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Stabilization of the γ -Sn phase in tin nanoparticles and nanowires

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Structures of Sn nanoparticles and nanowires are studied using density functional theory in conjunction with thermodynamic considerations. Besides the low-temperature α and room-temperature β phases, the high-temperature γ phase is considered. Results show that at ambient temperatures for sizes smaller than 50 nm, metallic β - and γ -Sn nanoparticles are more stable than semimetallic α -Sn ones because of their lower surface energies. Moreover, very small Sn nanostructures, exemplified by nanowires, are expected to exhibit the γ phase even at 0 K. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4931353>]

Tin (Sn) nanoparticles have gained increasing attention in Li-based batteries^{1–9} and optoelectronic applications.^{10–12} As an anode material, Sn has a much higher capacity than currently used graphite intercalation anodes.¹ Several groups have indeed fabricated working electrodes with considerable capacity and cycle life.^{2–5} In particular, small Sn particles of the size of several hundreds down to a few nanometers are used^{1,3–5,7–9} as they are less prone to crack formation and structural damages upon volume expansion during lithiation and thus exhibit better cycle life.⁶ Moreover, Sn is superior to carbon for the sodium battery chemistry.^{13,14}

Bulk Sn shows a first order phase transition at roughly 13 °C, where metallic β phase transforms into the non-metallic-zero-gap semiconducting α phase.¹⁵ This phase transition not only changes the atomistic structure but also increases the volume by $\sim 30\%$. Thus, a strong temperature impact on voltage, resistance, and degradation of Sn anodes is expected under operation conditions (typically between -20 and 50 °C). In order to understand temperature effects in Sn nanoparticles, we have recently studied their stabilities using density functional theory (DFT) by evaluating the impact of surface energies on the total Gibbs free energy. It was found that the metallic β -phase should be increasingly more stable than α -phase of Sn with reducing particle size.¹⁶ Experimental results on pure Sn nanoparticles are however rare and those so far reported are not consistent.^{17,18}

In this work, we report a DFT-based theoretical study of structure and stability of nanoparticles of the rarely studied γ polymorph of Sn. This phase is only slightly different from a simple hexagonal structure. We find that this polymorph is structurally very similar and energetically quasi-degenerate to bulk β -Sn for a wide range of exchange-correlation functionals (Table S1 in the supplementary material²⁶), which is also in correspondence to its experimental occurrence at temperatures higher than 170 °C.^{19–21} Here, we show that indeed lower surface energies are obtained for γ -phase compared to β -phase. The temperature-size phase diagram is determined,

revealing that γ -Sn is the most stable phase at room temperatures for nanoparticles smaller than 10 nm. On very small scales, as proved by calculations for Sn nanowires, the γ -phase is predominant even at 0 K.

The details of the theoretical method are given in the supplementary material.²⁶ The calculated bulk properties of α , β , and γ -Sn are tabulated in Table I. We find, in agreement with Ref. 19, that the γ -Sn polymorph is expected to have similar stability as β -Sn. When vibrations are included, the bulk $\alpha \rightarrow \beta$ phase transition temperature is reproduced qualitatively correct, however, within the Perdew, Burke, and Ernzerhof (PBE) generalized gradient approximation,²² the γ -Sn structure was found even more stable than β -Sn. On the other hand, a small correction to the absolute values of PBE bulk energies of -12 meV (-2 meV) for β -Sn (γ -Sn) results in accurate values for the bulk transition temperatures. Such a correction is necessary as DFT can have problems to reproduce the correct relative phase stability.^{23,24}

Surface properties of γ -Sn. The γ -Sn unit cell is depicted in Table I. It is closely related to a conventional hexagonal cell with the hexagonal z direction along the a direction of γ -Sn. Calculated surface energies of γ -Sn are tabulated in Table II and the most important surface terminations are depicted in Fig. 1. The lowest energy terminations of γ -Sn have surface energies of only ≈ 22 meV/Å² and they correspond to the possible bisections of the hexagonal structure without breaking

TABLE I. Structures and properties of different Sn polymorphs. A conventional unit cell was chosen for γ -Sn for a better comparison with the β structure.

	α -Sn	β -Sn	γ -Sn
			
a (Å)	6.65	5.95	6.16
b (Å)	6.65	5.95	5.64
c (Å)	6.65	3.21	3.27
ρ (atoms/Å ³)	0.0272	0.0352	0.0352
$E_0 - E_0(\alpha - \text{Sn})$ (meV)	0	39.0	38.6

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TABLE II. Surface energies of γ -Sn and relative contributions of surfaces to the Wulff shape.

γ -Sn surfaces {hkl}	{010}	{012}	{021}	{001}	{122}	{102}	{100}	{111}	{120}	{212}	{101}	{210}	{221}	{110}	{201}
γ_s (meV/Å ²)	21.7	21.7	22.2	22.5	23.7	24.5	24.6	25.4	26.0	27.3	27.5	27.6	27.8	28.0	28.7
% of Wulff shape	8.4	31.9	...	1.5	7.2	8.8	13.3	12.3	12.9	2.7	...	1.1

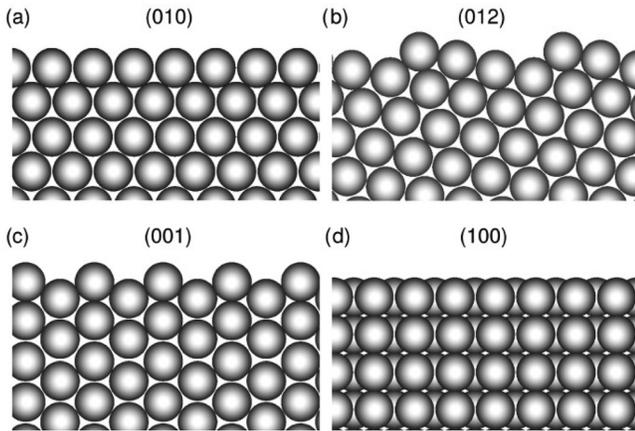


FIG. 1. Side views of relaxed structures of most important surface terminations of γ -Sn. (a) (010), (b) (012), and (c) (001) belonging to the very stable surface family which involves no bond breaking along the a axis (along the c axis for the corresponding quasi-hexagonal structure). (d) (100) is perpendicular to the surfaces (a)–(c). The calculated surface energies are listed in Table II.

the bonds to the two closest nearest neighbors along the a axis. The surface energies increase in the order $\{010\} \rightarrow \{012\} \rightarrow \{021\} \rightarrow \{001\}$ which is in line with the fact that these surfaces correspond to perfect and increasingly stepped “hexagonal” surfaces (see Figs. 1(a)–1(c)). The γ -Sn surfaces that cut through the bonds perpendicular to the hexagonal plane, e.g., $\{122\}$, $\{102\}$, and $\{100\}$, have higher surface energies between 23.7 and 24.6 meV/Å².

Wulff shape and nanoparticle stability at 0 K. In order to determine the lowest energy structure of Sn nanoparticles we constructed the Wulff shapes which are included in Fig. 2. The Wulff shape of α -Sn is dominated by the reconstructed

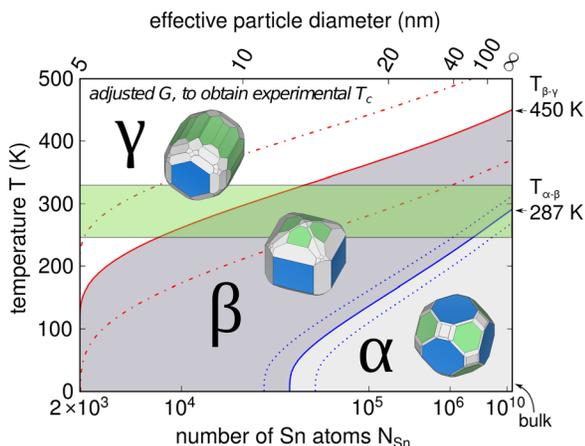


FIG. 2. Temperature-size phase diagram of Sn nanoparticles. The effective particle diameters correspond to equivalent spherical β -Sn particles with the same number of Sn atoms. The stability lines are obtained from DFT-derived free energies empirically shifted to reproduce the experimental bulk transition temperatures with the dashed lines indicating the effect of a 2 meV error. Typical battery operation temperatures are shaded with a green area.

$\{100\}$ (blue) and $\{111\}$ (green) surfaces. β -Sn is dominated by the $\{100\}$ (blue), $\{101\}$ (green), and $\{201\}$ terminations. For γ -Sn, we again adopted our approach to interpret surface energies as if they were obtained from calculations of a conventional hexagonal cell in order to apply hexagonal symmetry operations. We provide a mapping of the (hkl) notation of γ -Sn to a hexagonal primitive unit cell notation in the supporting information (Table S2²⁶). The γ -Sn Wulff shape is slightly elongated in the a direction due to the comparably large $\{100\}$ (blue) surface energy.

Nanoparticle stability at $T > 0$ K. The temperature-size phase diagram of Sn (the theoretical method is detailed in the supporting material²⁶) is illustrated in Fig. 2. The range of typical battery operation temperatures (-20°C – $+50^\circ\text{C}$) is shaded in green. For small particle sizes, the large surface energy contributions stabilize the β and γ phases. The bulk behavior is basically observed for particles larger than 100 nm. For nanoparticle sizes below 50 nm, the α - β phase transition falls out of the range of typical battery operating temperatures. Furthermore, nanoparticles of sizes below ≈ 11 nm should only be stable as γ -Sn or β -Sn at any temperature. However, the β - γ transition is less important for the electrode performance since the change in electronic and atomic structure is much less dramatic as in the case of α - β transition.

Sn nanowires. In order to confirm the extrapolations from the Wulff shaped nanoparticles, we also performed

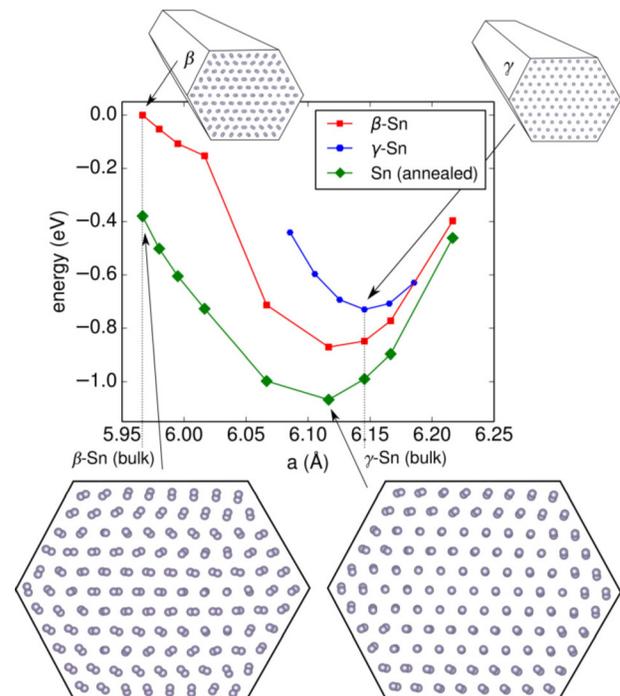


FIG. 3. Energy of DFT-relaxed ($T = 0, p = 0$) β -Sn and γ -Sn as well as annealed nanowires with hexagonal cross-sections as function of lattice parameter a .

computations for nanowires. By construction the simulated nanowires are infinitely extended along the a -direction and cut out of bulk β and γ -Sn with topologically equivalent hexagonal cross section (see Fig. 3) with β -Sn(101) and (010) as well as γ -Sn(010) surfaces exposed. The nanowire diameter is approximately 3.5 nm.

We find that increasing the lattice constant a from the β bulk value reduces the energy considerably. β -Sn nanowires with β bulk lattice parameters are clearly higher in energy than the equivalent γ -Sn ones. For the β -Sn derived nanowire (red squares), the minimum energy is obtained for the lattice constant a close to the γ -Sn value. However the slight energy discrepancy of ≈ 0.5 meV/atom between the bulk-truncated β and γ structures (red and blue curves) indicates a high degree of frustration if the axial lattice parameter a is fixed during relaxations. Therefore, we applied an *ab initio* molecular dynamics annealing procedure as explained in the supplementary material.²⁶ The calculated energies for different lattice parameters (green curve) as well as two relaxed structures are illustrated in Fig. 3. The minimum energy structure is obviously closely related to γ -Sn, especially in the center of the nanowire. This is in line with the observed low surface energies of γ -Sn(010) that drives the β -Sn nanowire into a γ -Sn-like nanowire. It should be noted that the elongation with respect to the lattice constant a exhibits no barrier for all considered structures. In other words, nanostructures with β -Sn bulk lattice parameters are not even metastable states of the system, which was also reported by others.²⁵ We showed here that the effect is due to the higher stability of the γ -phase with respect to the β phase in Sn nanostructures due to lower surface energies.

In this work, we studied the structure, stability, and phase transition in Sn nanoparticles and nanowires. According to the calculated temperature-size phase diagram, the phase stability of Sn changes dramatically by nanoscaling. It is found that the α – β phase transition temperature changes from 13 °C to below -20 °C in nanoparticles of sizes smaller than 50 nm. The β -Sn nanoparticles are metallic and exhibit a higher density which is favorable in terms of conductivity and potential volumetric energy density. We also found that surfaces should increase the stability of γ -Sn such that its stability range is shifted from high temperatures (close to the melting point) to room temperatures for nanoparticles smaller than 10 nm. The stabilization can be understood from the increased coordination number of Sn atoms in the γ polymorph (2 + 6 coordination), which makes bond cutting at surfaces easier than in β -Sn (4 + 2 coordination), as even surface atoms in γ -Sn have the same coordination as bulk atoms in β -Sn. We hope that this work motivates new

research efforts to study phase-sensitivity in the performance of nanostructured anode materials.

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- ¹J. W. Wang, X. H. Liu, S. X. Mao, and J. Y. Huang, *Nano Lett.* **12**(11), 5897 (2012).
- ²D. Larcher, S. Beattie, M. Morcrette, K. Edstroem, J. C. Jumas, and J. M. Tarascon, *J. Mater. Chem.* **17**, 3759 (2007).
- ³Y. Yu, L. Gu, C. Zhu, P. A. van Aken, and J. Maier, *JACS* **131**(44), 15984 (2009).
- ⁴H. Zhu, Z. Jia, Y. Chen, N. Weadock, J. Wan, O. Vaaland, X. Han, T. Li, and L. Hu, *Nano Lett.* **13**(7), 3093 (2013).
- ⁵J. Qin, C. He, N. Zhao, Z. Wang, C. Shi, E. Liu, and J. Li, *ACS Nano* **8**(2), 1728 (2014).
- ⁶N.-S. Choi, Y. Yao, Y. Cui, and J. Cho, *J. Mater. Chem.* **21**, 9825 (2011).
- ⁷Y. Zou and Y. Wang, *ACS Nano* **5**(10), 8108 (2011).
- ⁸X. Zhou, J. Bao, Z. Dai, and Y.-G. Guo, *J. Phys. Chem. C* **117**(48), 25367 (2013).
- ⁹Y. Xu, B. Yan, H. Zhang, J. Wang, G. Xu, P. Tang, W. Duan, and S. Zhang, *Phys. Rev. Lett.* **111**, 136804 (2013).
- ¹⁰M.-F. Ng and T. L. Tan, *Nano Lett.* **13**(10), 4951 (2013).
- ¹¹S. Küfner, J. Furthmüller, L. Matthes, M. Fitzner, and F. Bechstedt, *Phys. Rev. B* **87**, 235307 (2013).
- ¹²S. Küfner, J. Furthmüller, L. Matthes, and F. Bechstedt, *Nanotechnology* **24**(40), 405702 (2013).
- ¹³M. D. Slater, D. Kim, E. Lee, and C. S. Johnson, *Adv. Funct. Mater.* **23**(8), 947 (2013).
- ¹⁴B. Wang, B. Luo, X. Li, and L. Zhi, *Mater. Today* **15**(12), 544 (2012).
- ¹⁵G. Busch and R. Keibn, *Solid State Physics* (Academic Press, 1960), Vol. 11, pp. 1–40.
- ¹⁶N. G. Hörmann, A. Gross, and P. Kaghazchi, *Phys. Chem. Chem. Phys.* **17**, 5569 (2015).
- ¹⁷Y. Xu, Q. Liu, Y. Zhu, Y. Liu, A. Langrock, M. Zachariah, and C. Wang, *Nano Lett.* **13**(2), 470 (2013).
- ¹⁸H. S. Im, Y. J. Cho, Y. R. Lim, C. S. Jung, D. M. Jang, J. Park, F. Shojaei, and H. S. Kang, *ACS Nano* **7**(12), 11103 (2013).
- ¹⁹B. Wehinger, A. Bosak, G. Piccolboni, K. Refson, D. Chernyshov, A. Ivanov, A. Rumiantsev, and M. Krisch, *J. Phys.: Condens. Matter* **26**(11), 115401 (2014).
- ²⁰C. L. Mantell, *Tin* (Reinhold Publishing Corp., New York, 1949).
- ²¹N. Burns, *J. Fail. Anal. Prev.* **9**(5), 461 (2009).
- ²²J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- ²³C. Fang, M. van Huis, and H. Zandbergen, *Phys. Rev. B* **80**, 224108 (2009).
- ²⁴M. E. Arroyo-de Dompablo, A. Morales-García, and M. Taravillo, *J. Chem. Phys.* **135**(5), 054503 (2011).
- ²⁵Y.-S. Kim, S. M. Lee, and J. Y. Song, *Appl. Surf. Sci.* **256**(11), 3603 (2010).
- ²⁶See supplementary material at <http://dx.doi.org/10.1063/1.4931353> for more detailed information on the determination of the temperature-size phase diagram, the influence of the exchange-correlation functional, the mapping of γ -Sn surfaces onto those of a simple hexagonal structure and the AIMD annealing procedure as applied to the metallic Sn nanowire.