

Comment on “Large Melting-Point Hysteresis of Ge Nanocrystals Embedded in SiO₂”

In their Letter [1], Xu *et al.* study the melting behavior of Ge nanocrystals (NC) in a SiO₂ matrix. The observed melting-point hysteresis around the bulk melting point T_m is used with classical nucleation theory (CNT) to estimate the liquid-solid (LS) surface tension of Ge, γ_{LS} . We reconsider some of the numbers and arguments of [1].

(i) A key quantity is the latent heat of fusion L , but the value used in [1] is not given. On one hand, one can infer L from the discussion of Turnbull’s value for γ_{LS} . From the supercooling limit of Ge and a *calculated* $L = 25.5 \text{ kJ mol}^{-1}$, he deduced from CNT $\gamma_{LS} = 0.181 \text{ J m}^{-2} \propto L^{2/3}$ [2]. Xu *et al.* explain that a rescaling gives $\gamma_{LS} = 0.23 \text{ J m}^{-2}$, which indicates the use of $L_1 = 36.94 \text{ kJ mol}^{-1}$, the currently accepted value [3]. On the other hand, to reproduce their values for the nucleation barriers with $\gamma_{LS} = 0.26 \text{ J m}^{-2}$ [1], one needs to use $L_2 = 31.8 \text{ kJ mol}^{-1}$, but this is the average of two inconsistent early determinations [4]. L_1 should be preferred and leads to $\gamma_{LS} = 0.285 \text{ J m}^{-2}$. Coming back to Turnbull, we note that he studied Ge on a SiO₂ flake [5]: nucleation was heterogeneous as in [1]. Assuming a contact angle of $\pi/2$ on SiO₂ [1], we modify his analysis [2] by dividing the energy barrier by 2 and replacing the number of atoms n by $\approx n^{2/3}$, the number of atoms at the surface: γ_{LS} becomes 0.26 J m^{-2} , close to 0.285 J m^{-2} .

(ii) As Ge shrinks upon melting, Xu *et al.* consider the possibility that a gap opens between the molten droplet and the matrix. For a spherical vapor shell, they find that the surface energy cost is higher than the elastic strain energy, and conclude that a gap will not open. However, the vapor does not wet the matrix completely: the contact angle $\theta_c = \cos^{-1}[(\gamma_{LM} - \gamma_{MV})/\gamma_{LV}]$ is between 34° and 61° (based on tensions from [1]). The increase in surface energy can thus be lowered by creating a lenticular bubble rather than a spherical shell. A complete analysis should take the elasticity of the matrix into account, but it is complicated by the loss of spherical symmetry. To give an idea, we consider a rigid matrix and expand the liquid chemical potential linearly in density to calculate the change in Helmholtz free energy ΔF associated with the creation of the bubble. With a NC radius $r_0 = 2.5 \text{ nm}$ and $\theta_c = 49^\circ$, a shallow minimum exists for a cavitating droplet, but with $\Delta F > 0$: no bubble will appear. However, ΔF decreases when r increases, and it vanishes at 3.62 nm . Interestingly, such values exist in the sample: the average r is r_0 , with an rms deviation of 1.3 nm [1]. Moreover, the stretched and cavitating droplet are separated by an energy barrier of 3 eV , allowing a transition rate between the two states of 87 s^{-1} . As r increases, the cavitating droplet becomes more stable, but the energy barrier increases, and the transition rate is less than 1 s^{-1} for $r \geq 4.87 \text{ nm}$. For $\theta_c = 34^\circ$, the bubbles are always favored and the cavitation rates are huge.

Xu *et al.* also estimate the temperature $T_m + \Delta T$ at which molten and solid NC have the same free energy. Neglecting elasticity, $\Delta T \propto \gamma_{LM} - \gamma_{SM}$; the hysteresis being symmetric around T_m , they deduce $\gamma_{LM} = \gamma_{SM}$. We now include elasticity, starting with a stress free matrix-solid NC system and calculating the elastic energy E_{el} of the matrix-molten NC system. We follow [6], as did Xu *et al.* for cavitation. However, it seems that they have only considered the strain energy stored in *volume*, omitting the correction to the *surface* energy [Eqs. (16) and (17) of [6]]; the surface term is dominant for small r , and we include it in the following. We use different parameters for Ge [3], and Ref. [7] for SiO₂. We find an additional shift $\Delta T = T_m E_{el}/(4\pi r^3 L/3)$. We have tried different values of the interface stress f , close to γ_{LM} . The effect on ΔT is negligible for r_0 , between $+1.8 \text{ K}$ (respectively -1.3 K) for $f = 0.6 \text{ J m}^{-2}$ (respectively $f = 1 \text{ J m}^{-2}$), but it becomes important at small r : for 0.5 nm , ΔT is shifted by -30 K (respectively -81 K). A distribution with a lower average of r would allow to check this and to estimate f .

(iii) Finally, we consider the effect of annealing. The stress in the sample is relieved by annealing for 14 h at 1073 K [8]. When all the NCs are melted at 1450 K , the matrix is put under stress; using the thermally activated model from [8], we estimate that the stress relaxes in 34 s at this temperature, less than the 5 min duration of a temperature step in [1]. In this case, when cooling down, solidification results in a compressive stress. The above argument about ΔT can be invoked, but with a different value of the strain and the bulk modulus of the solid [3]. For $f = 0.6 \text{ J m}^{-2}$ (respectively 1 J m^{-2}), ΔT is shifted by $+24 \text{ K}$ (respectively $+28 \text{ K}$) for r_0 and by $+43 \text{ K}$ (respectively $+47 \text{ K}$) for $r = 0.5 \text{ nm}$. If such a mechanism is relevant, the whole picture would have to be modified, leading to different values for $\gamma_{LM} - \gamma_{SM}$ and γ_{LS} .

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Received 4 January 2007; published 17 August 2007

DOI: [10.1103/PhysRevLett.99.079601](https://doi.org/10.1103/PhysRevLett.99.079601)

PACS numbers: 64.60.-i, 61.46.Hk, 64.70.Dv

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