

Využití kalorimetrie při studiu nanočástic

Jindřich Leitner
VŠCHT Praha



- 1. Velikost a tvar nanočástic ...**
- 2. Povrchová energie ...**
- 3. Teplota a entalpie tání ...**
- 4. Tepelná kapacita a entropie ...**
- 5. Molární entalpie ...**

NANO ... Mediální bublina, nebo nový impuls vědeckého pokroku ?

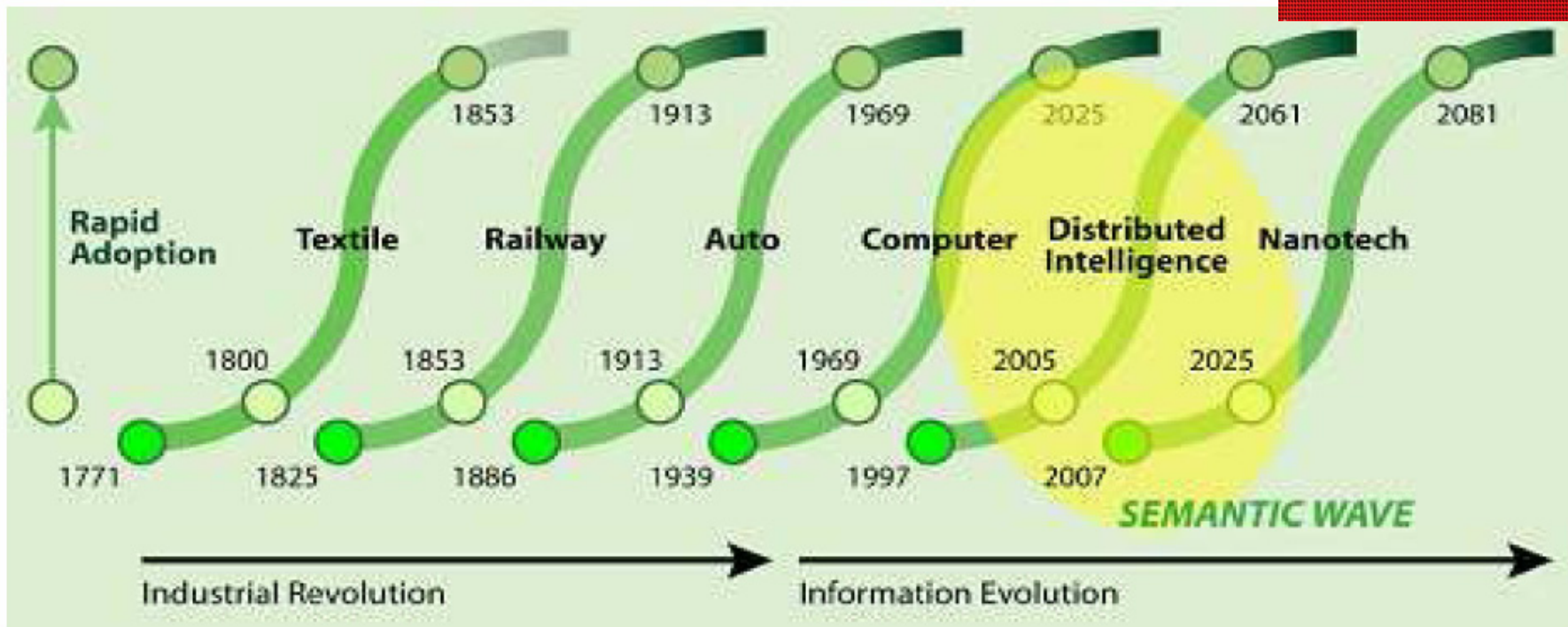
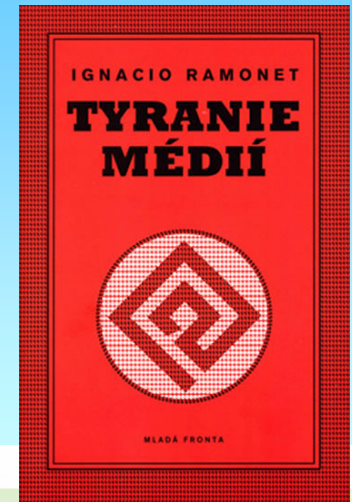
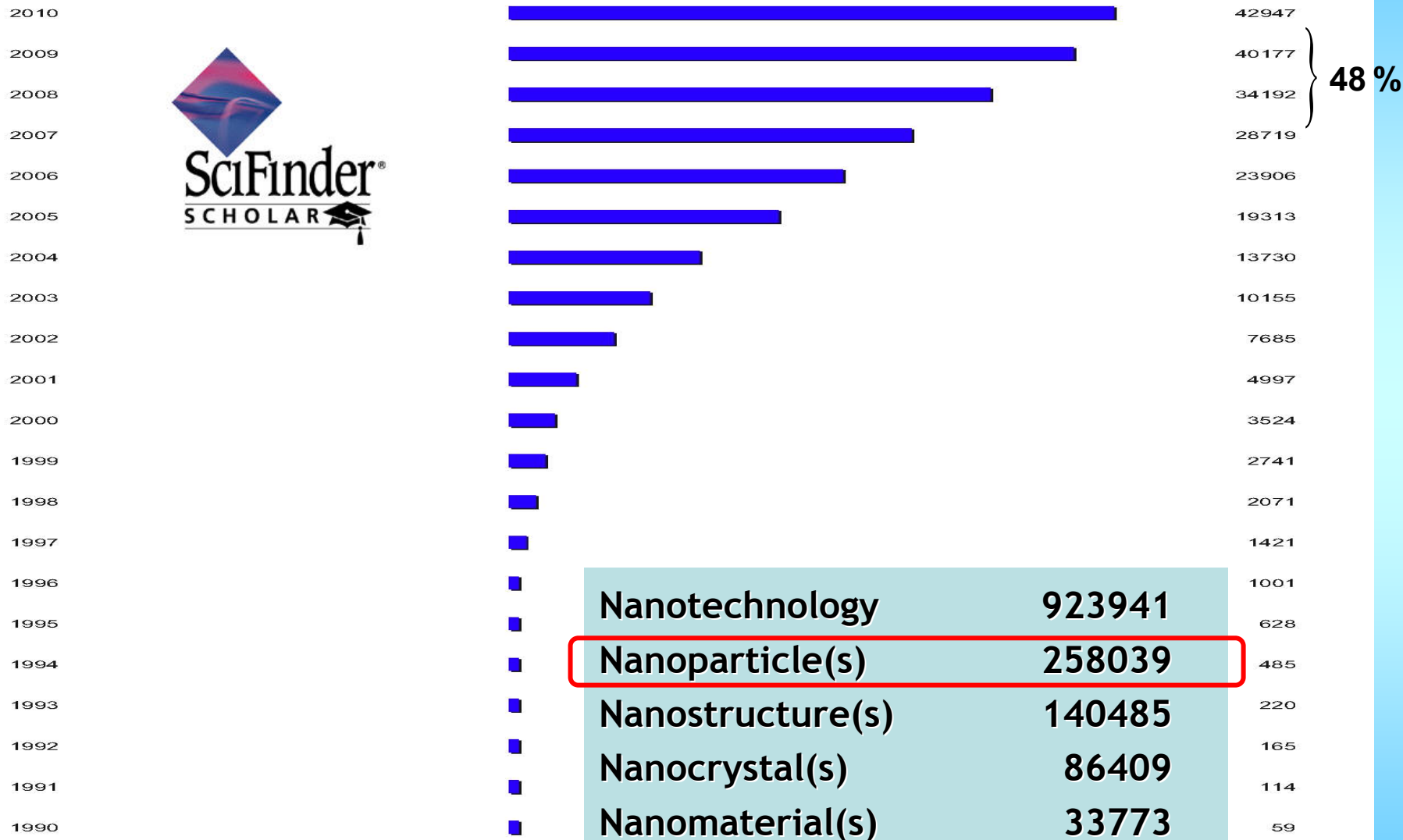


Figure 1. Semantic Wave (Source: Norman Poire, Merrill Lynch, 2006)



12.5.2011

Vliv povrchových atomů na „průměrné“ vlastnosti nanočástic

Journal of
Environmental
Monitoring

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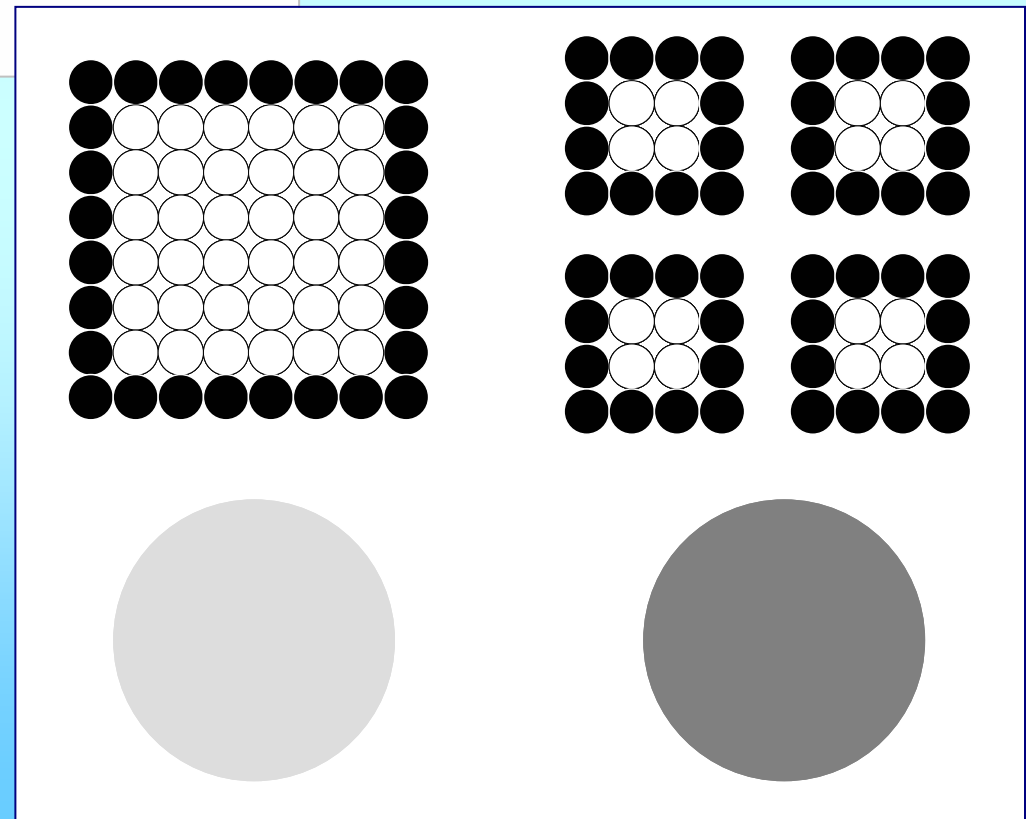
www.rsc.org/jem

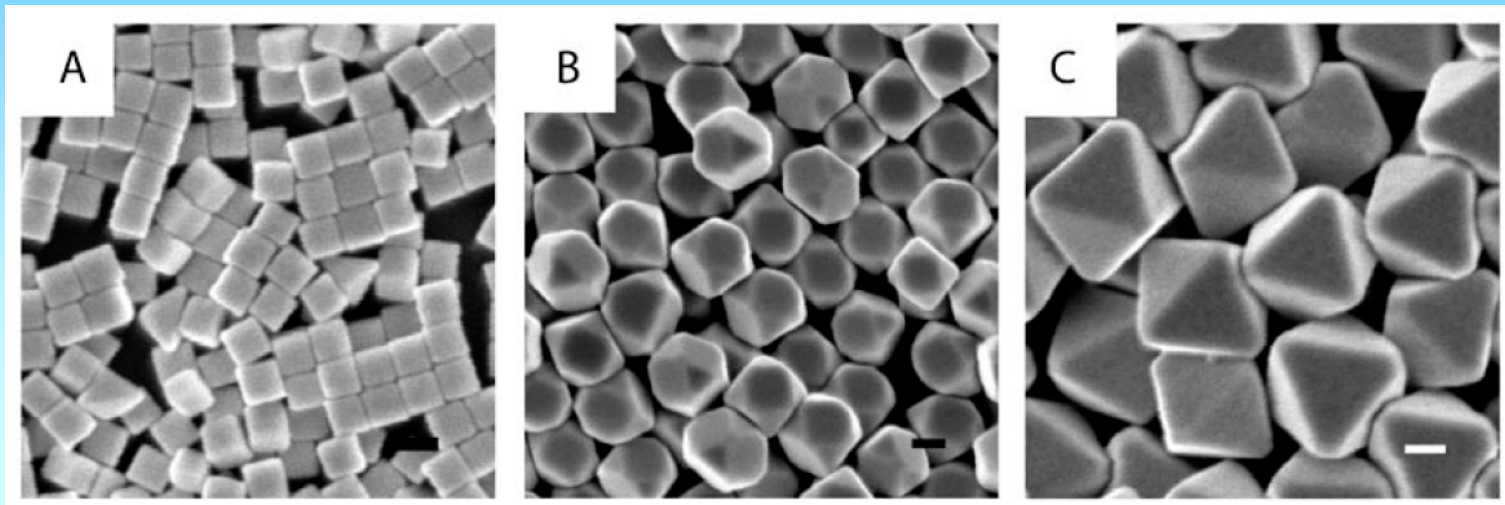
CRITICAL REVIEW

The devil is in the details (or the surface): impact of surface structure and surface energetics on understanding the behavior of nanomaterials in the environment†

Imali A. Mudunkotuwa and Vicki H. Grassian*

$$Z_{np} = \frac{N_{surf}}{N} Z_{surf} + \frac{N - N_{surf}}{N} Z_{bulk}$$





DOI: 10.1002/sml.200701295

Shape Control of Colloidal Metal Nanocrystals

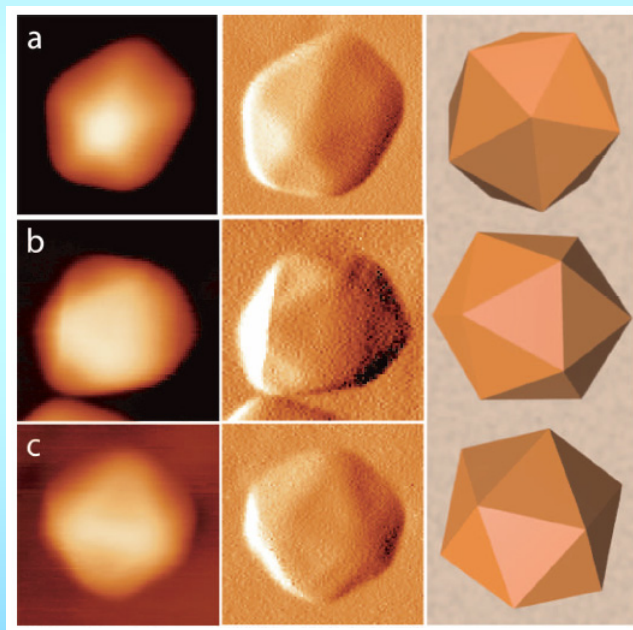
*Andrea R. Tao, Susan Habas, and Peidong Yang**

Volné nanočástice 10^0 - 10^2 nm

- atomová struktura jako *bulk* (vliv zvýšeného tlaku)
- vnější tvar odpovídá min F_{surf} (Wulffova konstrukce)

Volné nanočástice ≈ 1 nm

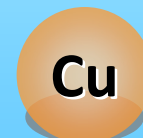
- atomová struktura jako *bulk*
- pseudokrystalická struktura (pětičetná osa symetrie)
- struktura s nízkou mírou uspořádání



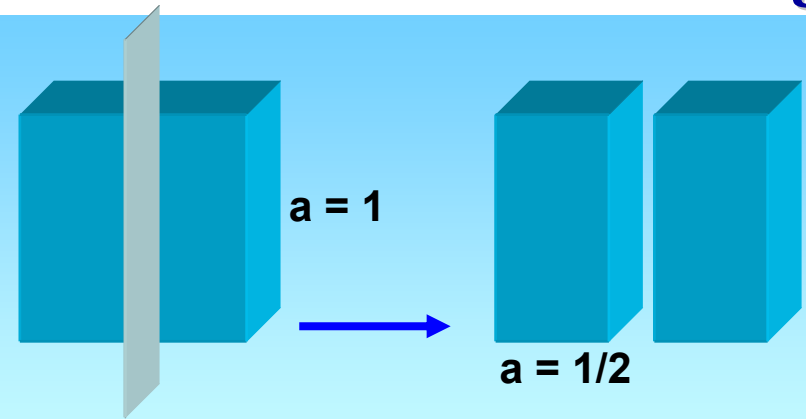
Temperature-Dependent Stability of Supported Five-Fold Twinned Copper Nanocrystals

Fabien Silly, and Martin R. Castell

ACS Nano, 2009, 3 (4), 901-906 • DOI: 10.1021/nn900059v • Publication Date (Web): 26 March 2009



Vytvoření nového povrchu



(γ_{surf}) - Reversibilně vykonaná práce při vzniku jednotkové plochy nového povrchu bez elastické deformace (skalární veličina). Jsou přerušeny vazby mezi atomy, na novém povrchu se objeví nové atomy, jsou zachovány délky vazeb, nemění se atomová hustota povrchu.

$$\delta w_{\text{surf}} = \gamma_{\text{surf}} dA, \quad w_{\text{surf}} = \gamma_{\text{surf}} A$$

$$\gamma_{\text{surf}} = \left(\frac{\partial U}{\partial A} \right)_{S,V,n} = \left(\frac{\partial H}{\partial A} \right)_{S,p,n} = \left(\frac{\partial F}{\partial A} \right)_{T,V,n} = \left(\frac{\partial G}{\partial A} \right)_{T,p,n}$$

Povrchová energie pevných látek:

- se liší od povrchového napětí (*surface stress*)
- je anizotropní (*hkl*)
- lze vypočítat (*ab-initio*, semiempirické metody, empirické metody a korelace)

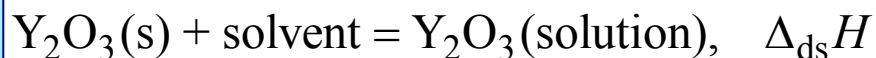
Rozpouštěcí kalorimetrie

Y_2O_3

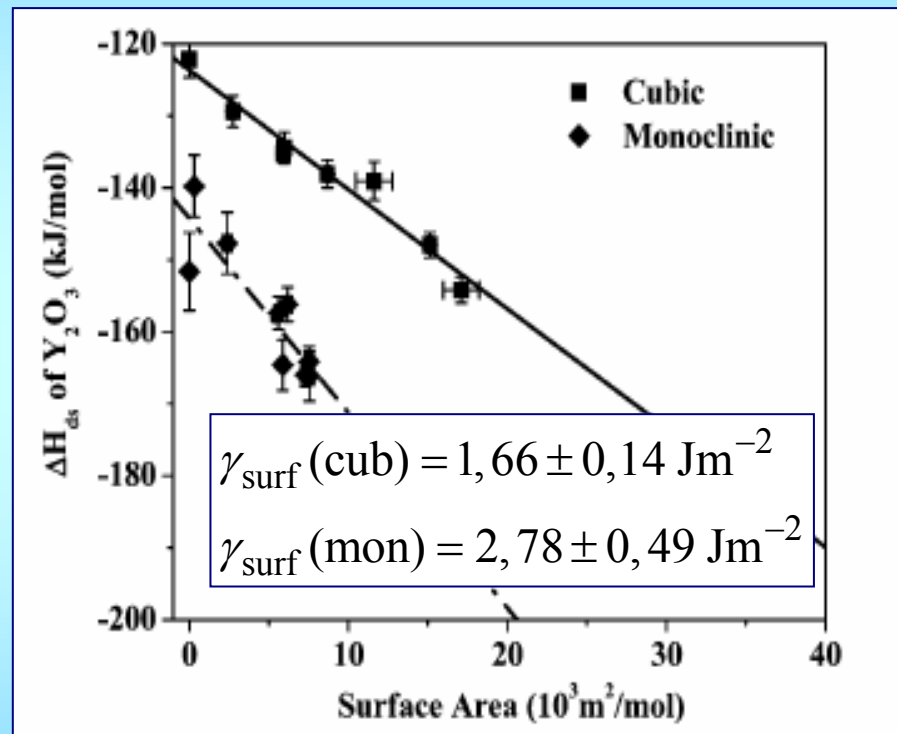
Kubická (p_{atm}) a monoklinická (HP) modifikace

Rozpouštěcí kalorimetrie

- Vzorky (cub) a (mon) o různém měrném povrchu
- Rozpouštědlo $3Na_2O \cdot 4MoO_3$
- Teplota $700\text{ }^\circ\text{C}$



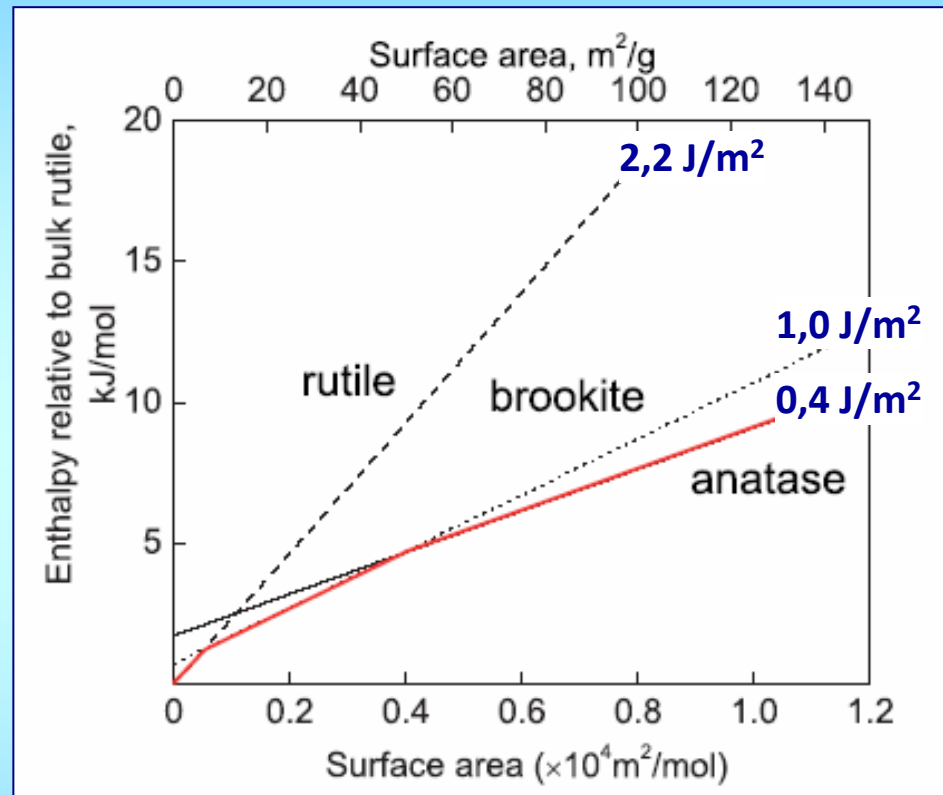
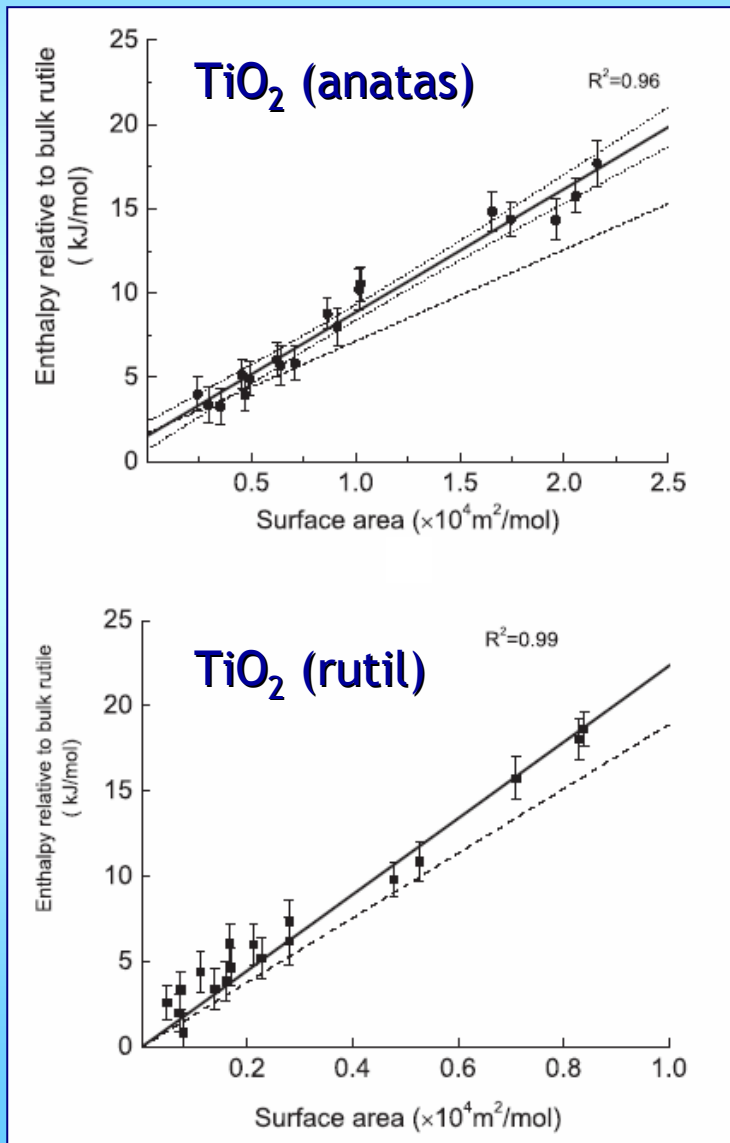
$$h_{\text{surf}} = \frac{\Delta H_{\text{ds},\infty} - \Delta H_{\text{ds},r}}{A_r} \approx \gamma_{\text{surf}}$$



Energetics of Cubic and Monoclinic Yttrium Oxide Polymorphs: Phase Transitions, Surface Enthalpies, and Stability at the Nanoscale

Peng Zhang,[†] Alexandra Navrotsky,^{*†} Bing Guo,[‡] Ian Kennedy,[§] Alisha N. Clark,^{||} Charles Lesher,^{||} and Qingyuan Liu[†]

Rozpuštěcí kalorimetrie



International Journal of Quantum Chemistry, Vol 109, 2647–2657 (2009)
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Energetics of Oxide Nanoparticles

ALEXANDRA NAVROTSKY

Peter A Rock Thermochemistry Laboratory and NEAT ORU, University of California at Davis, One Shields Avenue, Davis, CA 95616

Pawlow, 1909

$$\frac{T_r^F}{T_\infty^F} = 1 - \frac{2V_{m(s)}}{\Delta_{\text{fus}}H_\infty r_{(s)}} \left[\gamma_{(s)} - \gamma_{(l)} \left(\frac{V_{m(l)}}{V_{m(s)}} \right)^{2/3} \right]$$

Guisbiers, 2009

$$\frac{T_R^F}{T_\infty^F} = 1 - \frac{3V_m}{\Delta_{\text{fus}}H_\infty r} (\gamma_{(s)} - \gamma_{(l)})$$

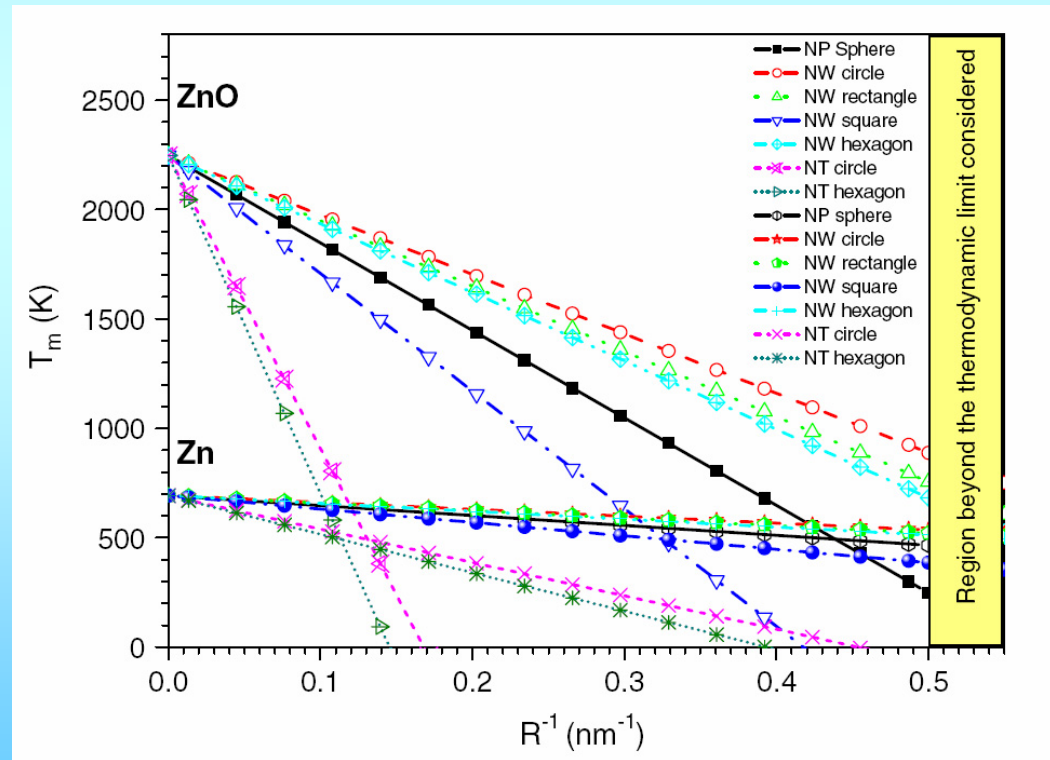
IOP PUBLISHING
Nanotechnology 18 (2007) 435710 (6pp)
doi:10.1088/0957-4484/18/43/435710

Theoretical investigation of size and shape effects on the melting temperature of ZnO nanostructures

G Guisbiers and S Pereira¹

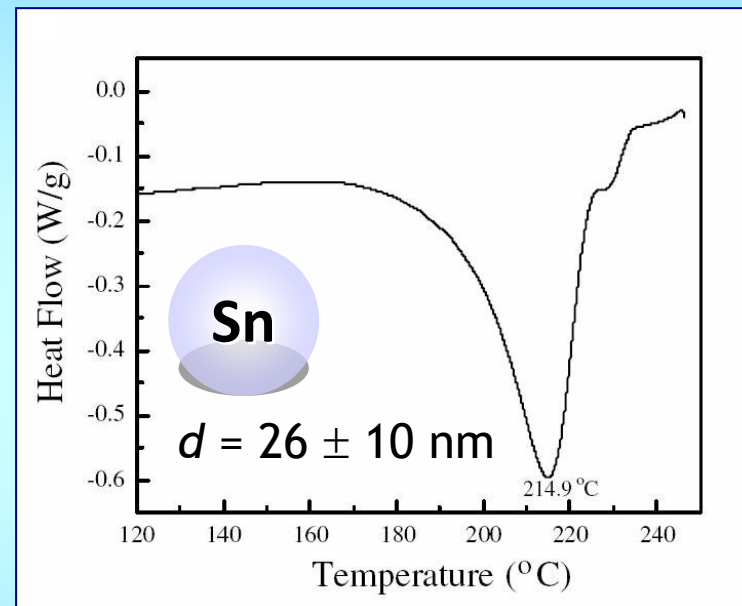
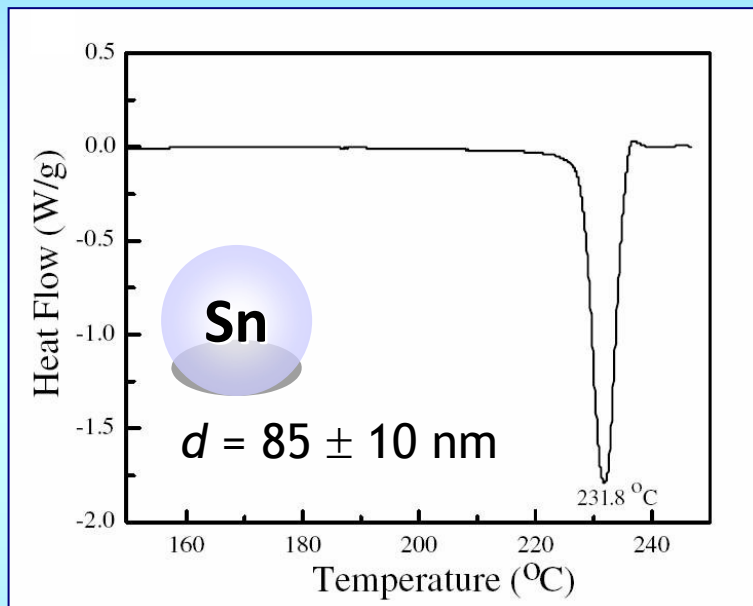


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DSC

TA 2970, ≈ 10 mg, 5 °C/min N_2 (gas)



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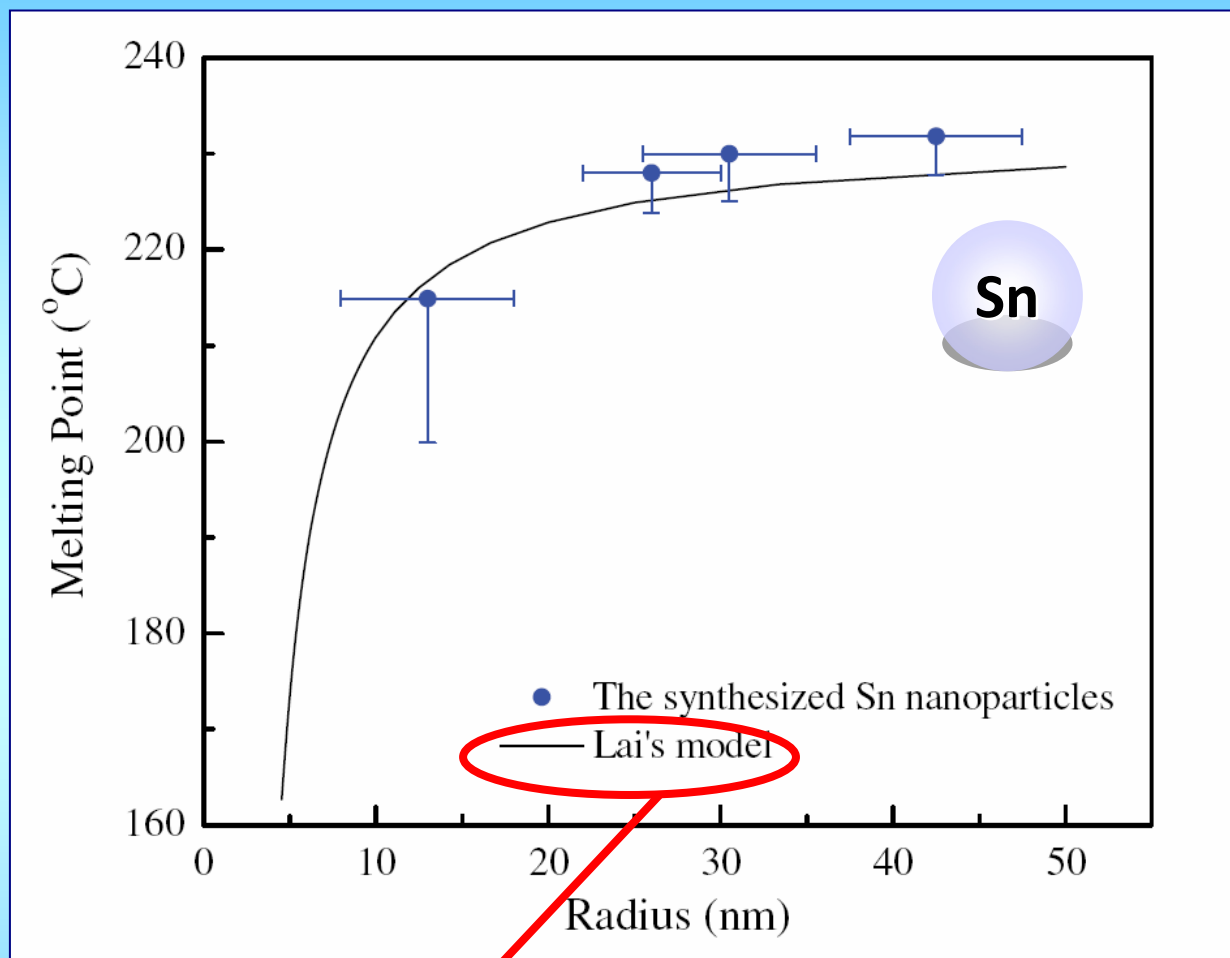
Chemical Physics Letters 429 (2006) 492–496

CHEMICAL
PHYSICS
LETTERS

www.elsevier.com/locate/cplett

Size-dependent melting properties of tin nanoparticles

Hongjin Jiang ^a, Kyoung-sik Moon ^a, Hai Dong ^a, Fay Hua ^b, C.P. Wong ^{a,*}



$$\frac{T_{\text{fus},r}}{T_{\text{fus},\infty}} = 1 - 3,37 \left[\frac{\gamma_{(sl)}}{15,8(r - \delta)} - \frac{1}{r} \right], \quad \delta = 1,8 \text{ nm}$$



Available online at www.sciencedirect.com



Chemical Physics Letters 429 (2006) 492–496

CHEMICAL
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www.elsevier.com/locate/cpl

Size-dependent melting properties of tin nanoparticles

Hongjin Jiang ^a, Kyoung-sik Moon ^a, Hai Dong ^a, Fay Hua ^b, C.P. Wong ^{a,*}

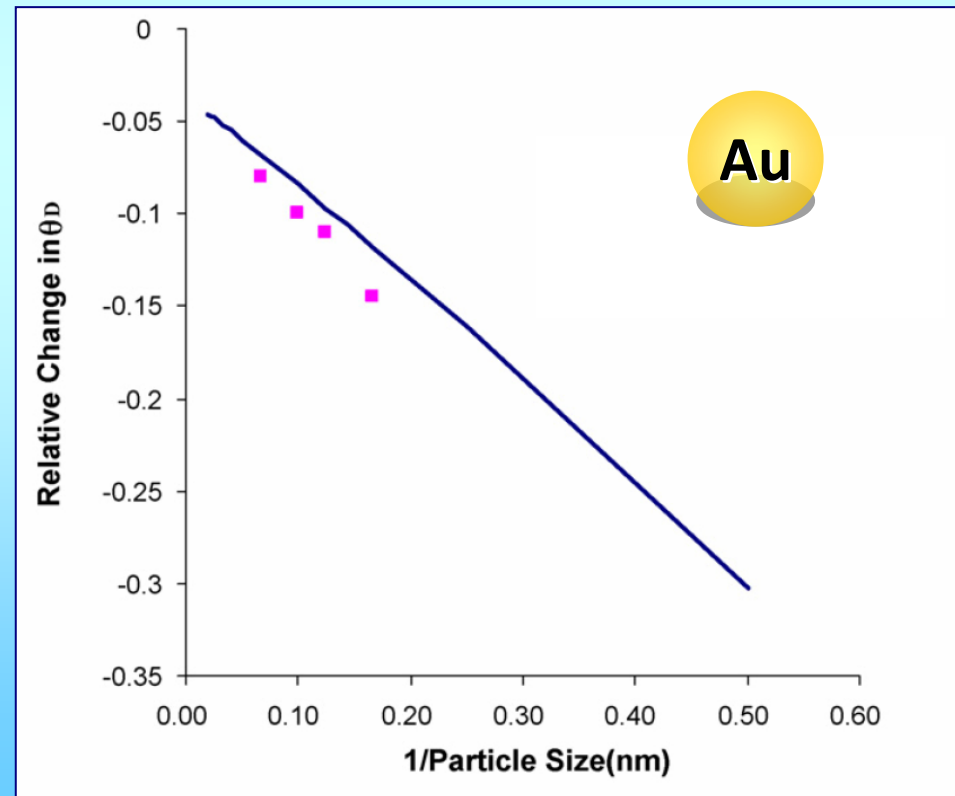
Tepelná kapacita

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V, \quad C_p = \left(\frac{\partial H}{\partial T} \right)_p$$

$$C_p = C_{\text{vib}} + C_{\text{dil}} + C_{\text{el}} + \dots$$

$$C_{\text{vib}}^D = 9NR \left(\frac{T}{\Theta_D} \right)^3 \int_0^{x_D} \frac{x^4 \exp(x)}{[\exp(x) - 1]^2} dx, \quad x_D = \Theta_D/T$$

$$\frac{\Theta_{D,r}}{\Theta_{D,\infty}} = \left(\frac{T_r^F}{T_\infty^F} \right)^{1/2}$$



Materials Chemistry and Physics 115 (2009) 703–706

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys



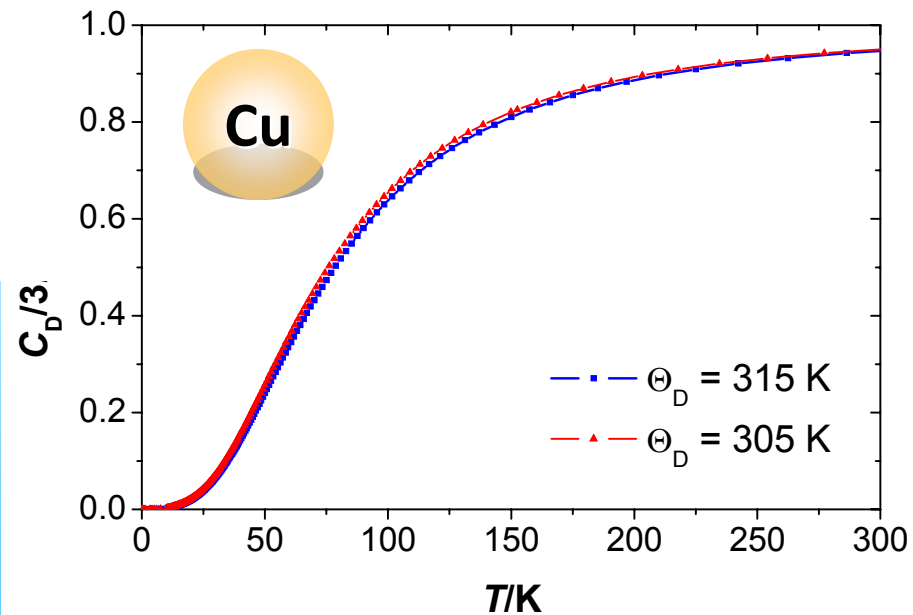
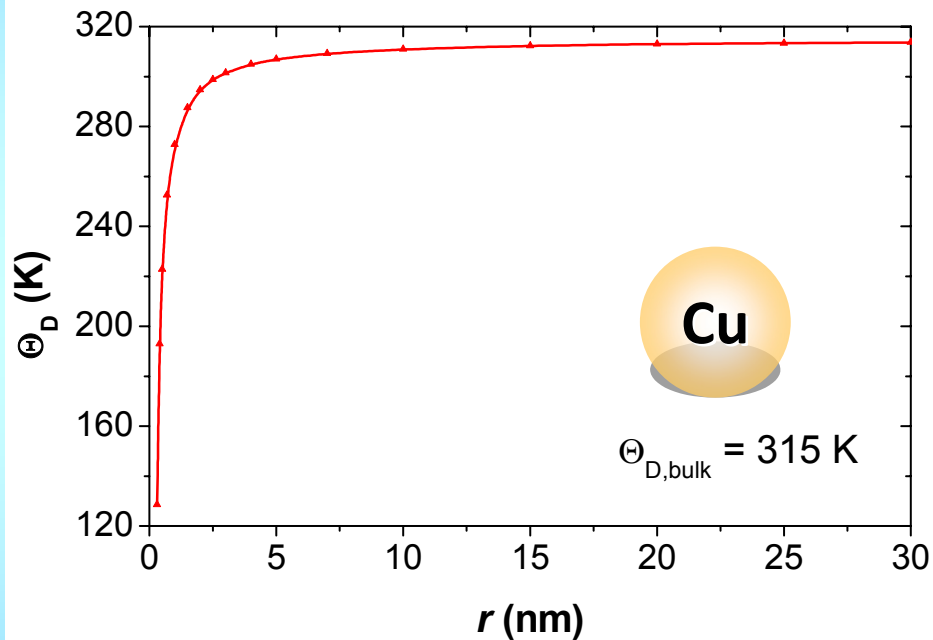
Size dependent Debye temperature and mean square displacements of nanocrystalline Au, Ag and Al

K. Sadaiyandi

Department of Physics, Dr.Sivashil Adinaray College of Engineering, Tiruchendur 628 215, India

Tepelná kapacita – oblast nízkých teplot ($T < 300$ K)

$$C_p \doteq C_{\text{vib}} (+ C_{\text{el}} + \dots)$$



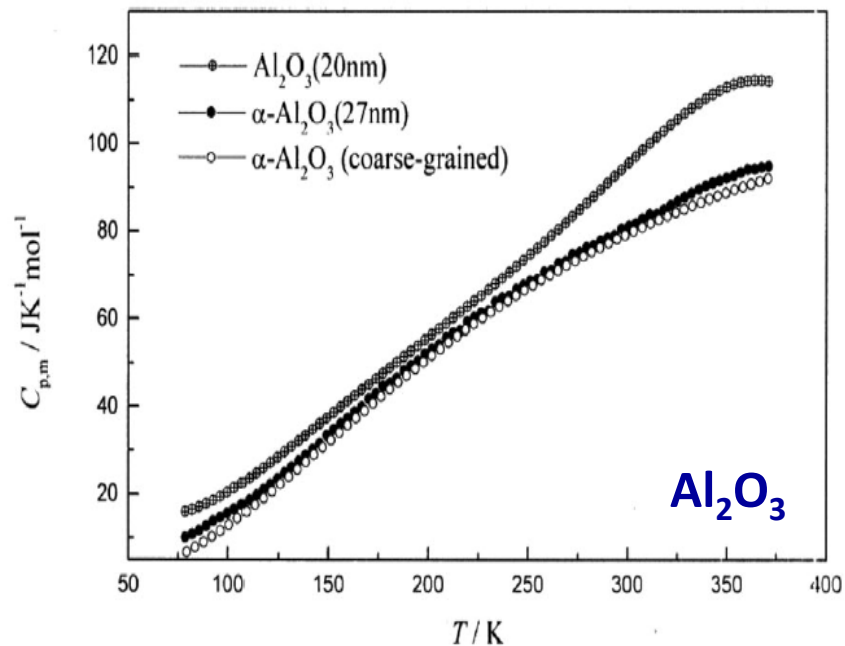
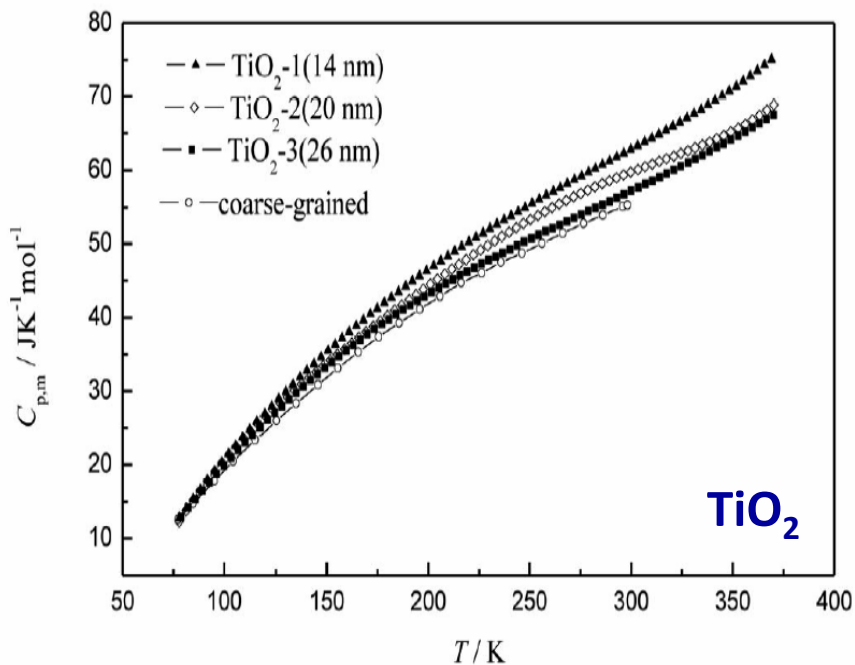
Tepelná kapacita

Materiál (velikost)	Metoda (obor teplot)	Ref.
Cu (8 nm)	DSC (150-300 K)	Rupp, PRB 1987
Pd (6 nm)	DSC (150-300 K)	Rupp, PRB 1987
Se (10 nm)	DSC (225-500 K)	Sun, PRB 1996
Ni (40 nm)	AC (78-370 K)	Wang, TCA 2002
CoO (7 nm)	RT (0,6-40 K), AC (10-320 K)	Wang, CM 2004
α -Fe ₂ O ₃ (15 nm)	RT (1,5-38 K), AC (30-350 K)	Snow, JCT 2010
Fe ₃ O ₄ (13 nm)	RT (0,5-38 K), AC (50-350 K)	Snow, JPC 2010
SiO ₂ (20 nm)	AC (9-354 K)	Wang, JNCS 2001
Al ₂ O ₃ (20 nm)	AC (78-370 K)	Wang, JNR 2001
TiO ₂ (14-26 nm)	AC (78-370)	Wu, JSSC 2001
ZnFe ₂ O ₄ (8-39 nm)	RT (1-40 K)	Ho, PRB 1995
ZnO (30 nm)	AC (83-350 K)	Yue, WHX 2005

DSC ... diferenční skenovací kalorimetrie, RT ... tepelně-pulzní kalorimetrie (měření relaxačního času), AC ... adiabatická kalorimetrie

AC

...



Pure Appl. Chem., Vol. 81, No. 10, pp. 1871–1880, 2009.

doi:10.1351/PAC-CON-08-09-15

© 2009 IUPAC, Publication date (Web): 25 September 2009

Study of heat capacity enhancement in some nanostructured materials*

Zhi-Cheng Tan[‡], Lan Wang, and Quan Shi

$$H_m = U_m + pV_m$$

$$dH_m = \left(\frac{\partial H_m}{\partial T} \right)_p dT = C_{pm} dT$$

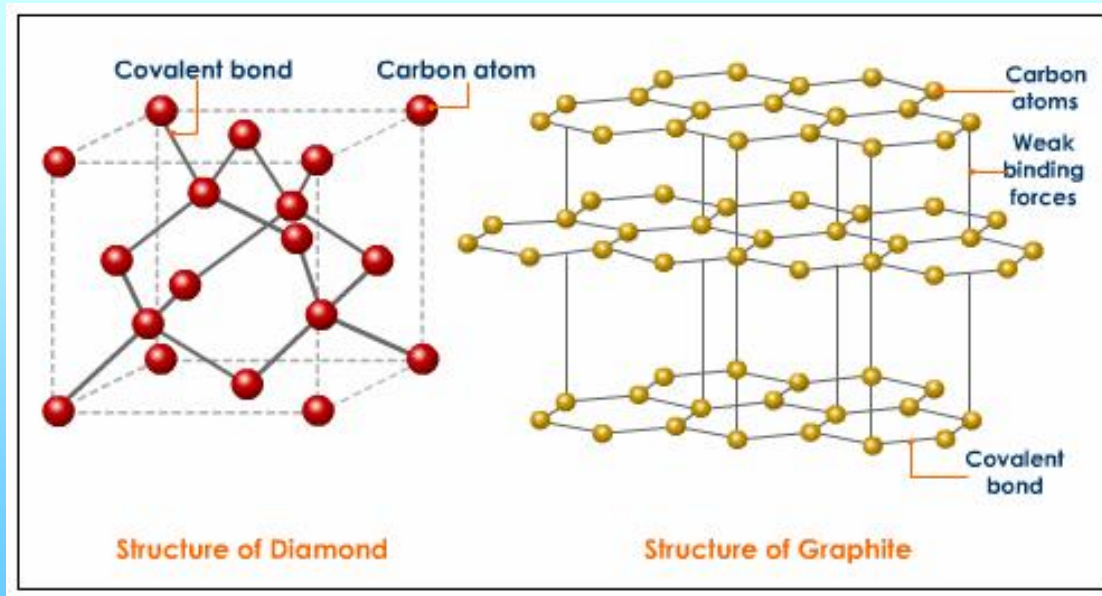
$$H_m(T) = H_m(T_{\text{ref}}) + \int_{T_{\text{ref}}}^T C_{pm} dT$$

$H_m(298, 15 \text{ K}) = 0$ ($p^\circ = 100 \text{ kPa}$)
pro prvky v termodynamicky stabilním stavu
(skupenství resp. strukturní modifikaci)

$H_m(298, 15 \text{ K}) = \Delta_{\text{tr}}H$ ($p^\circ = 100 \text{ kPa}$)
pro prvky v jiném stavu

$H_m(298, 15 \text{ K}) = \Delta_f H$ ($p^\circ = 100 \text{ kPa}$)
pro sloučeniny

Strukturní modifikace uhlíku

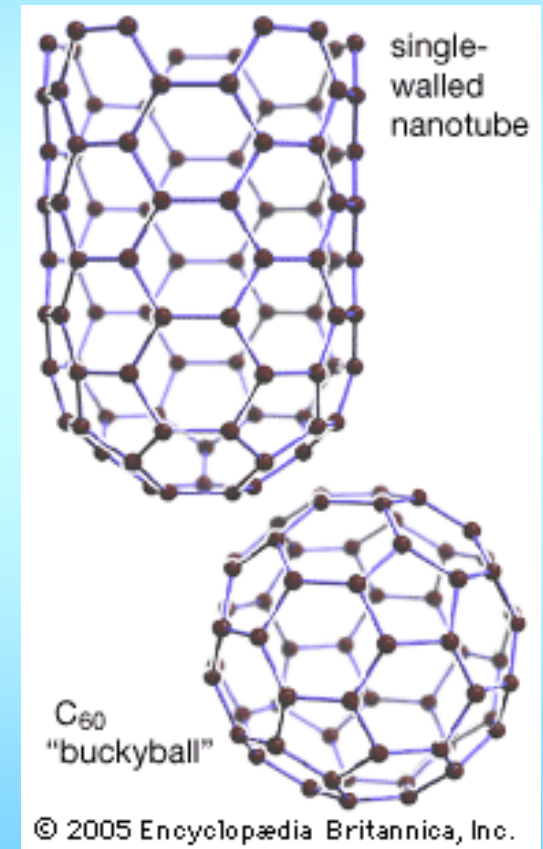


Strukturní modifikace uhlíku

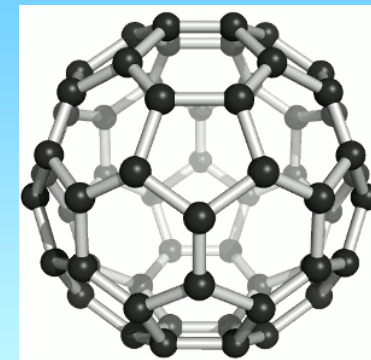
Fullereny

Duté struktury tvořené atomy uhlíku vázanými v pěti- resp. šestiatomových cyklech

- Sférické (buckyball) - konvexní polyedry se stěnami ve tvaru pravidelných pěti- resp. šestiúhelníků: Buckminsterfulleren C_{60} (Buckminster Fuller), komolý ikosaedr, jehož povrch je tvořen 20 šesti- a 12 pětiúhelníky, vyšší fullereny C_{70} , ..., C_{xxx} .
- Cylindrické (buckytube), též uhlíkové nanotrubky (*single-walled, multi-walled*)
- Fullerity (krystalová forma fullerenu)
- Fulleridy (fullereny dotované atomy jiných prvků)



Spalovací kalorimetrie



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Thermochimica Acta 437 (2005) 126–133

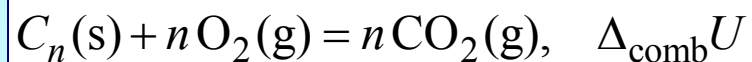
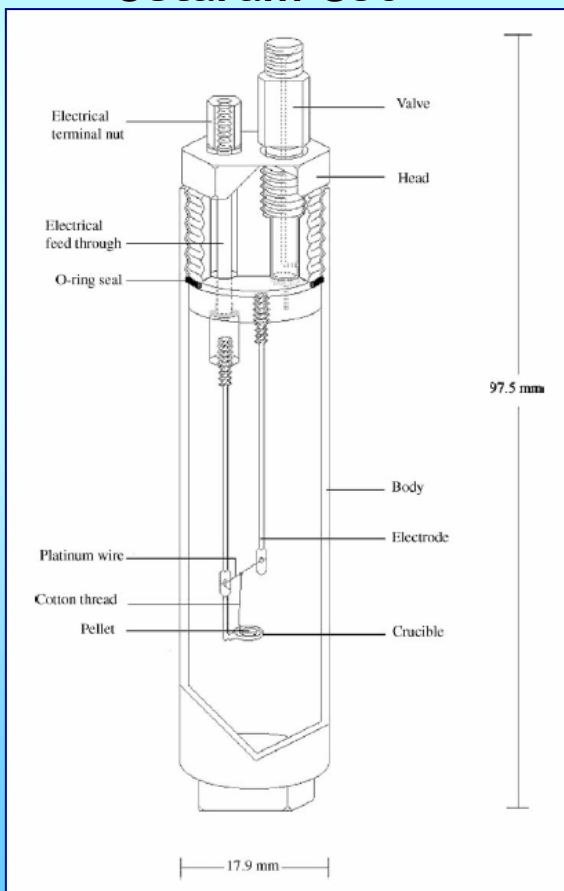
thermochimica
acta

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Enthalpies of combustion and formation of fullerenes by micro-combustion calorimetry in a Calvet calorimeter

Aarón Rojas-Aguilar*, Melchor Martínez-Herrera

Setaram C80 +



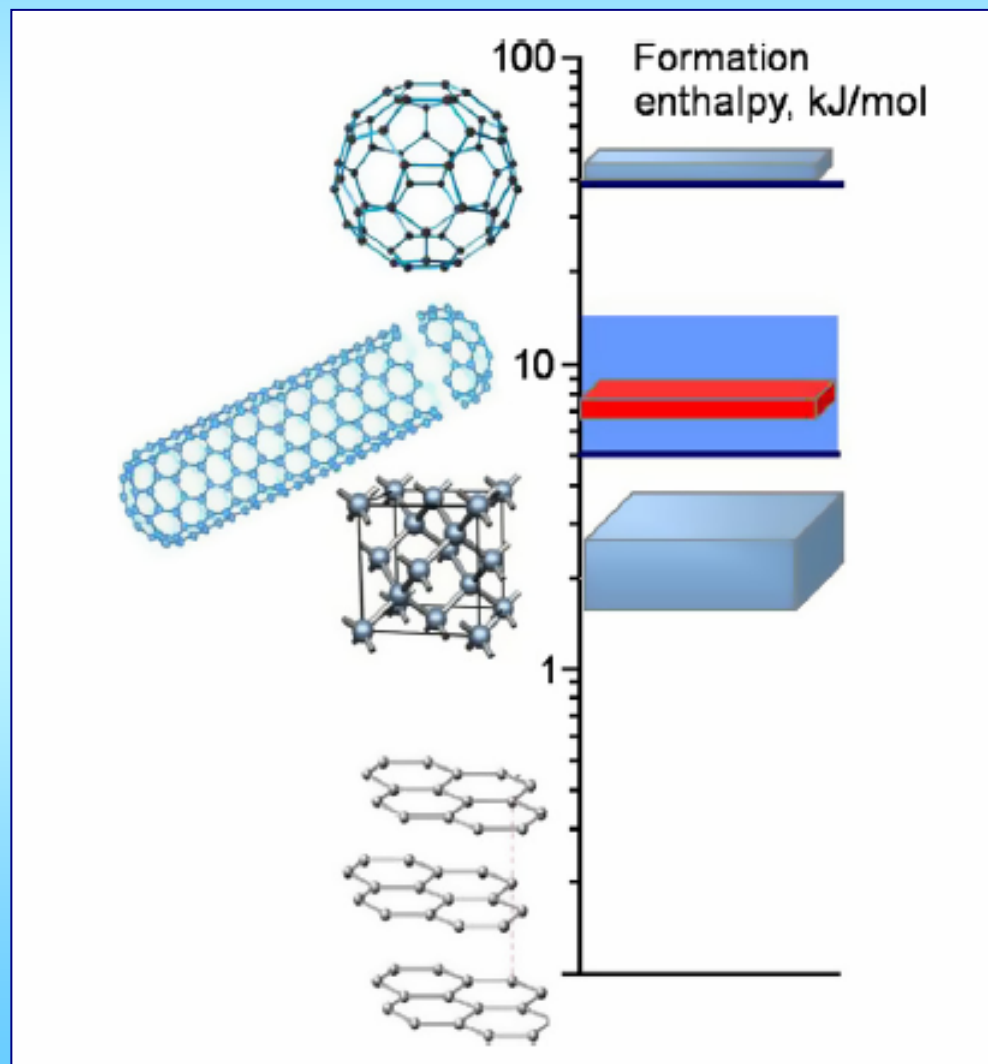
$$\begin{aligned} \Delta_{\text{comb}}H &= \Delta_{\text{comb}}U + p \Delta V \\ &= \Delta_{\text{comb}}U + \Delta n_g RT \end{aligned}$$

$$H_m(C_n, s) = n H_m(CO_2, g) - n H_m(O_2, g) - \Delta_{\text{comb}}H$$

Fáze	$H_m(298.15 \text{ K})$ (kJ mol ⁻¹)
Grafit	0
C60	2285,4
C70	2547,9

Stabilita forem uhlíku

Fáze	$H_m(298.15\text{ K})$ (kJ at ⁻¹)
Grafit	0
Diamant	2,5
C60	38,1
C70	36,4



CARBON 49 (2011) 949-954



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journal homepage: www.elsevier.com/locate/carbon



**Energetics of single-wall carbon nanotubes as revealed
by calorimetry and neutron scattering**

Andrey A. Levchenko^a, Alexander I. Kolesnikov^b, Olga Trofymuk^c,
Alexandra Navrotsky^{b,*}

1. Kalorimetrie je velice účinný a užitečný nástroj při studiu nanočástic.

2. Vztahy pro nanočástice platí „přiměřeně“ i pro jiné nanostrukturované materiály (vlákna, vrstvy, kompozity).

3. Další informace:

<http://www.vscht.cz/ipi/nanomaterialy/uvod.htm>



Na velikosti záleží !!!



Děkuji Vám za pozornost