than those of t-Te.

The temperature dependence of  $\sigma^2$  for the interchain interactions for t-Te and the 0.5-nm-thick films are shown in Fig. 4. The values of the interchain  $\sigma^2$  for the 0.5 nm-thick films are some scattered, but they are well fitted by the Debye model. The  $\Theta_D$  of the interchain interactions for t-Te and the 0.5-nm-thick films are also shown in Table 1 with compared to the Einstein temperatures. The  $\Theta_D$  of the 0.5-nm-thick films is lower than that of t-Te in contrast to the case of the intrachain interactions.

The  $\Theta_D$  reflects strength of atomic interactions. In t-

TABLE I: Debye and Einstein[1] temperatures of the intra- and interchains for t-Te and 0.5 nm-thick-films

	Intrachain		Interchain	
	$\Theta_D$ (K)	$\Theta_E$ (K)	$\Theta_D$ (K)	$\Theta_E$ (K)
t-Te	250	154	137	83
0.5nm	274	171	114	70

Te the  $\Theta_D$  of the intrachains is stronger than that of interchains [4]. This result is reasonable, considering that force constant of the intrachains is stronger than that of the interchains. If the relationship between the  $\Theta_D$  and the force constants is applied to consideration to the interactions of the nanoparticles, the covalent bonds of the nanoparticles are stronger than those of t-Te. The interchain interactions of the nanoparticles are weaker than those of t-Te with contrary to the case of the intrachain interactions. In the case of t-Te, an application of pressure induces elongation of the covalent bond length with contrary to shrinking of the interchain separation. If overlapping between the antibonding orbitals and the LP orbitals on the neighbor chains elongates the covalent bonds, the opposite change would be expected. In the Te nanoparti-

cles, the reduction of the interchain interactions induces the strengthening of the intrachain covalent bonds.

#### IV. CONCLUSION

The Debye temperatures ( $\Theta_D$ ) of the Te nanoparticles for the intra- and interchain interactions are investigated. While the  $\Theta_D$  of the intrachain interactions for the nanoparticles is higher than that for t-Te, the  $\Theta_D$  of the interchains for the nanoparticles is lower than that for t-Te. Weakening of the interchain interactions brings about the enhancement of the intrachain covalent bonds.

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- [1] H. Ikemoto and T. Miyanaga, Phys. Rev. Lett. **99**, 165503 (2007).  
 [2] A. L. Ankudinov, B. Ravel, J. J. Rehr, and S. D. Conradson, Phys. Rev. B **58**, 7565 (1998).

- [3] E. Sevillano, H. Meuth and J. J. Rehr, Phys. Rev. B **20**, 4908 (1979).  
 [4] H. Wendel, J. Phys. C: Solid State Phys. **9**, 445 (1976).