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Core-shell spin model of magnetization in Li-Zn-Co ferrite

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ABSTRACT

Nanoparticles of $Li_{0.35}Zn_{0.30}Co_{0.05}Fe_{2.3}O_4$ with average crystallite sizes of ~7.3 nm and 69.6 nm are prepared by sol-gel method. Size of nanocrystallite in each case plays an important role in the thermal variation of magnetization. For small size, each nanocrystallite may be considered as single domain ordered core surrounded by a surface shell of disordered spins, which are fluctuating randomly. Also, there is a large deviation of Bloch's law in case of magnetization vs temperature curves where exponent is larger compared to that of larger nanocrystallites. A steep increase in the magnetization is evidenced at lower temperatures, which is more prominent in case of nanocrystallites of smaller sizes. This additional magnetization comes from the surface spin contribution and is effective at $T \leq 100$ K. Thus various novel features of magnetism are being evolved once the particle/nanocrystallite size is quite low.

1. Introduction

Magnetic nanoparticles are of great interest in a wide field of research and applications. Nanoparticles of ferrite are one of the often used names in this field due to their superior magnetic properties. Recent applications of ferrite nanoparticles include microwave shielding devices, memory devices, high resolution imaging and greater precision target identification in military sectors, etc. [1–3]. Most importantly, ferrite nanoparticles are now being vastly used in biomedical applications as targeted drug delivery agent, magnetic resonance imaging, biosensors and magnetic separation [4–5]. Most recently, ferrite nanoparticles are proposed as an efficient heat mediator in magnetic hyperthermia treatment. All these applications are mainly based on the magnetic behavior of the nanoparticles either in the low frequency region (~kHz) or in the high frequency region (~GHz) and demand a clear idea about the origin of magnetism in these nanoparticles.

Spinel ferrites have two lattice sites viz., tetrahedral (A) and octahedral (B) sites, in which unequal magnetic spins are arranged in anti-parallel direction producing a net magnetic moment. More often, these spins are not exactly anti-parallel; rather they are canted at some angle. The net magnetic moment per formula unit in such case is estimated using canted spin model and expressed in Bohr magneton [6]. In this model, the net magnetic moment depends upon the cation distribution and hence magnetization can be tailored by a suitable choice of metal cations at A- and B-sites. Thus, a formula unit could be considered as a magnetic moment having a particular orientation. In a nanoparticle, a large number of such formula units having same direction of orientation form a domain. Depending on size of the nanoparticles, there can exist only a single domain or a multiple number of domains called the multi domain nanoparticles. Stoner Wohlfarth model is widely used to derive magnetization in such nanoparticles [7]. Moreover, the temperature dependence of magnetization in bulk materials at a temperature well below the Curie temperature (~850 K for Fe_3O_4) is described by well known Bloch $T^{3/2}$ law [8]. However, at the nanoscale, observed temperature variation of magnetization deviates significantly from $T^{3/2}$ law and follows an effective law where magnetization varies as a function of T^{α}. The exponent α is size dependent and generally, α is larger than 3/2 in nanoparticles and more often it is ~2 for nanoparticles of smaller sizes [9]. A significant increase in Bloch constant (B) is also found at nanoscale [10]. Such deviations in the values of α or B in nano regime could be explained by a core-shell model where surface spins play an important role [10]. A large number of broken exchange bonds for surface atoms result in spin disorder and the lack of coordination of surface ions to the core ions is the origin of these surface spins, which fluctuates at zero field and high temperature. In this direction, Hendriksen et al. in long past have studied small Fe clusters with 50–230 atoms and marked a lack of coordination between the surface spins and the spin arising from the central part which lead a faster decrease of magnetization at higher temperatures [9]. A decrease in the saturation magnetization with the decrease in the particle size of $MnFe_2O_4$

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