LETTER TO THE EDITOR

Curie temperature suppression of ferromagnetic nanosolids

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Abstract
Based on the recent bond-order–bond-length–bond-strength correlation mechanism (Sun C Q, Chen T P, Tay B K, Li S, Huang H, Zhang Y B, Pan L K, Lau S P and Sun X W 2001 *J. Phys. D: Appl. Phys.* **34** 3470) and the criterion of thermal-vibration–exchange-interaction energy equilibrium, an atomistic model has been developed for the Curie temperature (T_C) suppression of ferromagnetic nanosolids. At T_C, the atomic thermal vibration energy (E_V) overcomes the atomic cohesive energy (E_{coh}), which triggers the order–disorder transition of the spin–spin exchange interaction. Besides, the coordination-number (CN) imperfection at a surface enhances the strength of the bonds of the surface atoms. The CN reduction and bond-strength enhancement modifies the surface atomic E_{coh} from that of an atom inside the bulk. As such, the critical E_V for an atom at a free surface will be different from the bulk value and, hence, the T_C of a nanosolid will change with the portion of surface atoms. Matching between predictions and experimental observations on the T_C suppression of Fe, Ni and Co nanofilms evidences the validity of the current premise, in which no assumptions or freely adjustable parameters are involved.

1. Introduction

Ferromagnetic materials, such as Fe, Co and Ni and their alloys, exhibit many intriguing properties with miniaturization of the solid dimension [1–5]. One of the outstanding properties is the Curie temperature (T_C), that reduces with the particle size or the thickness of the films [4, 6–14]. The tunable T_C will be an advantage for magnetic sensors or switches that can function in a given temperature range. However, the understanding of the underlying

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mechanism for the T_C-tunability is still primitive, though models based on the criterion of spin–spin correlation-length (SSCL) limitation have been developed [15, 16].

According to the scaling theory [15], the correlation length is defined as the distance from a point beyond which there is no further correlation of a physical property associated with that point. Values for a given property at distances beyond the correlation length can be considered purely random. The SSCL, ξ, depends functionally on temperature as $\xi = \xi_0(1 - T/T_C)^{-\upsilon}$, where υ is a universal critical exponent. The SSCL limitation premise indicates that ξ is limited by the film thickness. If ξ exceeds the film thickness D, $\xi > k = D/d$, T_C will be lower compared with the bulk value. d is the atomic diameter of the ferromagnetic element concerned. The SSCL mechanism gives rise to the power-law form of the T_C–k relation which involves two freely adjustable parameters, λ and C (or C_0), for data simulation. The λ-value is in the range from 1 for the mean-field approximation to 1.59 for the three-dimensional Ising model [8, 15–17]:

$$\frac{\Delta T_C(k)}{T_C(\infty)} = \frac{T_C(k) - T_C(\infty)}{T_C(\infty)} = (C_0 k)^{-\lambda}. \tag{1}$$

In order to converge the numerical simulation with the measured data of ultra-thin films ($k \to 0$), Binder and Hohenberg [18] and Huang *et al* [19] revised equation (1) by replacing the reference $T_C(\infty)$ with the k-dependent $T_C(k)$ for normalization. With the revised premise, the numerical fit could be improved for ultra-thin films:

$$\frac{\Delta T_C(k)}{T_C(k)} = \frac{T_C(k) - T_C(\infty)}{T_C(k)} = (C' k)^{-\lambda'}. \tag{2}$$

Based on the mean-field approximation, Zhang and Willis [20] proposed an alternative to fit both the thinner and the thicker films with a step function:

$$\frac{\Delta T_C(k)}{T_C(\infty)} = \frac{T_C(k) - T_C(\infty)}{T_C(\infty)} = \begin{cases} -\left(\dfrac{\xi + 1}{2k}\right)^{\lambda}, & (k > \xi) \\[2ex] \dfrac{k - 1}{2\xi} - 1, & (k < \xi). \end{cases} \tag{3}$$

Equation (3) shows that, for $k < \xi$, T_C varies linearly with k, and if $\lambda \neq 1$ there is a discontinuity at $k = \xi$.

In addition to the freely adjustable parameters that need clearer indication in physics, existing models (equations (1) and (2)) diverge at the thinnest limit of a film and equation (3) possesses a singularity at the critical thickness. Although data fitting can be achieved with these models, physical interpretation of the origin for the T_C suppression is desired. Here we report a model based on the bond-order–bond-length–bond-strength (BBB) correlation mechanism [21] and the energy-equilibrium criterion. Without assumptions or freely adjustable parameters, model prediction based on the current premise matches well with observations of the T_C suppression of Fe, Co and Ni thin films, indicating that the T_C suppression of ferromagnetic nanosolids originates from the global CN imperfection of surface atoms.

2. Model

The BBB correlation mechanism [21] indicates that

(i) at a surface, the CN of the surface atom reduces and
(ii) the CN imperfection causes the surface bond to contract spontaneously, with a response of bond energy rise (in absolute value). The BBB correlation is expressed as [21]

$$c_i = d_i/d = 2/\{1 + \exp[(12 - z_i)(8z_i)]\}$$

$$\varepsilon_i = c_i^{-m}\varepsilon. \tag{4}$$

Subscript i denotes the ith atomic layer counted up to three from the outermost atomic layer to the centre of the bulk, as no CN imperfection is expected for $i > 3$. z_i is the effective CN of an atom in the ith atomic layer and m is a parameter defining the response of bond energy, ε, to the change of bond length d. It has been confirmed that for elemental solids, $m = 1$; for compounds or alloys, $m = 4$ [21].

The BBB correlation has consequences for both the cohesive energy E_{coh} (CN multiplies the single bond energy) of a surface atom and the binding energy density in the relaxed surface region as well. E_{coh} relates to thermodynamic properties such as self-assembly growth, melting, phase equilibrium and transition at a surface or a nanosolid of which the portion of surface atoms varies with its dimension. The binding energy density contributes to the Hamiltonian and related quantities of a surface and a nanosolid such as the bandgap and core-level shift. The binding energy density has been recognized to be responsible for the production of surface stress [22, 23]. The portion of surface atoms of a nanosolid is expressed by the surface-to-volume ratio [24, 25]. For a nanosolid consisting of several atomic layers, the surface-to-volume ratio is

$$\gamma i = N_i/N = v_i/V = \frac{R_{i\text{-}out}^\tau - R_{i\text{-}in}^\tau}{R_{1\text{-}out}^\tau}. \tag{5}$$

τ is the dimensionality of a nanosolid and $R = kd$ is the radius of a rod ($\tau = 2$) or a spherical dot ($\tau = 3$), or the thickness (D) for a thin plate ($\tau = 1$). $R_{i\text{-}out}$ or $R_{i\text{-}in}$ corresponds to the outer or inner radius of the ith atomic layer with respect to the centre of the bulk.

It is understandable that the total energy of a single bond is composed of two parts:

$$E_{total}(d, T_C) = E_b(d) + E_V(T_C) = E_C. \tag{6}$$

$E_b(d)$ is the binding energy at equilibrium atomic separation, ε, that is independent of the particular forms of the pair-wise interatomic potential. $E_V(T)$ is the thermal vibration energy. For a ferromagnetic system, $E_b(d)$ corresponds to the exchange energy. At the Curie temperature, the thermal vibration energy required to disorder the spin–spin exchange interaction is close to the exchange energy. Taking $E_{total}(d, T) = E_C$ as reference point ($=0$), we have

$$E_b(d) + E_V(T_C) = 0. \tag{7}$$

Figure 1 illustrates the BBB correlation mechanism. The separation between $E = 0$ and E_C may vary from material to material but it is constant for all bonds of a specific material. The distance between E_C and the minimal bond energy at equilibrium atomic separation (ε_i or ε) determines the thermal energy that causes the order–disorder transition.

Based on the mean-field approximation [20, 26], equation (7) leads to

$$-J_{ij} \times S \times (S + 1) + k_B T_c = 0, \qquad \text{and} \qquad T_C \propto J_{ij} \propto d_i^{-1}, \tag{8}$$

where S is the spin momentum and k_B the Boltzmann constant. J_{ij} is the spin–spin exchange–coupling coefficient that relates to the inverse equilibrium atomic separation. The atomic cohesive energy is given as

$$E_{coh,i} = \sum J_{ij} \propto z_i d_i^{-1}. \tag{9}$$

For a nanosolid with N atoms and dimension D, the total cohesive energy is

$$E_{coh}(D) = Nzd^{-1} + \left[\sum_{i \leqslant 3} N_i(z_i d_i^{-1} - zd^{-1})\right]. \tag{10}$$
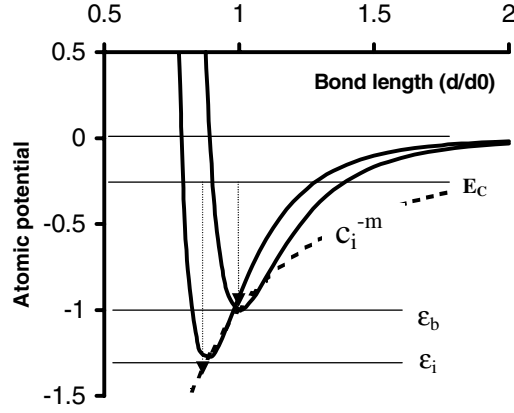
Figure 1. The typical pair-wise potential for interatomic interaction. The BBB correlation mechanism indicates that the bond length reduces with the CN of an atom at the surface with a response of bond energy rise (in absolute value). E_C corresponds to the total energy at T_C, which is taken as a reference point (=0) for total energy. The separation between $E_b = 0$ and E_C is constant for all the bonds of a specific material and the separation between E_C and the minimal $E_b(d)$ determines the thermal energy required per bond for the order–disorder transition of the spin–spin interaction.

Combining equations (8)–(10), we have

$$T_C(D) = NT_{C,b} + \sum_{i \leqslant 3} N_i(z_i T_{C,i} - z_b T_{C,b}),$$

and it is easy to derive

$$\frac{\Delta T_C(D)}{\Delta T_C(\infty)} = \left[\sum_{i \leqslant 3} N_i z_b T_{C,b}(z_{ib}T_{C,ib} - 1)\right] \Big/ (Nz_b T_{C,b}) = \sum_{i \leqslant 3} \gamma_i(z_{ib}c_i^{-1} - 1). \tag{11}$$

3. Analysis

Equation (11) indicates that the size-induced T_C suppression of a ferromagnetic solid originates from the difference in the E_{coh} between a surface atom and a bulk one: $z_{ib}c_i^{-1} - 1$. The trend of change depends on the portion of surface atoms, γ_i, in the first three atomic layers. Calculation based on equation (11) has been carried out with the following parameters: $z_{1b} = 1/3$, $z_{2b} = 1/2$; $d_{Co} = 0.125$ nm, $d_{Fe} = 0.126$ nm, $d_{Ni} = 0.124$ nm; $T_{C,Fe}(\infty) = 1043$ K, $T_{C,Co}(\infty) = 1395$ K, $T_{C,Ni}(\infty) = 631$ K.

Figures 2(a)–(c) compare the predicted curves with the experimental observations of Fe, Co and Ni thin films. Modelling prediction matches well with observations for most of the measured thicknesses. For ultrathin films, the measured data are closer to the predicted curve for a spherical dot. This indicates that at the beginning of film growth the films prefer to grow in island patterns, and transform gradually to a continuous plate.

The slight difference between predictions and observations at small k-values can be minimized by adjusting the c_i-value. In the calculation, we use $z_{1b} = 1/3$ as a standard, corresponding to $c_1 = 0.88$. In fact, z_{ib} should decrease with the particle size as the curvature of the surface increases. On the other hand, the bond contraction coefficient also varies from source to source. For instance, the bond lengths between Ag, Cu, Ni and Fe atoms and their neighbours were found to decrease with decreasing coordination. The bond lengths of the dimers (2.53, 2.22, 2.15 and 2.02 Å, for Ag, Cu, Ni and Fe, respectively [27]) are shorter than
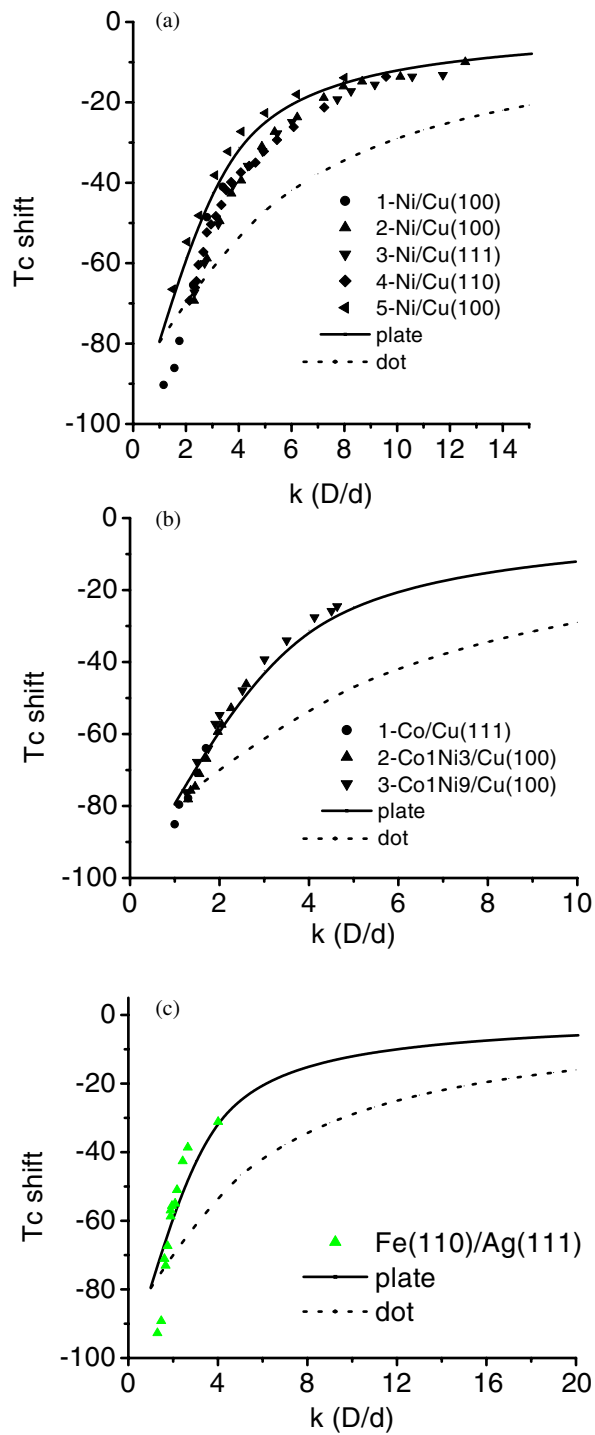
Figure 2. Comparison of the predicted T_C suppression with observation of (a) Ni thin films, data 1 [10], data 2, 3, 4 [20], data 5 [19], data 6 [32] and data 7 [9], (b) Co films [7] and (c) Fe films [4].

(This figure is in colour only in the electronic version)

the nearest-neighbouring distances in their respective bulk values by 12.5% for Ag, 13.2% for Cu, 13.6% for Ni and 18.6% for Fe [28]. A theoretical calculation conducted by Qian and Hübner [29] reveals that the Fe–W and Fe–Fe interlayer spacings contract by 10% compared with the corresponding bulk W–W and Fe–Fe interlayer spacings. Compared with the Fe bcc bulk moment of 2.2 μ_B, the magnetic moment for the surface layer of Fe has been found to be enhanced

(i) by 15% to 2.54 μ_B for 1 ML Fe/5 ML W(110) and

(ii) by 29% to 2.84 μ_B for 2 ML Fe/5 ML W(110).

The significant surface relaxation of Fe(310) (-12%) [30] and Ni(210) (-12%) [31] has also been found to enhance the atomic magnetic momentum by up to 27%. Therefore, bond contraction at a surface indeed has an enormous effect not only on the magnetic momentum but also on the transition of a ferromagnetic nanosolid. It is our opinion that knowing the origin for the T_C suppression is much more important than obtaining the precise fitting of the experimental data, that can be easily reached by adjusting the parameters.

4. Conclusion

In summary, a model of size and shape dependence of Curie temperature suppression for ferromagnetic nanosolids has been developed based on the BBB correlation premise and the energy-equilibrium criterion. Matching between predictions and experimental observations evidences the validity of the premise, which provides clearer physical indications but involves no assumptions or freely adjustable parameters.

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