Vibrational Properties of Ge Nanocrystals Determined by EXAFS

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Abstract. The vibrational properties of Ge nanocrystals (NCs) produced by ion implantation in SiO_2 followed by thermal annealing were determined from temperature dependent Extended X-Ray Absorption Fine Structure (EXAFS) spectroscopy measurements. Using a correlated anharmonic Einstein model and thermodynamic perturbation theory it was possible to extract information about thermal and static disorder, thermal expansion and anharmonicity effects for the Ge NCs. Comparison with results for bulk crystalline and amorphous Ge indicates that the Ge NCs bonds are stiffer than those of both bulk phases of Ge. Also, the values of the anharmonic linear thermal expansion and the thermal expansion coefficient obtained for the Ge NCs were considerably smaller those for bulk crystalline Ge. Similar trends are reported in the literature for other semiconductor NC systems. They suggest that the increased surface to volume ratio of nanocrystals and the presence of the surrounding SiO_2 matrix might be responsible for the different vibrational properties of the nanocrystal phase.

Keywords: Ge; nanocrystals; EXAFS; thermal expansion; anharmonic potential; vibrational properties.
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INTRODUCTION

Nanocrystalline particles are interesting subjects for materials science since their properties can deviate from those of bulk materials. Ge nanocrystals (Ge NCs), in particular, are promising candidates for several light emitting devices [1,2]. The structural properties of Ge NCs have recently been studied by synchrotron-based techniques [3,4] and in this contribution we study the short-range order vibrational or thermal properties of Ge NCs. Thermal properties of bulk crystalline Ge (c-Ge) have also been investigated and are compared to previous studies [5,6], reinforcing the validity of our approach. The deviations observed for the properties of Ge NCs relative to bulk c-Ge reveal further differences between both states and allow us to garner deeper insight about size effects and the influence of a matrix of SiO_2 surrounding the Ge NCs. Our results are also compared to temperature dependent EXAFS studies of other semiconductor nanoparticle systems reported in the literature [7-9], which exhibit similar trends.

EXPERIMENTAL

Ge NCs were formed in a 2 μm thick SiO_2 matrix by ion implantation followed by thermal annealing [4]. Cross section transmission electron microscopy (XTEM) results show that the NCs are spherical in shape and present crystallinity. Their size distribution had a mean diameter of 6 nm with a full width at half maximum of 3 nm. Figure 1 shows a high resolution image of a Ge NC in the SiO_2 matrix.

EXAFS measurements at the Ge K-edge (11.103 keV) were performed at temperatures from 8 to 300 K, at beam line 10-2 of the Stanford Synchrotron Radiation Laboratory, USA. Fluorescence spectra were recorded with a 30 element solid–state Ge detector and the Si (220) monochromator detuned by 50% for harmonic rejection. EXAFS spectra were isolated from the raw absorption by background subtraction and subsequent splining using ATHENA [10]. Structural parameters were then determined using ARTEMIS [10] with photoelectron wavenumber k and non-phase-corrected radial distance r ranges of 4.8 – 14.8 $Å^{-1}$ and 1.7 – 2.6 Å, respectively. Phases and amplitudes were calculated *ab initio* with the FEFF8.102 code [11]. The amplitude reduction factor

S_0^2 and threshold energy E_0 were determined from the polycrystalline standard and held constant thereafter. Multiple dataset fits were carried out with multiple k weightings of 1–4.

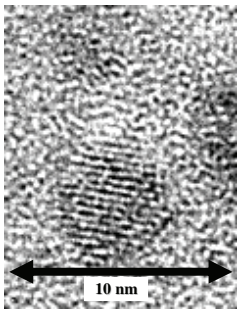

FIGURE 1. TEM image of a Ge NC in the SiO_2 matrix.

THEORETICAL

A model for the thermal evolution of the EXAFS cumulants in the quantum limit was derived by Frenkel and Rehr using a correlated anharmonic Einstein model and thermodynamic perturbation theory [12]. A one-dimensional anharmonic *effective* pair potential is assumed in such model, and it can be used as a reference to analyze the thermal behavior of the cumulants of the distance distribution obtained from experimental EXAFS data. A rigid shift of this *effective* potential relative to the crystallographic XRD potential has been previously observed for c-Ge [13]. This is probably a consequence of the difference in the minimum of the *effective* and *real* potentials, i.e. the difference between the maximum of the *effective* and *real* distributions of interatomic distances [14].

In the present work we have used the Frenkel and Rehr model [12] with the IFEFFIT code [15] to analyze our temperature dependant EXAFS data, as detailed in [16]. Additionally, static contributions to the cumulants were also considered. The values obtained from our experimental EXAFS data for the mean interatomic distance are equivalent to the *effective* first cumulant. From these values we have then evaluated the *real* first cumulant (not shown here) and the thermal expansion of interatomic distances using the relationships between these quantities as reported in [16].

RESULTS

The second cumulant values obtained for both c-Ge and Ge NCs from our experimental spectra are shown as a function of the measurement temperature in Figure 2(a), together with the data for c-Ge and a-Ge published in [5]. The lines are fits with the Einstein model. The values obtained from such fits for the static and thermal contributions to the total disorder are shown in Table 1, with the thermal component specified as the Einstein temperature. The results obtained in the present work for the third cumulant C_3 are shown in Figure 2(b). The results for c-Ge from [6] and a-Ge from [17] are included for comparison. The mean interatomic distances obtained for c-Ge and Ge NCs are shown in Figure 2(c). The thermal evolution of our first cumulant was observed to be best represented by the anharmonic contribution to the thermal expansion. The same quantity calculated by Dalba et al. [6] is also shown in the figure. Comparing the thermal evolution of the interatomic distances for c-Ge measured by EXAFS and XRD (from [18]), we can see they follow a very similar trend, despite the offset of about 0.003 Å between both data. This offset reflects what can be considered as a rigid shift of the *effective* interaction potential. Finally, it was also possible to evaluate the thermal expansion coefficient α_T from the measurements for both c-Ge and Ge NCs. The results are shown in Figure 2(d), where the thermal expansion coefficients determined by XRD measurements from [19,20] are also plotted.

CONCLUSIONS

The total values of C_2 for Ge NCs are intermediate between c-Ge and a-Ge. This indicates that the NCs are in a state of higher configurational energy than the crystalline samples. The Einstein temperature best fitting the NC data is higher than both c-Ge and a-Ge, indicating that the nanocrystals are stiffer than the bulk phases. This finding is in agreement with results obtained for ZnS NCs [7].

The total values of C_3 for the Ge NCs are higher than for c-Ge, due to the higher static disorder present in the NCs, which produces some asymmetry in the distribution of distances. On the other hand, the thermal only contribution to C_3 of the nanocrystals evolves with temperature at a slower rate than c-Ge. This indicates that the temperature induced asymmetry is lower for Ge NCs. As a result, the linear thermal expansion due to the *effective* potential anharmonicity, and the thermal expansion coefficient for Ge NCs are smaller than for c-Ge. These findings are in good agreement with data for other semiconductor NC systems [8,9].

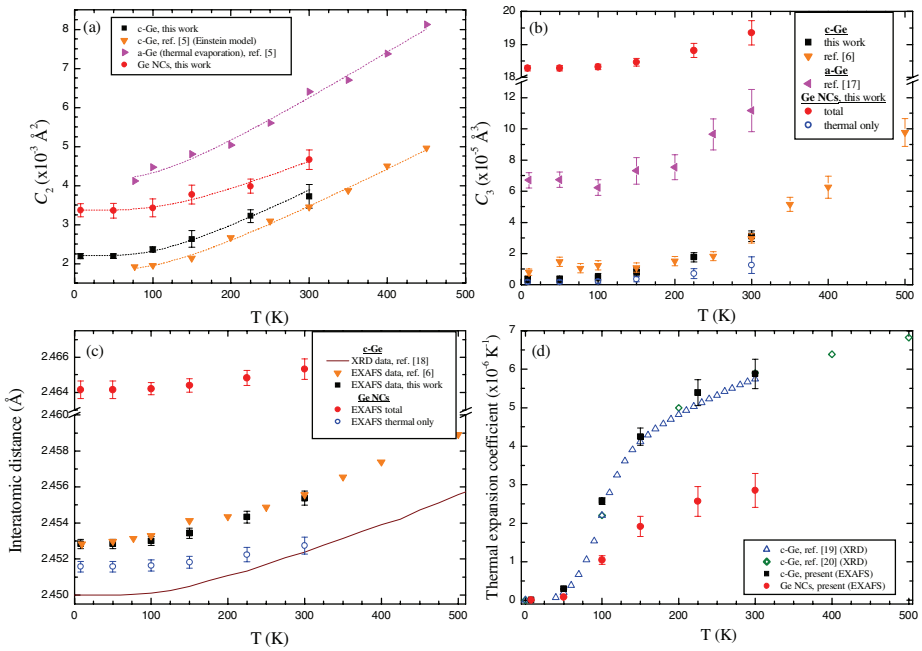

FIGURE 2. Results obtained from the EXAFS measurements on c-Ge and Ge NCs samples showing (a) second cumulants, (b) third cumulants, (c) *effective* first cumulants and (d) thermal expansion coefficients.

TABLE 1. Einstein temperatures and static components obtained from best fits to the experimental data.

System	Θ_E (K)	C_2 static (x10^{-3} Å^2)
c-Ge, ref. [14]	355.3 ± 5.7	0 (set)
c-Ge, present	351.1 ± 7.2	0.34 ± 0.05
Ge NCs, present	391.4 ± 11.2	1.70 ± 0.07
a-Ge, ref. [14]	323.3 ± 4.7	2.13 ± 0.10

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