

Size-, dimensionality-, and composition-dependent Debye temperature of monometallic and bimetallic nanocrystals in the deep nanometer scale

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A nanothermodynamic model was established to describe the Debye temperature of monometallic and bimetallic nanocrystals in the deep nanometer scale with respect to the effects of size, dimensionality, and also composition. The results indicate that the Debye temperature decreases with decreasing crystal size for both monometallic and bimetallic nanocrystals,

which is consistent with the experimental data. With considering the physicochemical properties of monometallic and bimetallic nanocrystals in the sub-5 nm scale, the developed model may provide new insight into the fundamental understanding of their thermal stability for applications in heterogeneous catalysis, sensors as well as microelectronic devices.

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1 Introduction In the past decade, ultra small monometallic and bimetallic nanomaterials, which contain a few to several thousand atoms, are the core components of optoelectronic, magnetic, heterogeneous catalysis, nanosensors, as well as microelectronic devices [1–3]. They possess unique electronic, magnetic, optic, catalytic, biomedical, and thermodynamic properties [4, 5]. In general, these physicochemical properties are intrinsically dominated by size, shape, dimensionality, crystallinity, structure, and composition. By tuning one or more of these parameters, one could approach the goal of designing materials with the desired properties. As a result, understanding the nature of these parameters effects on the physicochemical properties in the metallic nanocrystals has become one of the most important topics in the nanomaterials research community.

With the rapid development of metallic nanomaterials, some fundamental and challenging issues need to be addressed, such as the thermal stability. It is known that Debye temperature Θ_D is an essential physical parameter to characterize many materials properties. This is because it is directly related to thermal vibration of atoms and atomic bonding [6]. To date, a number of experimental [7–12] and theoretical [13–15] efforts have been made to investigate the

Θ_D of metallic nanocrystals. It is found that (1) Θ_D of isolated monometallic or bimetallic nanocrystals progressively reduces with the decreasing of crystals size; and (2) dimensionality of the materials also plays an important role in the Θ_D of nanocrystals. However, currently, there is a lack of a systematic investigation in the size, dimensionality, and composition-dependent Θ_D of metallic nanocrystals, especially in deep nanometer scale. The mechanism behind the Θ_D -variation in these nanocrystals is still unclear. Moreover, little attention has been directed to the Θ_D of bimetallic nanocrystals although they offer a natural avenue for further modifying the physicochemical properties of nanocrystals by changing their constituent stoichiometries. These have impeded the rapid development of nanocrystal- or nanocluster-assembled materials.

An extension of the classic thermodynamic theory to nanometer scale has generated a new interdisciplinary theory – nanothermodynamics, which is an indispensable tool for the investigation of size-dependent physicochemical properties in nanocrystals. In this work, a unified nanothermodynamic model was established to investigate the Θ_D of several monometallic and bimetallic nanocrystals in the deep nanometer scale. The accuracy of the developed model is verified with the available experimental data.

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2 Methodology It has been demonstrated that the size dependence of physicochemical properties is determined by cohesive energy $E_c(r)$, which is a function of the nanoparticles and nanowires radius or half thickness of thin films (r) in low-dimensional materials [6, 16]. Based on Lindemann's criterion [17] for melting, the correlation of $\Theta_D(\infty)$ and $E_c(\infty)$ could be obtained with ∞ denoting the bulk crystal. In the criterion, a crystal melts when the root of mean square amplitude reaches to a certain fraction of the equilibrium atomic distance. This criterion has been verified experimentally and is applicable for both bulk and nanocrystals, providing a base to establish $\Theta_D(r)$ function [18]. Combining with Einstein's explanation for the low-temperature specific heats of crystals, the $\Theta_D(\infty)$ is given as $\Theta_D(\infty) = c[T_m(\infty)/(MV_m^{2/3})]^{1/2}$, where c is a constant, $T_m(\infty)$ denotes bulk melting temperature, M the molar atomic or molecular weight, and V_m is the molar volume of crystals [19]. As a result, $\Theta_D^2(\infty) \propto T_m(\infty)$. It is noted that there are two other different opinions regarding to the relationship between $\Theta_D(\infty)$ and $T_m(\infty)$. One was proposed as $\Theta_D(\infty) \propto T_m(\infty)$ [20] and another was $\Theta_D^2(\infty) \propto T_m(\infty) - T$ based on the bond-order-length-strength correlation mechanism [21–23], where T is the temperature of measurements. Further theoretical efforts will be directed toward this issue. Moreover, on the basis of Lindemann's criterion, $T_m(\infty) \propto E_c(\infty)$ can be obtained [6, 18]. Thus, $\Theta_D^2(\infty) \propto T_m(\infty) \propto E_c(\infty)$. It is assumed that this relationship is also applicable in the deep nanometer scale as a first order approximation and thus we have $\Theta_D^2(x, r, d)/\Theta_D^2(\infty) = T_m(x, r, d)/T_m(\infty) = E_c(x, r, d)/E_c(\infty)$, where $0 \leq x \leq 1$ shows the composition of alloys and d denotes the dimensionality. In general, the dimensionality of materials can be defined as the dimensions of which the characteristic length is not at nanometer scale (typically less than 100 nm). In this case, $d = 0$ for isolated nanoparticles or nanoclusters, $d = 1$ for nanowires, $d = 2$ for thin films, and $d = 3$ for bulk materials. Note that the Θ_D is also a temperature-dependent parameter [21]. In this work, the size dependence of Θ_D in metallic nanocrystals was investigated at room temperature. As a result, the temperature dependence of Θ_D will not be considered.

Combining the $E_c(x, r, d)$ function reported in literature [24] and the above consideration of $\Theta_D^2(x, r, d)/\Theta_D^2(\infty) = E_c(x, r, d)/E_c(\infty)$, the $\Theta_D^2(x, r, d)/\Theta_D^2(\infty)$ function can be written as

$$\frac{\Theta_D^2(x, r, d)}{\Theta_D^2(x, \infty)} = \left\{ 1 - \frac{1}{12r/[(3-d)h(x)] - 1} \right\} \times \exp \left\{ -\frac{2S_b(x)}{3R} \frac{1}{12r/[(3-d)h(x)] - 1} \right\}, \quad (1)$$

where $S_b(x)$ is the composition-dependent bulk evaporation entropy of crystals, R denotes the ideal gas constant, and $h(x)$ is the composition-dependent atomic or molecular diameter. As a first-order approximation, the Fox equa-

tion can be used to determine the $h(x)$ and $S_b(x)$ as following [25]:

$$\frac{1}{h(x)} = \frac{1-x}{h(0)} + \frac{x}{h(1)}, \quad (2)$$

$$\frac{1}{S_b(x)} = \frac{1-x}{S_b(0)} + \frac{x}{S_b(1)}, \quad (3)$$

where $S_b(0)$, $S_b(1)$, $h(0)$, and $h(1)$ denotes the corresponding values with $x = 0$ or $x = 1$.

3 Results and discussion Figures 1 and 2 plot: (i) the calculation results from Eq. (1); (ii) the experimental data of $\Theta_D(r, d)$ for monometallic Au nanoparticles and thin films, Co nanoparticles, as well as Ni and Cu thin films; and (iii) the

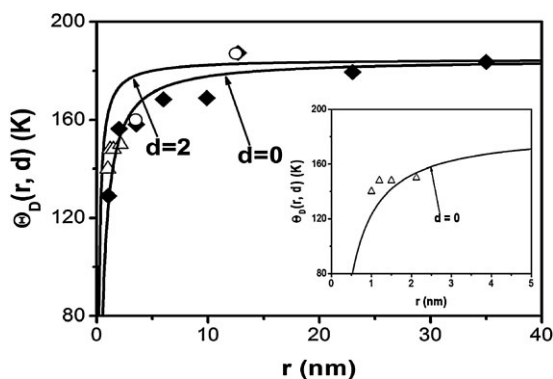


Figure 1 $\Theta_D(r, d)$ of Au nanoparticles ($d = 0$) and thin films ($d = 2$). The solid lines denote the model predictions from Eq. (1). The symbol Δ [7] denotes the experimental data of Au nanoparticles. In order to be shown clearly, the $\Theta_D(r, d)$ of Au nanoparticles is also plotted in the inset. The symbols $\circ$ [11] and $\blacklozenge$ [12] are experimental data of Au thin films.

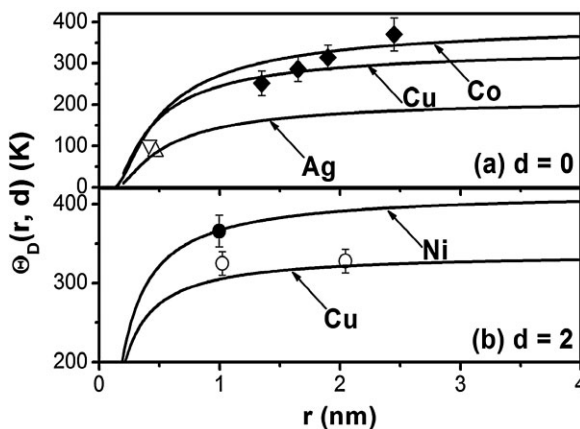


Figure 2 $\Theta_D(r, d)$ of (a) Co nanoparticles, Cu and Ag nanoclusters ($d = 0$); and (b) Ni and Cu thin films ($d = 2$). The solid lines denote the model predictions from Eq. (1). The symbols $\bullet$ [9], $\circ$ [9], and $\blacklozenge$ [10] are experimental data of Ni thin films, Cu thin films, and Co nanoparticles, respectively. The symbols ∇ and Δ denote computer simulation results of Cu and Ag nanoclusters, respectively [14].

Table 1 Parameters used in the model predictions. h , E_b , and T_b values of monometals are cited from Ref. [26] whereas h values of $Zr_{90}Al_{10}$ and $Zr_{84}Al_{16}$ are determined by Eq. (2). S_b values of monometals are calculated by $S_b = E_b/T_b$ whereas S_b values of $Zr_{90}Al_{10}$ and $Zr_{84}Al_{16}$ are determined by Eq. (3).

	$\Theta_D(\infty)$ (K)	h (nm)	E_b (kJ mol ⁻¹)	T_b (K)	S_b (J mol ⁻¹ K ⁻¹)
Au	184.59 [12]	0.2884	368	3129	117.61
Ni	416.00 [9]	0.2492	431	3186	135.28
Cu	338.00 [9]	0.2556	338	3200	105.63
Co	400.00 [10]	0.2507	426	3200	133.13
Ag	216.00 [27]	0.2889	285	2435	117.04
Zr		0.3232	605	4682	129.22
Al		0.2863	326	2792	116.76
$Zr_{90}Al_{10}$	290.32 [8]	0.3191			127.86
$Zr_{84}Al_{16}$	286.70 [8]	0.3167			127.05

computer simulation results of $\Theta_D(r, d)$ for Cu_{34} and Ag_{34} nanoclusters by using model interaction potentials as derived from the embedded atom method and invoking the harmonic approximation of lattice dynamics. The related parameters used in the modeling are listed in Table 1. Note that the radii of the Cu_{34} and Ag_{34} nanoclusters are determined by the correlation of $r = hn^{1/3}/2$, where n is the number of atoms in the materials [16]. As shown in the figures, it is discernible that the $\Theta_D(r, d)$ function decreases with decreasing r due to increased surface/volume ratio and such size effect is pronounced when $r < 5$ nm. With the reduction in crystal size, the surface/volume ratio increases, resulting in higher energetic state of surface atoms, thus causing the instability of nanocrystals. As a result, the atomic vibrational amplitude increases with r decreasing, effectively depressing the Debye temperature. From the figures, it is also found that our calculated results are consistent with the experimental data and the computer simulation results even when $r < 2$ nm, thereby verifying the accuracy of the developed model.

Moreover, for the same r , the sequence, from strong to weak, of size effects on the $\Theta_D(r, d)$ determined by Eq. (1) is nanoparticles, nanowires, and then thin films due to their different surface/volume ratios, of $3/r$, $2/r$, and $1/r$, respectively. This can be clearly found from the $\Theta_D(r, d)$ of Au (Fig. 1) and Cu (Fig. 2) nanocrystals with different dimensionalities. Therefore, the developed model can also be used to determine the dimensionality dependence of $\Theta_D(r, d)$ in metallic nanocrystals. From Fig. 2a, we can see that the $\Theta_D(r, d)$ of Cu_{34} (denoted as ∇ [14]) and Ag_{34} (denoted as Δ [14]) nanoclusters with coordination 12 are about one-third of those of the bulk form due to strong size effect, which are in good agreement with our calculation results. On the other hand, the simulated $\Theta_D(r, d)$ of Cu_{34} and Ag_{34} nanoclusters with coordination 9, 8, and 6 are much smaller than our model predictions [14]. This is because the coordination imperfection may shorten the bonds of under-coordinated atoms and depress the cohesive energy [15].

Figure 3 shows the calculation results from Eqs. (1)–(3) and the experimental data of $\Theta_D(x, r, d)$ in bimetallic

$Zr_{90}Al_{10}$ and $Zr_{84}Al_{16}$ nanoparticles. The related parameters used in the modeling are also listed in Table 1. It is found that the $\Theta_D(x, r, d)$ of bimetallic nanoparticles decreases with decreasing r , which is in good agreement with our model predictions. It verifies the accuracy of the developed model and demonstrates the applicability of the Fox equation in bimetallic nanocrystals. Moreover, there is no adjustable parameter in Eqs. (2) and (3), substantially simplifying the calculation of $h(x)$ and $S_b(x)$. From Fig. 3, it can be seen that the size effects on $\Theta_D(x, r, d)$ of $Zr_{90}Al_{10}$ and $Zr_{84}Al_{16}$ nanoparticles are different. This is ascribed to the strong composition effect in bimetallic nanocrystals, in particular for the mixture of alloy components with distinct lattice constants. It should be noted that the interaction energy between the composed elements can also affect the $\Theta_D(x, r, d)$ values of bimetallic nanocrystals, which was not considered in our modeling. This would have a limited influence on the determination accuracy because the metallic interaction energy is also size-dependent and it decreases with decreasing r in nanocrystals [28].

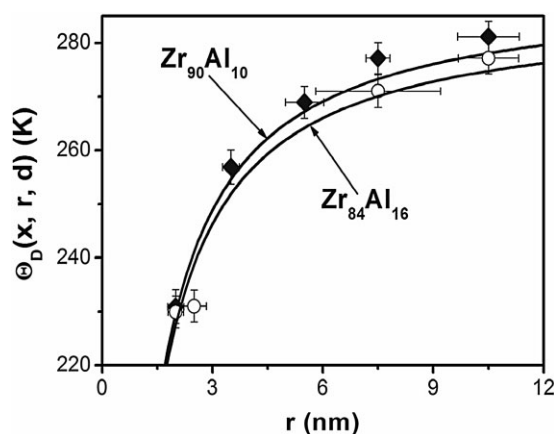


Figure 3 $\Theta_D(x, r, d)$ of bimetallic $Zr_{90}Al_{10}$ and $Zr_{84}Al_{16}$ nanoparticles ($d=0$). The solid lines denote the model predictions from Eqs. (1)–(3). The symbols $\blacklozenge$ and $\circ$ are experimental data of $Zr_{90}Al_{10}$ and $Zr_{84}Al_{16}$, respectively [8].

4 Conclusion A nanothermodynamic model is established to calculate the $\Theta_D(x, r, d)$ of monometallic and bimetallic nanocrystals in the deep nanometer scale based on the cohesive energy model and Fox equation. It is found that (i) $\Theta_D(x, r, d)$ decreases with decreasing r for both monometallic and bimetallic nanocrystals while the size effect on $\Theta_D(x, r, d)$ from strong to weak is nanoparticles, nanowires and thin films; (ii) the Fox equation could be used to determine the thermodynamic parameters of bimetallic nanocrystals; and (iii) our simple model offers a new avenue for investigating the physicochemical properties of alloys. These findings provide new insight into the fundamental understanding of the evolution of physicochemical properties for metallic nanocrystals with the size, dimensionality, as well as composition.

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References

- [1] S. Sun, C. B. Murray, D. Weller, L. Folks, and A. Moser, *Science* **287**, 1989 (2000).
- [2] S. Alayoglu, P. Zavalij, B. Eichhorn, Q. Wang, A. I. Frenkel, and P. Chupas, *ACS Nano* **3**, 3127 (2009).
- [3] S. Y. Jo, B. R. Kang, J. T. Kim, H. W. Ra, and Y. H. Im, *Nanotechnology* **21**, 055604 (2010).
- [4] Y. Sun and Y. Xia, *Science* **298**, 2176 (2002).
- [5] F. Tao, M. E. Grass, Y. Zhang, D. R. Butcher, J. R. Renzas, Z. Liu, J. Y. Chung, B. S. Mun, M. Salmeron, and G. A. Somorjai, *Science* **322**, 932 (2008).
- [6] C. C. Yang and S. Li, *Phys. Rev. B* **75**, 165413 (2007).
- [7] A. Balerna, E. Bernieri, P. Picozzi, A. Reale, S. Santucci, E. Burattini, and S. Mobilio, *Phys. Rev. B* **31**, 5058 (1985).
- [8] U. Herr, M. Geigl, and K. Samwer, *Philos. Mag. A* **77**, 641 (1998).
- [9] M. Kiguchi, T. Yokoyama, D. Matsumura, H. Kondoh, O. Endo, and T. Ohta, *Phys. Rev. B* **61**, 14020 (2000).
- [10] M. Hou, M. E. Azzaoui, H. Pattyn, J. Verheyden, G. Koops, and G. Zhang, *Phys. Rev. B* **62**, 5117 (2000).
- [11] G. Kästle, T. Müller, H.-G. Boyen, A. Klimmer, and P. Ziemann, *J. Appl. Phys.* **96**, 7272 (2004).
- [12] G. Kästle, H.-G. Boyen, A. Schröder, A. Plettl, and P. Ziemann, *Phys. Rev. B* **70**, 165414 (2004).
- [13] C. C. Yang, M. X. Xiao, W. Li, and Q. Jiang, *Solid State Commun.* **139**, 148 (2006) and references therein.
- [14] H. Yildirim, A. Kara, and T. S. Rahman, *J. Phys.: Condens. Matter* **21**, 084220 (2009).
- [15] G. Ouyang, Z. M. Zhu, W. G. Zhu, and C. Q. Sun, *J. Phys. Chem. C* **114**, 1805 (2010).
- [16] C. C. Yang and S. Li, *J. Phys. Chem. C* **113**, 14207 (2009).
- [17] F. A. Lindemann, *Z. Phys.* **11**, 609 (1910).
- [18] Q. Jiang and C. C. Yang, *Curr. Nanosci.* **4**, 179 (2008).
- [19] J. G. Dash, *Rev. Mod. Phys.* **71**, 1737 (1999).
- [20] M. Blackman, *Proc. R. Soc. Lond. Ser. A* **148**, 365 (1935).
- [21] M. X. Gu, C. Q. Sun, Z. Chen, T. C. Au Yeung, S. Li, C. M. Tan, and V. Nosik, *Phys. Rev. B* **75**, 125403 (2007).
- [22] C. Q. Sun, *Prog. Solid State Chem.* **35**, 1 (2007).
- [23] C. Q. Sun, *Prog. Mater. Sci.* **54**, 179 (2009).
- [24] C. C. Yang and S. Li, *J. Phys. Chem. C* **112**, 2851 (2008).
- [25] T. G. Fox, *Bull. Am. Phys. Soc.* **1**, 123 (1956).
- [26] <http://www.webelements.com/>, Web Elements Periodic Table.
- [27] Q. Chen and B. Sundman, *Acta Mater.* **49**, 947 (2001).
- [28] L. H. Liang, D. Liu, and Q. Jiang, *Nanotechnology* **14**, 438 (2003).