Origin of ferromagnetism in BaTiO₃ nanoparticles

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Based on a microscopic approach we demonstrate that the unexpected ferromagnetic properties of BaTiO₃ (BTO) or PTO observed recently at room temperature are due to oxygen vacancies at the surface of the nanocrystalline materials. Such vacancies lead to the appearance of Ti^{3+} or Ti^{2+} ions with nonzero net spin. The resulting different valence states composed of Ti^{3+} or Ti^{2+} offer a nonzero magnetization which decreases with increasing particle size. The system shows a multiferroic behavior below a critical size of the nanoparticles and the related polarization tends to a saturation value when the particle size is enhanced.

Recently, there has been a great effort in studying magnetism in nonmagnetic semiconductors diluted with magnetic impurities due to possible applications in spin-based electronic systems. Moreover, nanoparticles (NP) of inorganic materials including otherwise nonmagnetic oxides such as CeO_2, Al_2O_3, MgO, ZnO, In_2O_3 and SnO_2, nitrides, chalcogenides and other functional materials like superconductors and ferroelectrics were shown to be ferromagnetic at room temperature. The magnetism in these NP has been suggested to be intrinsic and originates from cation or anion vacancies at the surfaces of the NP. Very recently, it was reported from both experiments and first-principles calculations that typical ferroelectric materials such as BaTiO₃ (BTO) and PbTiO₃ (PTO) become multiferroic when they are prepared at the nanoscale [1−8]. So, nanocrystalline BTO offers a room-temperature magnetic hysteresis as well as temperature-dependent dielectric constant and a polarization. Multiferroics that exhibit magnetoelectric coupling are widely discussed from quite different context, see [9−12]. However, apart from a density functional calculation as vacancy-induced magnetism in BTO(001) thin films [13] a well accepted theoretical description of the ferroic properties of nanocrystalline BTO is still missing. In a previous paper [14] the static and dynamic properties of KH_2PO_4 (KDP)-type and BTO-type ferroelectric NP have been reviewed. Based on that approach we propose a statistical model which reflects the multiferroic properties of BTO-NP. While the spontaneous polarization in a classic ferroelectric material like BTO is expected to diminish when the particle size is reduced [14−16], ferromagnetism cannot occur in bulk material [17]. It is observed experimentally that the multiferroic nature emerges in an intermediate size range of nanocrystalline BTO. Whereas the ferromagnetism is arising from the oxygen vacancies or point defects at the surface of the NP the ferroelectricity is originated from the core of the material [1−3].

As demonstrated in [14] the Ising model in a transverse field is also appropriate to describe the properties of ferroelectric NP. The Hamiltonian reads

$$H^{\mathrm{e}} = -\Omega \sum_i S_i^x - \frac{1}{2} \sum_{ij} J_{ij} S_i^z S_j^z \ . \tag{1}$$

Since the ferroelectricity in BTO is originated from the off-centering of the Ti ions with respect to the cubic perovskite crystal we assume as the simplest model that there are two positions of the Ti atoms in a double-well potential. These two states are mapped on the S^z-component of a pseudo spin-1/2 operator whereas the S^x-component
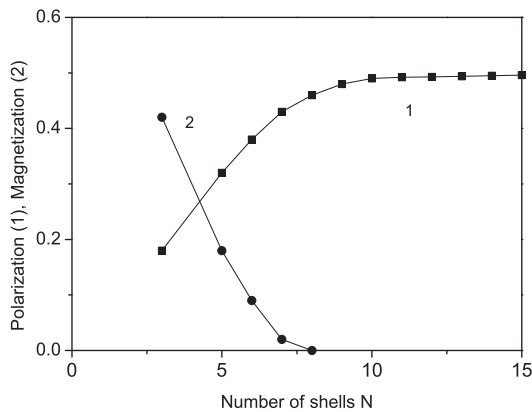
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Figure 1 Size dependence of the polarization P (1) and magnetization M (2) of a BTO-NP for $T = 300$ K, $J_b = 700$ K, $\Omega_b = \Omega_s = 10$ K, $A_b = 250$ K, $S = 1/2$ (Ti^{3+}), and different exchange interactions: (1) $J_s = 0.5 J_b$, (2) $A_s = 2 A_b$.

characterizes the tunneling between the wells with the frequency Ω. The quantity J_{ij} denotes the nearest-neighbor pseudo-spin interaction. The Hamiltonian in Eq. (1) is conventionally applied for bulk material. For nanocrystalline material we have to define an NP by fixing the origin at a certain spin in the center of the particle and including all spins within the particle into shells. The shells are numbered by $n = 1, \ldots, N$, where $n = 1$ denotes the central spin and $n = N$ represents the surface shell of the system. Hence the number N is a measure of the extension of the NP. The real size of the NP is obtained by multiplying N with the lattice constant. Surface effects are included by different coupling parameters within the surface shell and within the bulk, which will be characterized by the suffix s or b, respectively. The thermodynamic Green's function method enables us to calculate the size dependence of the polarization P in BTO-NP for $J_s < J_b$ [14]. The results confirm that P shrinks when the particle size N is decreasing and is vanishing at a critical value $N_c = 3$. The result for the polarization is shown as curve 1 in Fig. 1.

The polarization is enhanced with increasing shell number N and becomes saturated for large NP size. The observation is in agreement with experimental data presented in [14–16].

To analyze the magnetic properties let us come back to the structure of conventional perovskite-based ferroelectrics like BTO more specifically. As mentioned before the ferroelectricity arises in that material as the result of the displacement of the so-called B-site cation (Ti^{4+}) with respect to the oxygen octahedral cage. Consequently the transition metal ion (Ti^{4+} in BTO) needs an empty d-shell since the ferroelectric displacement occurs due to the hopping of electrons between the d-state Ti and p-state O atoms. Usually this process excludes the occurrence of any net magnetic moment because magnetism requires partially filled d-shells of the transition metal. Practically, all ferroelectric perovskites contain transition metal ions with an empty d-shell, such as Ti^{4+}, Ta^{5+}, W^{6+}. The ferroelectricity

in these systems is caused by the off-center shifts of the transition metal ion, which forms strong covalent bonds with one or three oxygen atoms using their empty d-states. And somehow, the presence of real d-electrons in the d^n configurations of magnetic transition metals is able to suppress this process, preventing ferroelectricity in magnetic perovskites. This effect is well known as the so-called 'd^0 versus d^n problem'. Notice that this problem had been studied as one of the initial points at the beginning of the recent revival of multiferroics [17, 18]. Mangalam et al. [2] have carried out magnetic measurements of BTO samples with 60 nm, 100 nm and 2 μm. While the sample on the nanometer scale reveals clearly ferromagnetism at room temperature the sample of μm scale shows a diamagnetic behavior as it is also expected for the bulk BTO material. The smaller the particle size is the higher is the saturation magnetization. The effect that larger particles lead to a lower magnetization is consistent with the suggestion that surface defects decrease with increasing particle size. As argued in [2] the observed ferromagnetism in such BTO-NP can be correlated with the presence of oxygen vacancies at the surface of the NP. So positron annihilation studies in BTO-NP reveals a lower annihilation rate of positrons with the 2p electrons of oxygen in the sample of 100 nm and 60 nm in comparison to the bulk system. This observation indicates the presence of oxygen vacancies [2]. Each oxygen vacancy is expected to donate two electrons to the empty d-state of a single Ti^{4+}(d^0) ion in order to produce a Ti^{2+}(d^2) ion with spin $S = 1$. An alternative mechanism is that each oxygen electron goes to different Ti^{4+} ions and generate two Ti^{3+} ions in state d^1 with spin $S = 1/2$ [1, 19]. With decreasing particle size the number of oxygen vacancies increases and hence the number of Ti^{2+} or Ti^{3+} ions is also enlarged. This enhancement of Ti ions with nonzero spin gives rise to a weak ferromagnetism. Probably there is also the creation of a mixed valence state composed of a superposition of both states d^2 and d^1. The presence of the mixed valence state of the Ti-ions due to point defects could be also the origin for the observed room-temperature ferromagnetism in TiO$_2$ NP suggested in [5, 6].

The magnetic properties of BTO are analyzed using the Heisenberg model for the resulting different valence states on the surface composed of Ti^{3+} or Ti^{2+}. The Hamiltonian reads

$$H^m = -\frac{1}{2} \sum_{ij} A_{ij} \mathbf{B}_i \cdot \mathbf{B}_j \,, \tag{2}$$

where $\mathbf{B}_i$ is the Heisenberg spin operator at the site i, A_{ij} is the exchange integral between the nearest neighbors of for instance the Ti^{3+}-ions. Different to many oxides the exchange coupling is positive as it was explained previously by [1, 2]. In a similar manner like for the ferroelectric system we calculate the magnetization M based on Eq. (2). The NP is composed of distinct shells indicating the size of the NP. Different to the ferroelectric case the surface ex-
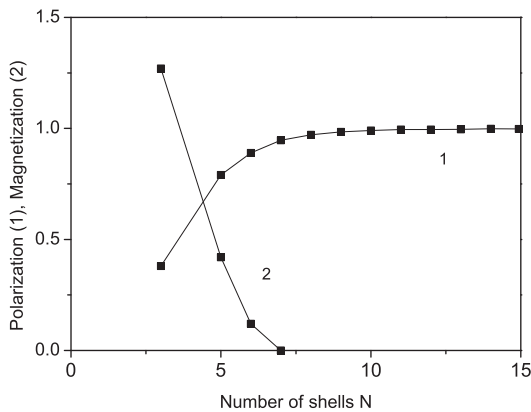
Figure 2 Size dependence of the polarization P (1) and magnetization M (2) of a BTO-NP for $T = 300$ K, $J_b = 700$ K, $\Omega_b = \Omega_s = 10$ K, $A_b = 344$ K, $S = 1$ (Ti^{2+}), and different exchange interactions: (1) $J_s = 0.5 J_b$, (2) $A_s = 2 A_b$.

change interaction A_s is assumed to be larger as the related bulk coupling A_b. Therefore only the surface spins yield a significant contribution to M, which is again found by the finite temperature Green's function approach. The result for M depending on the NP-size N is depicted as curve 2 in Fig. 1 in case of Ti^{3+} on the surface with $S = 1/2$.

The temperature is assumed to be $T = 300$ K. The magnetization increases with decreasing particle size above a critical size N_c, which is in qualitative agreement with the experimental data presented in [2]. The critical size depends on the model parameters. Comparing the two curves for the polarization (curve 1) and the magnetization (curve 2) one argues that ferroelectricity exists also for bulk material whereas the magnetization disappears. However, with decreasing size a weak ferromagnetic behavior is observed below a critical size of $N_c \simeq 8$. The magnetization increases with decreasing particle size, while the polarization decreases. In an intermediate size interval the BTO-NP offer multiferroic properties characterized by the coexistence of a finite polarization and magnetization. Figure 2 shows the magnetization for $S = 1$, i.e. originated from magnetic Ti^{2+} ions on the surface. The result is quite similar to Fig. 1, indicating that the mechanism for the appearance is the same as for Ti^{3+}-ions. The ferromagnetism is stronger compared to the case of Ti^{2+}. Because in that case the shells are smaller the magnetization disappears for a lower critical size N_c and as a consequence the polarization becomes higher. For a further clarification of the situation we would like to suggest to study experimentally the influence of an external electrical field on the magnetic properties or vice versa the influence of a magnetic field on the electric properties which is one of the important features of multiferroics compounds. Such a measurement should give more evidence of the magnetoelectric coupling in BTO or PTO NP.

In conclusion, we have shown that the observed ferromagnetic properties in BTO- or PTO-NP at room temperatures could be originated due to the oxygen vacancies at the surface and to the appearance of a different valence state composed of Ti^{3+} or Ti^{2+}. As the result one observes multiferroic properties of the NP. Whereas the polarization decreases with decreasing particle size, the magnetization increases below a critical particle size N_c which is of the order of $1-8$ Å. The critical size should be enhanced by an increasing external magnetic field as suggested in [1, 2]. BTO is multiferroic in a small size interval below a critical one of the BTO-NP. Let us remark that our approach can be also used to analyze BTO-NP doped with transition metal ions like Fe, Mn, Co or Ni. Such system are studied experimentally for instance in [20].

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