Thermal properties of size-selective nanoparticles: Effect of the particle size on Einstein temperature

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Abstract. Characterizing size related thermal properties of nanoclusters is challenging due to the requirement to accurately control both their average sizes and the size distributions. In this work, temperature-dependent Extended X-ray Absorption Fine Structure spectroscopy and the phenomenological bond-order-length-strength (BOLS) model were employed to investigate the size-dependent Einstein temperature of Au nanoclusters. Theoretical calculations of Einstein temperature and average bond distance for clusters with different sizes agree quantitatively with experiment. The BOLS model is thus useful for predictive understanding of structure and thermal properties in well-defined metal clusters.

1. Introduction

Nanoparticles are characterized by high fraction of uncoordinated surface atoms, asymmetric bond length distributions and non-bulk like electronic structure, all of which affect their properties.[1] Experimental investigations of effects of temperature and pressure on these properties are subjects of continuous research,[2-4] although fundamental theory of thermodynamics of nanoparticles is yet to be developed. The greatest challenge towards that goal is twofold. First, it is difficult to isolate nanoparticles from their environment, such as support and adsorbates, to investigate metal-metal bonding structure and dynamics in a broad temperature range. Second, due to inherent heterogeneities of sizes, shapes, states of crystalline order,[5] and due to the ensemble-averaging nature of most structural probes, it is difficult to interpret the average measurements over an ensemble in terms of the behavior of a "representative" nanoparticle.[6] Computational methods, such as molecular dynamics simulations, are commonly employed to address some of the challenges.[7, 8] Alternative methods, based on analytical approaches and/or phenomenological models, are also sought, as there is a strong need to understand what factors are responsible for the thermal behaviors.

Characteristic temperatures such as melting point and Einstein temperatures are important factors defining thermodynamic properties of materials. From known behavior of these factors, many thermal properties can be deduced.[2, 9, 10] In previous studies, their relationships with the particle size were not easy to understand without accounting for the interaction between particle and environment.[11-13] Here we isolate the effect of particle size on Einstein temperature using dendrimer-encapsulated nanoparticles (DENS). Their Einstein temperatures and structural characteristics were measured by temperature-dependent Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy. The bond-order-length-strength (BOLS) model was used to interpret the data.[14] Agreement between measured and calculated changes in Einstein temperature with particle size demonstrated the usefulness of the BOLS model for prediction of thermodynamic properties of self-supported metal clusters.

2. Experimental

Au nanoclusters with two different average sizes were prepared using the wet chemical method as previously reported.[15] The size of particles was controlled by tuning surfactant and $HAuCl_4$ salt ratio. The two samples, denoted S1 and S2 were characterized by transmission electron microscopy (TEM) at the University of Texas, using a JEOL-2010F TEM operating at 200 kV. Temperature-dependent XAFS spectra at Au L_3 edge were collected in transmission mode at beamline X18B, NSLS at Brookhaven National Lab. Two Au cluster samples and Au foil were placed side by side onto a closed cycle Displex cryostat sample holder to avoid difference in sensed temperature.

3. Results and Discussion

Analysis by TEM showed that for sample S1 the average particle size was 1.6±0.2 nm and for S2 - 1.4±0.2 nm. The temperature-dependent Au L_3 XAFS spectra for Au foil are shown in Fig. 1(c). The amplitudes of Fourier transform (R-space) spectra decrease with increasing temperature, as expected, due to the enhanced bond-length disorder at elevated temperature. Similar trend was observed in the temperature-dependent XAFS spectra of samples S1 and S2.

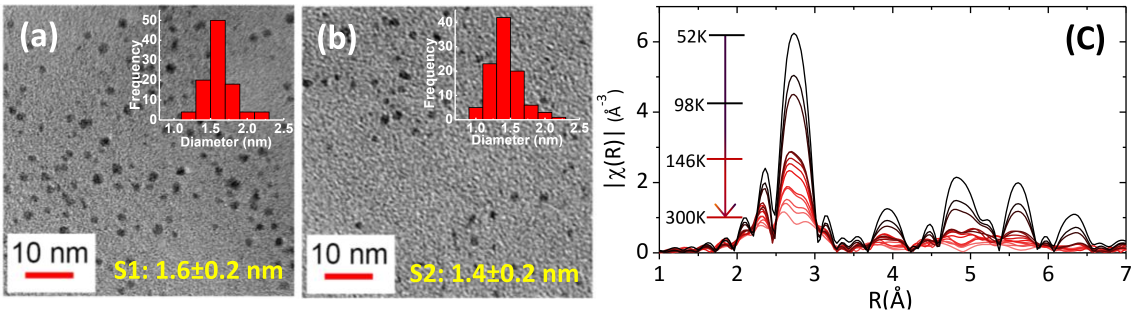

Figure 1. (a,b) The image and histogram (inset) of size distribution for samples S1 and S2. (c) The temperature-dependent Fourier transformed XAFS spectra for Au foil.

In the quantitative EXAFS data analysis, we varied the disorder factor and kept the coordination number constant, as no change in particle size or shape is expected in the temperature range below room temperature. In the multiple data-set modeling process, the total bond length disorder (Debye-Waller factor) was separated into the static (σ_s) and thermal disorder (σ_d) parameters, that were assumed to be statistically independent from each other:[16]

$$\sigma^2 = \sigma_s^2 + \sigma_d^2. \tag{1}$$

We used Einstein model to model the change of the dynamic disorder with temperature.[17] The coordination number of the first nearest Au-Au bond in S1 was obtained to be 8.8 ± 0.4, slightly larger than that in S2 (8.6 ± 0.4), which agrees with the trend observed in TEM measurements. The first nearest Au-Au bond distances in sample S2 with smaller particle size are smaller than those of S1 with larger particle size (Fig. 2(a)).[18] The average (over the measured temperature range) Au-Au distance in sample S2 and S1 is 2.4% and 1.7% shorter, respectively, than that in Au foil.

Debye-Waller factors for all samples are shown in Fig. 2 (b). The static disorder contribution to the total disorder (Eq. (1)) can be visualized as y-intercept in Fig. 2 (b). It is clearly larger for smaller particles, as shown previously.[5, 19, 20] Einstein temperature follows the opposite trend, increasing from 117.7±9.6 to 124.9±9.4K with particle size and to 134.5±0.8K for Au foil. This effect is expected for small particles, dating back to the works of F. von Lindemann, who demonstrated a monotonic relationship between the Einstein and melting temperatures,[21] and the fact that melting temperature decreases with decreasing size in small particles was reported by many groups.[2, 3, 7]

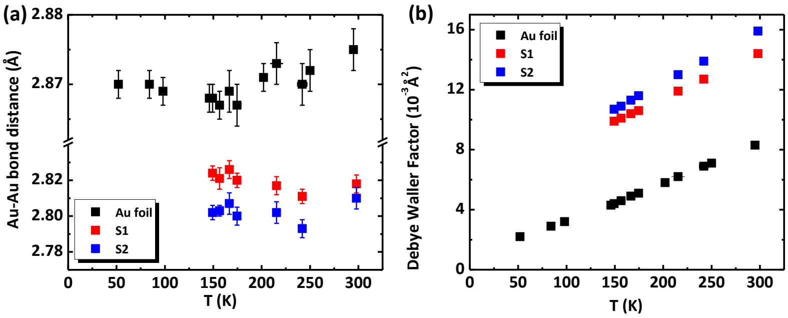

Figure 2. The temperature-dependent values of (a) the Au-Au bond distance and (b) Debye Waller factors for samples S1, S2 and Au foil.

These results were compared with those predicted by BOLS model, which calculates average bond distance and melting temperature based on the atomic structure of nanoclusters.[9] The change in melting temperature of nanoclusters relative to that of bulk structures can be expressed as:[9]

$$\frac{\Delta T_m(\mathrm{D})}{T_m(\infty)}=\frac{T_m(\mathrm{D})-T_m(\infty)}{T_m(\infty)}\cong\frac{\Delta E_T(\mathrm{D})}{E_T(\infty)}=\sum_{i\le 3}\gamma_i(z_{ib}c_i^{-m}-1);$$
$$\gamma_i=\frac{N_i}{N};\; z_{ib}=\frac{z_i}{z_b};\; c_i(z_i)=\frac{d_i}{d}=2/[1+\exp\left(\frac{12-z_i}{8z_i}\right)]. \tag{2}$$

The average bond distance ($\bar{d}$) over all atoms in the cluster is:[22]

$$\bar{d}=d[1+\Delta d],\; \Delta d=\sum_{i\le 3}\gamma_i(c_i-1). \tag{3}$$

In Eq. 3, d is the bond distance of bulk. From Eqs. 2 and 3, it is obvious that only the low-coordinated atoms on the surface are responsible for changes in average bond distance and melting temperature of the cluster.

Calculations were performed on cuboctahedral Au clusters containing 55, 147 and 309 atoms because the coordination numbers of these three regular cluster types (N_{55}=7.86, N_{147}=8.98 and N_{309}=9.63)[23] and their diameters of 1.1, 1.7 and 2.3 nm, respectively are comparable to those expected in "average" particles within samples S1 and S2. To directly compare experimental results with calculations, melting temperature was converted to Einstein temperature.[21] The ratio of Einstein temperature of cluster with diameter D to bulk can thus be derived in terms of the corresponding ratio for the melting temperature:

$$\frac{T_E(\mathrm{D})}{T_E(\infty)}=\sqrt{\frac{\Delta T_m(\mathrm{D})}{T_m(\infty)}+1}\,. \tag{4}$$

Experimental and calculated results on average bond distance and relative Einstein temperatures for Au clusters with different sizes are listed in Table 1.

Table 1. Comparison of BOLS model predictions and experimental results.

BOLS model prediction			EXAFS results		
	$\bar{d}$ (Å)	$T_E(\mathrm{D})/T_E(\infty)$		$\bar{d}$ (Å)	$T_E(\mathrm{D})/T_E(\infty)$
55	2.756	0.823			
147	2.793	0.875	S2	2.802±0.005	0.88±0.08
309	2.813	0.903	S1	2.820±0.005	0.93±0.08
Au foil	2.870*	1	Au foil	2.870±0.002	1

* Obtained by EXAFS analysis of Au foil

Similar to the experimental results, BOLS model calculations (Table 1) also predict the decrease of the average bond distance and Einstein temperature with decrease of particle size. The combination of results obtained from TEM, XAFS and BOLS model indicates that cuboctahedral Au_{147} is the appropriate model to describe the size and shape of sample S2 (the smaller sample). The agreement of the experimental and calculated results for that sample validates the BOLS model and its application to unsupported metal clusters. On the other hand, though the average diameter of sample S1 is close to that of S2, the average bond distance and Einstein temperature of sample S1 are closer to those of Au_{309}. Taken together, these latter observations suggest that a small portion of large particles dominates the thermal properties of the sample S1, which is a reasonable conclusion, taken into account that XAFS averaging is done according to the volume, not diameter, of nanoparticles. Hence, even a few large particles not accounted for in TEM images, can dominate the XAFS signal. The BOLS model, therefore, should be used with caution in its predictive capacity, and its validity should be tested against the measured particle size distribution whenever possible.

4. Conclusions

Temperature dependent EXAFS data in unsupported Au clusters of two different sizes demonstrated that both the average metal-metal bond length and Einstein temperature decreased with particle size. Phenomenological relationship between these two quantities can be also obtained analytically, within BOLS model that utilizes no free parameters. The agreement between the experiment and the calculation validates both the Einstein model in EXAFS data analysis of Au clusters and the use of the BOLS model for predicting their thermal and structural properties. An important prediction validated in this work is the role of surface atoms in tuning thermal properties of nanoclusters.

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