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Martensitic and austenitic transformations in core-surface cubic nanoparticles

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ABSTRACT

As a continuation of our recently published work, we have used the pair approximation in Kikuchi version to investigate martensitic and austenitic transformations in homogeneous (HM) and composite (CM) cubic nanoparticles (CNPs) based on the Blume–Emery–Griffiths model. A single cubic nanoparticle made of a core surrounded by a surface is considered as shaped in two dimensional (2D) square arrays instead of hexagonal array. From the phase diagrams of HM and CM-CNPs it has been observed that the martensitic–austenitic transformations (MT–AT) occurred. The influence of the exchange coupling and single-ion anisotropy parameters in the model Hamiltonian on the MT–AT is studied and analyzed in comparison with the results for hexagonal nanoparticles. Significant changes of the phase transition points and hysteresis behaviours depending upon the particle structure have been discussed.

1. Introduction

The cubic nanoparticles (CNPs) have provoked continuous broad interest for understanding the magnetism of very small magnetic structures. Their applications are significantly focused on science in the direction of brand new philosophy [1,2]. An interesting feature of the CNPs is that they attach face to face to the surrounding particles and form a two dimensional (2D) square array instead of hexagonal one [3]. For the CNPs, 2D array is one of the closed-packed arrangements. Nanoparticles (NPs) in these arrays have large surface-to-volume ratios and therefore they can evidence to have as important different selectivity and reactivity in catalysis [4–6]. In understanding the surface effects on various physical properties, the particles have been synthesized and characterized by different experimental techniques [7–15]. Owing to their observed electronic nature which is markedly different from those of the bulk materials [16], CNPs have received much attention and mostly have applications in materials science, sensor technology and semiconductor devices [17–19]. On the other hand, magnetic properties of the CNPs have been very sensitive to the particle shape due to the dominating role of surface anisotropy in magnetization [20–23]. A number of physical and chemical methods have been applied to the synthesis of magnetic NPs in a cubic lattice [24–29]. Single-domain CNPs with surface anisotropy were also simulated using Monte-Carlo (MC) methods [30–33].

As noted from the literature, there are several articles on cubic Ising and Heisenberg type NPs consisting of core-shell architecture. Based on the MC simulation technique, various thermodynamic and magnetic properties for these particles were widely studied under the constant and oscillating external magnetic fields [34–40]. A number of characteristic phenomena, such as the effects of shell and interface couplings on the critical magnetic properties of the particles were discussed. However, despite constant progress in both experimental and computational techniques, ferromagnetic (FM) and antiferromagnetic (AF) CNPs have not been fully understood yet. In this work, we have made use of theoretical framework proposed by us for the hexagonal nanoparticles (HNPs) [41] to investigate the various magnetic properties of CNPs. Particularly, we investigate the martensitic–austenitic transformations (MT–AT) which are related to hysteresis splitting in core-surface CNPs and analyze the results in comparison with that of HNPs.

The formulation mentioned in Ref. [41] is based on the Blume–Emery–Griffiths (BEG) model [42] and its solution in pair approximation (PA) devised by Kikuchi for some bulk materials [43]. The

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BEG model is an important lattice-spin model in statistical mechanics. Besides rich variety of multicritical phenomena [44–46], MT problems for the various bulk materials have been discussed successfully in relation with this model [47–51]. But, its solution in PA [46] considers no finite size effects which dominate the magnetic behaviour of some Ising clusters, increasing their relevance as the particle size decreases [52]. In this article (also in Ref. [41]), we have firstly proposed a relationship between bond/pair variables in PA and the number of spins so that core and surface contributions to total magnetization can be identified for the nanostructured particles. Then, based on the numerical solutions of the pair variables magnetization and hysteresis curves for CNPs are obtained and analyzed. Our results indicate that by changing the biquadratic exchange constant, it is possible to observe MT–AT transformations.

2. Basics of model and methodology

Since the details of theoretical formulation used in this study are expressed in Ref. [41] clearly, here we give a brief summary including some important points. For a smart cubic nanoparticle (CNP), we simply consider a square lattice in any 2D arrays as in Fig. 1. In the figure, the coloured arrays form the shells which are connected with sizes (R) of the CNPs. We suppose an Ising spin (σ_i) at each lattice site i which takes on the values ± 1, 0. The inner spins (red circles) are called the core (C) region which is surrounded by the outer spins (blue circles) that are known as the surface (S) of the particle. As in the hexagonal nanoparticle (HNP) [41], we consider the classical model Hamiltonian with bilinear (J) and biquadratic (K) exchange interactions in the presence of single-ion anisotropy parameter (D) and external magnetic field (h) as follows:

$$H\{\sigma_i\} = -J\sum_{\langle i,j\rangle}\sigma_i\sigma_j - K\sum_{\langle i,j\rangle}\sigma_i^2\sigma_j^2 - D\sum_{\langle i,j\rangle}(\sigma_i^2+\sigma_j^2) - h\sum_{\langle i,j\rangle}(\sigma_i+\sigma_j), \quad (1)$$

which is also called the BEG model. All parameters appearing in Eq. (1) are in units of k_BT (k_B Boltzmann constant and T temperature). For the core-surface (CS) type CNPs we separate Eq. (1) into three terms (H_C, H_{CS}, H_S) including all interactions between nearest neighbouring spins in core (J_C, K_C, D_C), core-surface (J_{CS}, K_{CS}) and surface (J_S, K_S, D_S) regions. Then, the exchange interaction energy in PA for a single CNP can be expressed in terms of the bond/pair variables (P_{ij}) shortly as

$$\beta E = \sum_{i,j=+,0,-}(N_P^C\varepsilon_{ij}^C + N_P^{CS}\varepsilon_{ij}^{CS} + N_P^S\varepsilon_{ij}^S)P_{ij},\ (\beta = 1/k_BT) \quad (2)$$

where $N_P^C = (N_C\gamma_C/2) - N_{CS}$, $N_P^{CS} = 2N_{CS}\gamma_{CS}/2$, $N_P^S = N_S\gamma_S/2$ are the numbers of spin pairs (i, j) and ε_{ij}^C, ε_{ij}^{CS}, ε_{ij}^S are called the bond energies of the pairs for C, CS, S parts, respectively. Number of spins for each region (N_C, N_{CS}, N_S) can be found by counting the sites in the square lattice in 2D (see Table 2 in Ref. [53]. The bond energies were computed easily and listed in Ref. [41]. From Fig. 1, the coordination numbers for three parts are determined as $\gamma_C = 4$, $\gamma_{CS} = 2$, $\gamma_S = 0$. In Ref. [41], we reported nine self-consistent equations for P_{ij} (with symmetry $P_{ij}=P_{ji}$) in the form:

$$P_{ij} = Z^{-1}(p_ip_j)^{(\gamma-1)/\gamma}\exp\left[-\beta(N_P^C\varepsilon_{ij}^C + N_P^{CS}\varepsilon_{ij}^{CS} + N_P^S\varepsilon_{ij}^S)\right] \equiv e_{ij}Z^{-1},$$
$$(i,j = +,\ 0,\ -) \quad (3)$$

where p_i ($i=+, 0, -$) is the point/state variable, γ ($\gamma=\gamma_C$) is the coordination number of a given lattice site and $Z$is the partition function defined by the relation $Z = \sum_{i,j=+,0,-}e_{ij}$. Eq. (3) is solved numerically by using Newton–Raphson or iteration method for the normalized magnetization (m) which is calculated via the definition [46]

$$m = P_{++} + P_{+0} + P_{+-} - (P_{-+} + P_{-0} + P_{--}). \quad (4)$$

Using Eq. (4), the behaviours of the magnetization curves, phase diagrams, and hysteresis loops for the homogeneous (HM) and composite (CM)-CNPs are obtained as in Figs. 2–5. In our calculations, the results for the HM-CNPs correspond to the FM core and FM core-surface interactions, i.e., $J_0 = J_C = J_{CS} = 1$ while FM core and AF core-surface interactions are considered for the CM-CNPs with $J_0 = J_C = 1$, $J_{CS} = -1$. For simplicity, we selected $K = K_C = K_{CS}$ and $D = D_C = D_S$ in both cases. As for the bilinear and biquadratic interactions between surface spins (J_S,K_S) we considered no contribution to total magnetization coming from particle's surface because of zero lattice coordination ($\gamma_S = 0$) in Fig. 1.

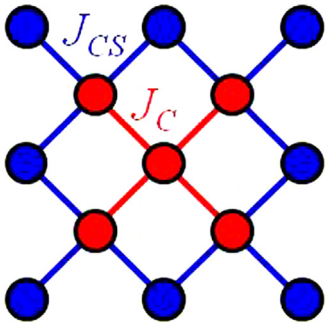

Fig. 1. Schematic representation of a CNP on a square lattice in 2D exhibiting two shells of spins. Solid red and blue lines correspond to the core and core-surface pairs, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3. Result and discussion

The temperature (k_BT/J_0) dependence of magnetization (m) for several values of single-ion anisotropy (D) and related phase diagrams for the HM-CNPs are shown in Fig. 2. In the figure, all curves are obtained for both small CNP with R=3 shells and a big particle with R=10 shells in the presence of a repulsive biquadratic interaction ($K=-0.4$) with no magnetic field ($h=0.0$) [45]. The magnetization of big CNP decreases continuously from one (1) with increasing temperature and converges to zero (0) as the temperature approaches to second-order phase transition temperature (T_{C2}) when $D=-0.3585$. Similarly, m also decreases as the temperature raised but induces a jump at the Curie temperature (T_{C1}) for $D=-0.3650$, seen in Fig. 2a. The discontinuity of m at T_{C1} is truly a first-order phase transition behaviour and not due to proximity of critical behaviour via a tricritical point. In addition to these results, there exist for $D=-0.3591$ and -0.3605 values big and small hillocks depending upon the heating and cooling processes, respectively. Here, the FM behaviour is first observed in the martensitic (M) phase on heating and then magnetization decreases with temperature for $D=-0.3591$. Further increasing of k_BT/J_0 causes a jump of magnetization at T_{Ci}. Finally, the austenitic (A) phase is reached in transition from FM phase to paramagnetic (PM) phase. A well defined endothermic peak appears in the transition from M phase to A phase during heating process, while an exothermic peak is observed in the transition from A phase to M phase during cooling process, illustrated also in Fig. 2b. These peaks are also seen for small particle (R=3) when $D=-0.6565$, -0.6545. Thus, the hillocks emerge at temperatures between 211 and 273 k_BT/J_0 for R=10 and temperatures between 18 and 24 k_BT/J_0 for R=3. The characteristic temperatures indicated in Fig. 2b are called martensitic start temperature (M_S), martensitic finish temperature (M_F), austenitic start temperature (A_S) and austenitic finish temperature (A_F). The magnetization sharply increases from A_S toA_F which corresponds