Physica A 496 (2018) 663–675

Contents lists available at ScienceDirect

Physica A

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

Surface effects and discontinuity behavior in nano-systems composed of Prussian blue analogues

L.B. Drissi [a,b,*], S. Zriouel [a,b,c,*], L. Bahmad [d]

[a] Lab-PHE, Modeling & Simulations, Faculty of Sciences, Mohammed V University in Rabat, Morocco
[b] CPM, Centre of Physics and Mathematics, Faculty of Sciences, Mohammed V University in Rabat, Morocco
[c] Department of Physics, Polydisciplinary Faculty, Sultan Moulay Slimane University in Beni Mellal, Morocco
[d] Laboratory of Condensed Matter and Interdisciplinary Sciences (LaMCScI), Faculty of Sciences, Mohammed V University in Rabat, Morocco

HIGHLIGHTS

- We study a ferrimagnetic surface–bulk Prussian blue analogues (PBA) using Monte Carlo calculations.
- We show the effects of the surface on thermodynamic quantities.
- We give the conditions for the occurrence of compensation temperature.
- We describe the influence of the system's parameters on the hysteresis curves.

ARTICLE INFO

Article history:
Received 7 July 2017
Received in revised form 22 December 2017
Available online 3 January 2018

Keywords:
Prussian blue analogues
Surface–bulk nano-systems
Ferrimagnets
Monte Carlo calculations
Discontinuity and critical temperatures
Hysteresis cycles

ABSTRACT

Magnetic properties and hysteresis loops of a nano-ferrimagnetic surface–bulk Prussian blue analogues (PBA) have been studied by means of Monte Carlo simulations. We have reported the effects of the magnetic and the crystal fields, as well as the intermediate and the bulk couplings, the temperature and the size on the phase diagram, the magnetization, the susceptibility, the hysteresis loops, the critical and the discontinuity temperatures of the model. The thermal dependence of the coercivity and the remanent magnetization are also discussed. This study shows a number of characteristic behaviors, such as the discontinuities in the magnetizations, the existence of Q- and N-types behaviors in the Néel classification nomenclature and the occurrence of single and triple hysteresis loops with high number of step-like plateaus. The obtained results make ferrimagnetic surface–bulk PBA useful for technological applications such as thermo-optical recording.

1. Introduction

Recently, nano-ferrimagnetic materials have attracted a lot of theoretical and experimental interest [1–5] and the references therein. The possible existence of a compensation temperature, under certain conditions, makes the ferrimagnets promising for advanced permanent magnetic applications particularly high-density magneto-optical recording [6]. This temperature is usually found below the critical temperature, at which the magnetic moments located on different sublattices of the model counteract each other, giving a zero total moment [7].

A simple model exhibiting the ferrimagnetic behavior is the model composed of two sublattices with opposite spin directions. In these models, the magnetic reorientation phase transition (MRPT) is the result of the competing forces that

---

* Corresponding authors.
E-mail addresses: ldrissi@fsr.ac.ma (L.B. Drissi), sanae.zriouel@usms.ma (S. Zriouel), bahmad@fsr.ac.ma (L. Bahmad).

https://doi.org/10.1016/j.physa.2017.12.125

favor different directions of the magnetization [8]. In [9], the study of a spin-1 two-sublattice ferrimagnetic monolayer on a simple square lattice confirms the existence of two magnetic phases in the ferrimagnets.

Surface–bulk provides another model of ferrimagnets. Several surface/bulk materials display a different magnetic behavior at the surface than in the bulk due to the different coordination number and the symmetry of the atoms at the surface [10]. Using the mean-field theory (MFT) and the Monte Carlo (MC) calculations, the occurrence of a higher critical temperature in the surface compared to the bulk is shown for the semi-infinite cubic Ising model [11]. By the mean of MC simulations, it is found that the finite size effects affect the magnetic properties of the surface and the bulk differently [12].

Besides the two-sublattice ferrimagnetic systems and the surface/bulk materials, other morphologies such as Ising core/shell nanostructures are used to study ferrimagnets. In [13], a model explaining the formation process of a single spin core–shell nanocrystal, using a reverse micellar system is presented using the MC technique and the post-core route. The coercive force increasing as a function of the antiferromagnetic shell thickness is the result obtained for a composite spin-1/2 core–shell nanoparticles [14]. The influence of a transverse field on the thermodynamic quantities of a cylindrical core/shell spin-1 Ising nanowire shows two distinct magnetic susceptibility peaks and some magnetic reversal events [15]. Within the Green's function technique, the size and the anisotropy effects on the static and dynamic properties of ferromagnetic spherical nanoparticles with spin $S = 2$ were investigated in [16].

Mixed spin ferrimagnets have also attracted great interest because they exhibit many new phenomena which cannot be observed in their single spin counterparts. The study of the nonequilibrium properties [17] and the equilibrium behavior [18] of the spin $(1/2, 1)$ Ising model shows that the phase diagram contains three phases separated by two continuous transition lines. In [19,20], MC simulations are used to examine the effect of the shell and the intermediate coupling on the magnetic properties and the thermodynamic quantities of a ferrimagnetic $(1/2, 1)$ hexagonal nanoribbon and $(1/2, 1, 3/2)$ hexagonal core–double shell graphyne-like, respectively.

More complicated ferrimagnets with higher spin, as $(1, 3/2)$ and $(2, 5/2)$, have also been studied employing different techniques such as the mean-field approximation (MFA) based on Bogoliubov inequality for the Gibbs free energy [21], the effective-field theory (EFT) [22], the MC calculations [23,24] and the Glauber stochastic dynamics [25,26].

Up to now, the tailoring of nanostructured magnetic materials has reached a high level of sophistication due to the advanced development of the experimental techniques. Special interest is devoted to magnetic nanocubes, the ideal building blocks for the formation of three-dimensional 3D nanocrystals. Superlattices of iron nanocubes are synthesized via the thermal decomposition of relevant organometallic compounds for magnetic applications because of their high magnetization and their adjustable anisotropy [27]. The shape-controlled synthesis and the self-assembly of FePt nanocubes are reported as an approach for single particle recording and for maximization of energy product in an exchange-spring nanocomposite system [28]. Cobalt nanoparticles with cubic shape are prepared by the wet-chemical processing [29]. In [30], single-crystalline $La_{1-x}Ba_xMnO_3$ nanocubes with an adjustable Ba doping level are fabricated using the hydrothermal synthesis for producing colossal magnetoresistivity in mixed valence manganites.

On the other hand, the most extensive class of magnetic structures based upon a simple cubic, however, is that exemplified by Prussian blue analogues (PBA) $M_3[M\prime(CN)_6]_2$, where M is a divalent metal and $M\prime$ is a trivalent metal [31]. These materials have attracted a notable attention in the last decade because of their unusual and multiple magnetic [32,33], electrical [33,34], optical [33,35], and gas storage properties [33,36]. Of the many known Prussian Blue analogues, the $V_3[Cr(CN)_6]_2$ and the $Ti_3[V(CN)_6]_2$ have important magnetic properties. Indeed, the $V_3[Cr(CN)_6]_2$ exhibits the highest critical temperature ($T_c = 315K$) among the Prussian blue analogs [37,38].

In parallel, there are extensive theoretical studies modeling nanocube structures and showing some interesting magnetic results. Using the MC simulations, the $(3/2, 1)$ core/shell ferrimagnetic nanoparticles on a simple cubic lattice show a dynamic phase transition from paramagnetic to a dynamically ordered phase in the presence of ultrafast switching fields [39]. This core–shell system defined on a body-centered-cubic lattice is also investigated in [40,41]. The effects of the crystal field and the exchange interactions on the thermal and the magnetic properties of the system are reported in [40]. In [41], it is found that the nearest-neighbor interactions influence clearly the compensation behavior. This compensation temperature dependence on the particle size is now known as a characteristic property of ferrimagnetic systems. The investigation of the hysteresis loops of a spin $(1, 3/2)$ core/shell cubic nanowire in terms of the transverse field, the crystal field and the exchange interactions, in the framework of EFT, leads to triple, pentamerous and heptamerous hysteresis loops [42]. The study of a mixed spin $(2, 5/2)$ ferrimagnet for a simple cubic lattice using MFA shows the possibility of many compensation points at low temperatures depending on the values of anisotropies [43].

As reported above, the ferrimagnetic materials in their different morphologies exhibit interesting magnetic phenomena beside the existence of the compensation temperature which is a characteristic property of these nanostructures. Previous works on systems having surface–bulk morphology show that the magnetic properties of the surfaces differ drastically from those of the bulk to which they are coupled leading to novel properties. However, to date there are no reports on the magnetic behavior of ferrimagnetic surface–bulk ferrimagnets with regular cubic structure even if cubic geometry is the simplest model for the study of the critical phenomena and a majority of the important engineering materials crystallize in this geometry [44].

The purpose of the present work is to study the magnetic behavior of ferrimagnetic surface–bulk PBA made of $V_3[Cr(CN)_6]_2$ surface with spins $S_{V^{II}} = S_{Cr^{III}} = \pm 3/2, \pm 1/2$ above the $Ti_3[V(CN)_6]_2$ bulk with spins $\sigma_{Ti^{II}} = \sigma_{V^{III}} = \pm 1, 0$. Using the Monte Carlo simulations, we determine the role of the interaction between surface and bulk and the effect of some relevant parameters such as the bulk coupling, the crystal and external magnetic fields, the size and the temperature on the occurrence of the discontinuity temperature and the hysteretic properties of the model.