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# Size dependence of the Mössbauer recoilless fraction in $\beta$ -Sn nanocrystals

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## Abstract

We study the size dependence of the Mössbauer recoilless fraction in  $\beta$ -Sn nanocrystals by performing conversion electron Mössbauer spectroscopy at different temperatures. The Mössbauer recoilless fraction is intimately related to dynamical processes involving the nuclei during the  $\gamma$ -ray emission. The  $\beta$ -Sn nanocrystals are embedded in a SiO<sub>2</sub> matrix, and they have a mean diameter ranging from 7 to 17 nm. A lowering of the recoilless fraction with decreasing cluster size is observed. The smallest nanocrystals reveal a 60% reduction of the recoilless fraction compared to the bulk value, while for the largest clusters we observe the same Mössbauer recoilless fraction as in the bulk. This suggests that the dynamical properties of the  $\beta$ -Sn nanocrystals in SiO<sub>2</sub> approach those of the bulk for a critical mean diameter above 16 nm. The experimental results are compared with theoretical values obtained by a continuum model in which the relevant parameters are determined *ab initio*.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

The physical properties of low-dimensional systems could be very different from those of their bulk counterparts. Small clusters exhibit interesting optical, mechanical, electronic and thermal properties due to the large atomic surface-to-volume ratio. For example, isolated Sn metallic nanoparticles reveal melting properties which are size dependent [1, 2]. The vibrational density of states (VDOS) of metallic nanocrystals depends on their size, and the phonon spectrum can be very different with respect to the bulk [3].

The Mössbauer effect (ME) allows one to measure the dynamics of the atoms forming the nanostructures, if they contain Mössbauer-active nuclei. The probability for occurrence of the ME, i.e. the Mössbauer recoilless fraction  $f$ , is intimately related to the phonon spectra of the resonant atoms via the mean square displacement  $\langle x^2 \rangle$  of the emitting or absorbing nucleus along the  $\gamma$ -ray direction. Equation (1) displays  $f$  in the harmonic approximation [4], together with its explicit expression, as obtained in the second

quantization formalism:

$$f = e^{-k^2 \langle x^2 \rangle} = \exp \left\{ -k^2 \sum_s \frac{\hbar}{3mN\omega_s} \left( n_s + \frac{1}{2} \right) \right\} \quad (1)$$

where  $k$  is the incident  $\gamma$ -ray wavevector, the label  $s$  runs over the vibrational modes (frequency  $\omega_s$  and thermal occupation number  $n_s$ ) of a crystal composed of  $N$  atoms having mass  $m$ . Equation (1) links  $f$  to the eigenfrequencies of the system under study. The recoilless fraction of a particular phase is proportional to the corresponding resonant area in the Mössbauer spectrum, the physical quantity directly accessible in the experiment. Any size dependence of the VDOS for the nanocrystals should be reflected in a corresponding dependence of their  $f$  values.

A considerable reduction of  $f$  for nanometre-sized Sn, Au, W and Fe particles has previously been observed exploiting the ME [5–8].

There is a great interest in metallic nanocrystals embedded in SiO<sub>2</sub>, due to their potential applications as information storage elements in emerging non-volatile memory devices [9]. Koops and colleagues have applied the ME to measure an extreme lowering of the Debye temperature ( $\Theta_D$ ) for very

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small (3–4 nm diameter)  $\beta$ -Sn clusters in  $\text{SiO}_2$  [10, 11]. However, the critical nanocrystal size above which the dynamical properties resemble those observed in the bulk is still not known. Our results fill the gap that exists between the vibrational properties of very small clusters and those observed in bulk  $\beta$ -Sn. We study the size dependence of  $f$  in  $\beta$ -Sn nanocrystals embedded in a  $\text{SiO}_2$  matrix by measuring the  $f$  values of the nanocrystals in the 7–17 nm diameter range. A direct comparison with the dynamical properties of bulk  $\beta$ -Sn is possible through the measurement via the ME of  $\Theta_D$  for the bulk phase. We observe a drastic lowering of the Mössbauer recoilless fraction for the smallest nanocrystals, while the  $f$  value for the 17 nm clusters is indistinguishable from that observed in the bulk reference sample.

## 2. Experimental details

$\beta$ -Sn nanocrystals are obtained by  $^{119\text{m}}\text{Sn}$  ion implantation followed by rapid thermal annealing (RTA) [9]. Amorphous  $\text{SiO}_2$  layers (85 nm thick) are implanted with  $^{119}\text{Sn}^+$  ions at room temperature (RT), with an energy of 80 keV and fluence of  $1 \times 10^{16} \text{ cm}^{-2}$ . RTA is performed after ion implantation, to both recover the implantation damage and to obtain a thermally activated and controlled redistribution of the implanted ions by phase separation. Details about the ion beam synthesis of Sn nanocrystals in  $\text{SiO}_2$  can be found in [9].

We consider a set of three samples annealed at 900 °C for 30 s, 900 °C for 120 s and 1100 °C for 30 s, respectively. In these samples, the mean diameter ( $d$ ) of the clusters identified as crystalline  $\beta$ -Sn is determined by transmission electron microscopy (TEM), and the results are 7.4(6), 10.9(9) and 16.9(7) nm, respectively [9]. In the following, we label the samples by their  $d$  values.

The local structure of the Sn-implanted  $\text{SiO}_2$  samples has been investigated in detail by conversion electron Mössbauer spectroscopy (CEMS) at RT and extended x-ray fine absorption spectroscopy [9]. By using a simple model based on CEMS results at RT and Rutherford backscattering spectroscopy (RBS) data providing the total number of Sn atoms in the samples, we have estimated  $f$  for  $\beta$ -Sn nanocrystals of different sizes [9]. We have reported a considerable reduction in  $f$  for small  $\beta$ -Sn nanocrystals embedded in  $\text{SiO}_2$  [9], while for the biggest ones we have observed an  $f$  value approaching that reported for the bulk  $\beta$ -Sn compound [12].

In order to carefully study this peculiar size dependence of  $f$ , we performed CEMS at 295 K (RT) and at low temperature (LT) down to 123 K. We use an experimental set-up that is based on a sealed parallel-plate avalanche counter (PPAC) especially developed for LT CEMS experiments [13].

The PPAC detector body is made of aluminium, and a Mylar front window is used for lowering the absorption of the  $\gamma$ -rays coming from the Mössbauer source. The parallel plates are made of Plexiglas, and thin graphite layers are used to build the anode and the sample back contact. We use a 90%He + 10%CH<sub>4</sub> mixture as a counting gas at a pressure of 220 and 60 mbar at RT and LT, respectively. Typical operating voltages are in the range of 600–800 V [13]. Gaseous nitrogen flowing through a serpentine tube immersed in liquid nitrogen

is used to cool down the sample (the detector). We tested our LT CEMS system by measuring the  $\Theta_D$  for a bulk  $\beta$ -Sn reference sample having a thin native  $\text{SnO}_2$  surface layer [13]. This sample is also used as a reference in the discussion of the size dependence of  $f$  for the  $\beta$ -Sn nanocrystals. The measured  $\Theta_D$  values for  $\beta$ -Sn and  $\text{SnO}_2$  were 120(1) K and 215(18) K, respectively. The  $\Theta_D$  ( $\beta$ -Sn) value we find is consistent with those reported in the literature, ranging from 122 to 136 K [12]. The  $\Theta_D$  ( $\text{SnO}_2$ ) is found to be lower than the values reported for the crystalline and amorphous bulk phases, but this is in accordance with a lowering of  $\Theta_D$  for  $\text{Sn}^{4+}$  atoms on the sample surface [13].

The Mössbauer source consists of  $^{119\text{m}}\text{Sn}$  atoms embedded in a  $\text{CaSnO}_3$  matrix, and it is moved by a standard constant acceleration drive system. The Mössbauer drive system was properly isolated in order to avoid artefacts in the spectra due to thermal drift [13].

## 3. Results and discussion

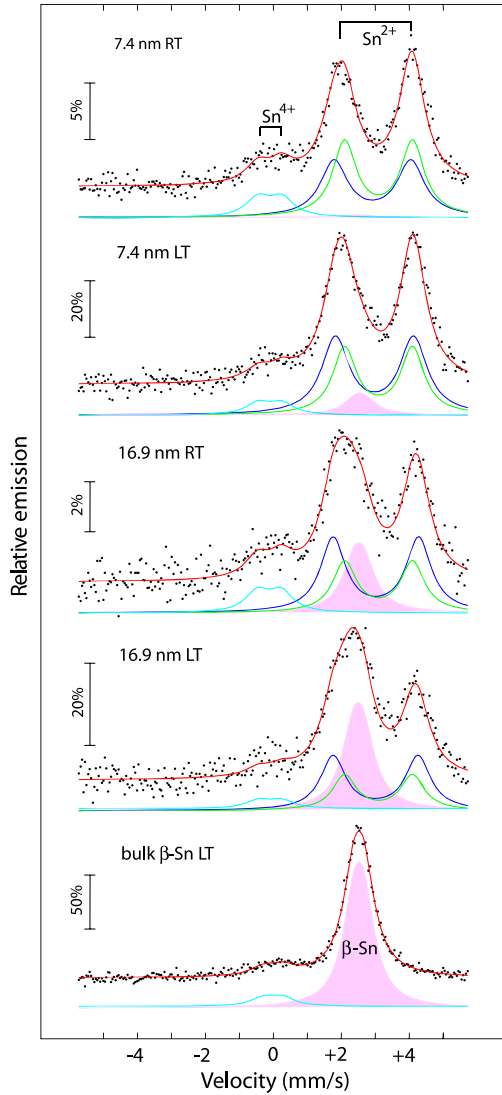
### 3.1. CEMS results

Figure 1 shows the RT and LT spectra for the 7.4 and 16.9 nm samples, together with the CEM spectrum at LT for the reference  $\beta$ -Sn bulk sample. The isomer shifts are relative to  $\text{CaSnO}_3$  at RT.

The CEM spectra of the samples containing nanocrystals are fitted with four distinct components. The fit is obtained by using the least-squares-fitting NORMOS-90 program [14]. The two doublets showing the highest centre shift are related to small  $\text{SnO}$  clusters and to Sn atoms dispersed in the  $\text{SiO}_2$  matrix, respectively [15]. The doublet centred at 0  $\text{mm s}^{-1}$  is due to the presence of  $\text{Sn}^{4+}$  atoms close to the sample surface [15]. The remaining component is centred at 2.5  $\text{mm s}^{-1}$  and it is related to the  $\beta$ -Sn nanocrystals [9]. All the experimental linewidths are 0.85  $\text{mm s}^{-1}$  at RT and at LT, indicating no line broadening. The experimental set-up used in this study allows a more detailed investigation of the nature of the Sn oxide phases [15] when compared to source Mössbauer measurements performed on similar systems [11], as the latter are affected by larger Mössbauer linewidths.

The  $\beta$ -Sn component has a higher spectral intensity at LT than at RT. The resonant area  $A$  of a particular component in a CEM spectrum is proportional to the product  $n \times f$ , where  $n$  is the number of atoms in that phase and  $f$  is the appropriate Mössbauer recoilless fraction. In principle one can calculate the absolute  $f$  value from  $A$ . However, since we do not know the exact number of Sn atoms constituting the  $\beta$ -Sn nanocrystals in the different samples, we use the temperature dependence of  $A$  to extract their  $f$  values. The  $\Theta_D$  of the  $\beta$ -Sn nanocrystals is determined by fitting the temperature dependence of the  $A$  values within the Debye model, and  $f$  is then calculated from equation (1) in the Debye approximation. Table 1 summarizes the results, together with the  $f$  values we computed in [9]. The results for the reference  $\beta$ -Sn sample are reported as well.

The  $f$  values (at RT) displayed in table 1 are in agreement with those reported in [9], where the  $f$  values were determined



**Figure 1.** CEM spectra of the 7.4 and 16.9 nm samples at RT and LT. The LT spectrum of the bulk  $\beta$ -Sn sample is reported as a reference. Dots show experimental data. The CEM spectra of the samples containing the nanocrystals are fitted with four components. The apparent single line relates to  $\beta$ -Sn, the doublet centred around zero accounts for  $\text{Sn}^{4+}$  and the remaining quadrupole-split doublets are related to  $\text{Sn}^{2+}$ . The CEM spectrum of the reference sample at LT is fitted with the two characteristic lines related to  $\beta$ -Sn and  $\text{SnO}_2$ .

by using our simple model based on the CEMS results at RT and the RBS data. In this simple model, the oxidized phases were considered as having the  $f$  values of their bulk phases ( $f = 0.2$  for both the  $\text{Sn}^{2+}$  phases and  $f = 0.5$  for  $\text{Sn}^{4+}$ ) [9]. By performing CEMS at different temperatures, we have determined the actual  $f$  values for the Sn oxides present in the sample annealed at 900 °C for 30 s [15]. For the two  $\text{Sn}^{2+}$  phases we have measured different  $f$  values, being equal to 0.06 and 0.153, respectively, and the  $\text{Sn}^{4+}$  phase shows  $f = 0.294$  [15]. By using the same model as described in [9] but considering the actual  $f$  values for the Sn oxides [15], we find an  $f$  value of about 0.0022 for the 7.4 nm  $\beta$ -Sn nanocrystals, in accordance with the previous estimate [9]. For those samples having larger clusters the error in determining the  $f$  in oxides is large, preventing any definitive conclusion.

**Table 1.** Debye temperature  $\Theta_D$  and Mössbauer recoilless fraction  $f$  at RT and LT, as deduced by using the Debye model to fit the temperature variation of the  $\beta$ -Sn resonant area. The  $f$  values reported in [9] are also given for comparison.

Sample	$\Theta_D$ (K)	$f$ (RT)		$f$ (LT)
		This work <sup>a</sup>	Reference [9]	This work
3–4 nm	82(8) <sup>b</sup>	0.00076(69) <sup>c</sup>	—	—
7.4 nm	98(18)	0.0098(96)	0.003(3)	0.110(81)
10.9 nm	115(7)	0.0195(89)	0.022(8)	0.182(41)
16.9 nm	117/124	0.0262(55)	0.034(5)	0.211(24)
Bulk $\beta$ -Sn	120(1)	0.0256(16)	—	0.208(10)

<sup>a</sup> Except for the 3–4 nm clusters.

<sup>b</sup> Taken from [11].

<sup>c</sup> Calculated with the Debye model by using the  $\Theta_D$  reported in [11].

The  $f$  values at LT increase by one order of magnitude when compared to those at RT. According to equation (1), our  $f$  values (at RT) correspond to  $\langle x^2 \rangle$  equal to 0.032, 0.027 and 0.025 Å<sup>2</sup> for the 7.4, 10.9 and 16.9 nm nanocrystals, respectively. The vibrational amplitude in the smallest clusters shows an increase of approximately 30% compared to the largest one. The  $f$  value for the 16.9 nm nanocrystals approaches the  $f$  that we have measured for the bulk  $\beta$ -Sn, by using the same experimental approach (table 1), while  $f$  (at RT) for the 7.4 nm clusters displays more than a 60% decrease. This is consistent with the even more pronounced reduction of  $\Theta_D$  measured by Koops *et al* for the 3–4 nm clusters [11] (table 1). Our experimental results show that the dynamical properties of  $\beta$ -Sn nanocrystals embedded in  $\text{SiO}_2$  resemble those observed in the bulk when the mean diameter is above 16 nm.

The increase in  $\langle x^2 \rangle$  that we observe for the smallest particles is considerably higher than that observed by Askelrod *et al* for even smaller particles (i.e. 4.5 nm mean diameter) [5]. Askelrod *et al* report a reduction of  $\langle x^2 \rangle$  of only 8% for their particles with respect to the bulk. This is apparently in contrast with our results. The differences from Askelrod *et al*'s results must be attributed, at least in part, to the effects of the matrix embedding the nanocrystals. Indeed, the matrix determines the force constants of the cluster surface layers by modifying their VDOS. In our system, the  $\beta$ -Sn nanocrystals are immersed in a  $\text{SiO}_2$  matrix while in Askelrod *et al*'s work they are mainly surrounded by Sn oxides, i.e. SnO and  $\text{SnO}_2$ .

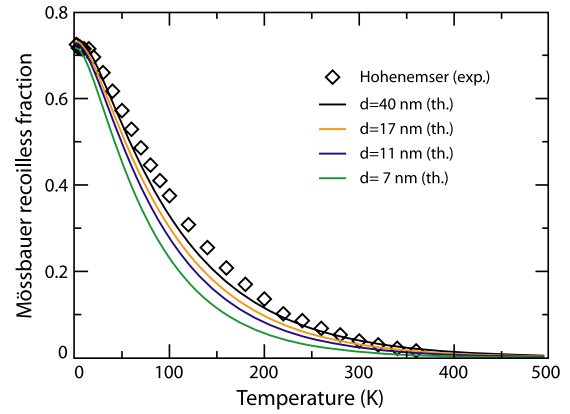
### 3.2. Theoretical model

The remarkable size dependence of  $f$  detected for the  $\beta$ -Sn nanocrystals, can be explained by means of a continuum model of a spherical nanocrystal developed by Tamura *et al*, in which the relevant parameters are determined *ab initio* [16–18]. In the model of Tamura *et al* the spherical nanocrystals are approximated by a sphere of radius  $R_0$  ( $R_0 = d/2$ ) made of a continuous elastic medium, allowing the eigenfrequencies of the lattice vibrations to be computed with a reduced computational effort. Relaxation effects of the surface atoms can be included in the model, as described in [16] and briefly illustrated below. This model accounts well for the size dependence of the frequency spectrum in small particles, since

it includes both the temperature and size dependence of  $\langle x^2 \rangle$ . The existence of a size-dependent term should explain the dependence of the Mössbauer recoilless fraction on  $d$ . To calculate  $\langle x^2 \rangle$  for small particles, different boundary conditions from those assumed for bulk materials must be used. The VDOS of the nanocrystals is characterized by a discreteness of the eigenfrequencies,  $\omega_S$  in equation (1), that becomes more evident as the particle size is reduced, while the distribution of  $\omega_S$  is denser as the particle size increases [16–18]. We have considered the effect of atomic relaxation at the surface of the nanocrystal. According to the model described by Tamura *et al* [16], this effect is taken into account by the *relaxed displacement*  $\delta$  that describes the inward (or the outward) relaxation of the atoms at the surface with respect to the ideal surface, where the atoms are located at the corresponding bulk positions. The nanocrystal is therefore divided in an inner region of radius  $R_i$  having the density and elastic constants of the bulk and an outer region of thickness  $R_0 - R_i$  having different elastic constants and with an increased (or decreased) density with respect to the bulk value, according to the sign and magnitude of the relaxed displacement. In the model developed by Tamura *et al*, the spheroidal and torsional vibrational modes have the boundary conditions of disappearance of stress at the cluster boundary, and a continuity of stress and displacements at the interface between the inner and outer region of the cluster-sphere [17].

Since  $f$  decreases by increasing the temperature (table 1), we expect that the main effects are due to the acoustic vibrational modes, thermally populated also at low temperatures when the  $f$  value is still significant. We can conveniently reproduce and explain the effect detected in the experiment with a reduced computational effort by using a continuum model for the acoustic vibrational modes of the nanoparticles. The parameters of the model are chosen in such a way that when the nanoparticles diameter goes to infinity, the VDOS of the acoustic modes reproduces the essential features of the bulk  $\beta$ -Sn. The vibrational properties of bulk  $\beta$ -Sn are easily computed by first principles within the density functional perturbation theory by plane-wave pseudopotential techniques [19], and these quantities can be used as input parameters for the continuum model<sup>4</sup>. The notation is the same as Tamura *et al*'s. According to our simulation, the ratio between longitudinal and transverse sound velocity is  $c_{li}/c_{ti} = 2.11$ , where the subscript  $i$  labels the quantities referred to the inner region of the nanocrystal, assumed the same as in the bulk. This value well matches the experimental sound velocities in bulk Sn [20]. As done in [16–18], we assume that this ratio is unchanged in the surface region of the nanosphere. The ratio of the Lamè elastic constant [21] between the surface and the inner region is taken to be equal to 2/3 as in [16]. The reader can refer to [16] and to references therein for a detailed discussion of the approximation used in choosing this value. In this model the inward relaxation of the surface atoms

<sup>4</sup> A rough estimation of the quantities related to the surface relaxation in the Sn nanocrystals is made by relaxing a super cell of a 16-layer slab of  $\beta$ -Sn along the [001] direction. However, the trends of the  $f$  factor as a function of nanocrystal size do not depend on the specific choice of the parameters involved in the surface relaxation.



**Figure 2.** Calculation of the Mössbauer recoilless fraction in the 0–500 K temperature range. The calculation is performed for nanocrystals having a mean cluster diameter  $d$  of 7, 11, 17 and 40 nm. The experimental  $f$  values for bulk  $\beta$ -Sn, as reported in [12], are also shown.

of the nanocrystal is taken into account by considering the parameter  $\delta$ . In our case we take  $\delta = 0.2 \text{ \AA}$  for all the nanocrystals (see footnote 4). This relaxation is responsible for the increase in the atomic density of a surface layer of thickness  $R_0 - R_i = 7.4 \text{ \AA}$  (see footnote 4). The atomic density in the inner volume of the sphere representing the nanocrystal is assumed to be the same as in the bulk  $\beta$ -Sn, i.e.  $0.038 \text{ \AA}^{-3}$ . Figure 2 displays the theoretical results for the temperature dependence of the Mössbauer recoilless fraction, as obtained using the Tamura model to compute  $\langle x^2 \rangle$  for nanocrystals of different sizes. Figure 2 shows also, for comparison, the experimental data for bulk  $\beta$ -Sn taken from [12].

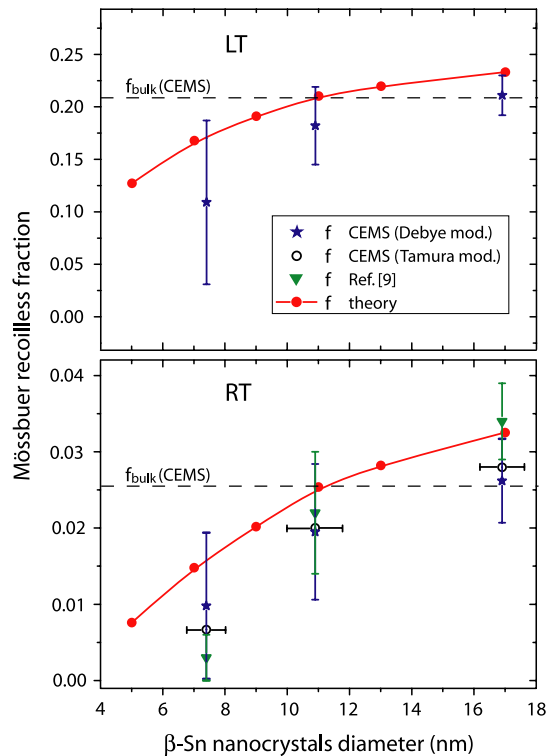
Due to their finite size and spherical symmetry, the vibrational modes of the nanocrystals have a different quantization with respect to those having an infinite  $d$ . This fact changes qualitatively the VDOS of the nanoparticles when compared to that in the bulk, and it is responsible for the size dependence of  $f$ . Since the population of vibrational modes increases by increasing the temperature, the percentage difference between  $f$  in nanocrystals and in the bulk becomes larger by increasing the temperature. On the other hand,  $f$  decreases with temperature due to the increase of  $\langle x^2 \rangle$  (equation (1)). According to our calculation, the combination of these two competing effects gives the largest size dependence of  $f$  in the 110–130 K temperature range (figure 2). This is the range of our LT CEMS measurements.

### 3.3. Comparison between experiment and theory

Figure 3 shows a comparison between the Mössbauer experiment and the theoretical results. The  $f$  values of the  $\beta$ -Sn nanocrystals of different radii are reported at RT (bottom panel) and at LT (top panel). The dashed lines represent the  $f$  values for the bulk  $\beta$ -Sn reference sample, as deduced by using the Debye model to fit the temperature dependence of the resonant area.

The Mössbauer recoilless fraction decreases with decreasing  $\beta$ -Sn nanocrystal size. The mean  $f$  values, as deduced by





**Figure 3.** Size dependence of the Mössbauer recoilless fraction in  $\beta$ -Sn nanocrystals at LT = 123 K (top panel) and RT = 295 K (bottom panel). (Blue) stars and (black) open circles show experimental data, as obtained by fitting the temperature variation of  $A$  with the Debye and Tamura models, respectively; (green) triangles show data taken from [9]; (red) filled circles show theoretical results. The (red) continuous line is given as a guide for the eyes. The horizontal dashed lines indicate the  $f$  values for bulk  $\beta$ -Sn, as measured with CEMS (table 1). Note the different vertical axis scales in the top and bottom panels.

CEMS, are slightly lower than those predicted by our calculation. This is possibly due to a larger atomic surface-to-volume ratio for the nanocrystals than the value corresponding to the ideal spheres. Indeed, TEM shows the presence of both perfectly spherical nanocrystals and others having a less regular shape [9]. By using our theoretical results, we estimate the  $f$  values at RT without considering the Debye model. We extract the proportionality constant  $C$  between  $A$  and  $f$  by dividing the  $A$  at LT, which presents a smaller error with respect the one at RT (table 1), by the  $f$  values at LT we have computed (figure 2). The  $f$  values at RT are then calculated by dividing the  $A$  at RT by  $C$ . The results are 0.0067, 0.02 and 0.028 for the 7.4 nm, 10.9 nm and 16.9 nm samples, respectively. They are indicated in the bottom panel of figure 3 with open circles (Tamura model). The agreement we find by following the two distinct approaches in interpreting the experimental data (Debye and Tamura models) confirms that the qualitative and quantitative behaviours found in the experiment are model independent.

#### 4. Conclusions

In summary, we find that the Mössbauer recoilless fraction in  $\beta$ -Sn nanocrystals embedded in  $\text{SiO}_2$  matrix is strongly

size dependent. We determine  $f$  for the nanocrystals by performing Mössbauer spectroscopy at room temperature and at low temperature (123 K). The corresponding mean square displacement of the constituting atoms is deduced from the general expression of  $f$ . The largest nanocrystals have a recoilless fraction approaching the bulk value, while (at room temperature) the smallest clusters display a 60% decrease, which corresponds to a 30% increase of mean square displacement. We find that the nanocrystals with mean diameter larger than 16 nm exhibit the bulk dynamical properties. Our results fill the gap between the existing data of  $f$  for very small clusters (3–4 nm) and those observed in bulk  $\beta$ -Sn. The experimental results are in agreement with those predicted *ab initio* using a continuum model of spherical nanocrystals in the elastic body approximation. The size dependence of  $f$  is due to the remarkable contribution of the surface vibrational modes in determining the VDOS in the smaller nanocrystals, i.e. the surface relaxation effect, and this effect is more pronounced as the atomic surface-to-volume ratio becomes higher.

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