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Thermodynamics at the nanoscale: A new approach to the investigation of unique physicochemical properties of nanomaterials

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ABSTRACT

An extension of the classic thermodynamics theory to nanometer scale has generated a new interdisciplinary theory – nanothermodynamics. It serves as a bridge between macroscopic and nanoscopic systems. Over the past decade, nanothermodynamics theories have developed rapidly owing to their critical role in investigating the size-dependent physicochemical properties of nanomaterials. This review examines up-to-date research results on this cutting-edge topic. The focus and emphasis are on the utilization of nanothermodynamics models to investigate the size-dependent thermal stability, magnetic properties, photoelectric behaviors, thermoelectric phenomena, mechanical properties, electrical properties, etc. of nanomaterials.

A range of properties have been studied with respect to the effects of size, dimensionality and composition through a quantitative nanothermodynamics model. It is found that (a) the size dependence of these properties can be universally reconciled to the effect of severe bond dangling; (b) for the same material size, the sequence of size effects on the properties, from strong to weak, is nanoparticles, nanowires and thin films; and (c) the composition effects on the properties of nanoalloys are substantial, having a nonlinear relationship. It also reveals that vacancy formation determined by the cohesive energy variation is one of the intrinsic factors which dominate the size-dependent physicochemical properties of nanomaterials.

Contents

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List of symbols and abbreviations

a, c	lattice parameter
a_h	hole Bohr radius
A_c	a material constant
A_m	gram-atom (g-atom) surface area
b	bowing parameter
B	bulk modulus
BOLS	bond-order-length-strength
c_G	Gruneisen constant
c_i	coordination number-dependent reduction of bond length
C	a constant
C_p	heat capacity
C_v	equilibrium vacancy concentration
C_0	a size-independent pre-exponential coefficient
d	dimensionality of materials
d_{hkl}	inter-planar distance of (hkl)
D	thermal diffusivity
D_d	diffusion coefficient
DFT	density functional theory
D_0	a size-independent pre-exponential coefficient
e	electrical charge of one electron
E_a	first absorption peak energy
EAM	embedded-atom method
E_c	cohesive energy
E_{ca}	catalytic activation energy
E_d	diffusion activation energy
E_{exc}	spin–spin exchange interaction
E_g	bandgap energy
E_{lv}	lattice thermal vibrational energy
E_r	exciton Rydberg energy
E_v	vacancy formation energy
f	surface stress
$fwhm$	full width at half-maximum
FGS	fullerene-like graphite shells
G	Gibbs free energy