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Origin of ferromagnetism in transition metal doped $BaTiO_3$

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We have calculated the temperature, magnetic field, and ion doping dependence of the magnetic and electric properties in Fe-doped $BaTiO_3$ using a microscopic model and the Green's function technique. It is shown that the ferromagnetic and multiferroic properties observed at room temperature in Fe doped $BaTiO_3$ could be due to the super exchange interactions between Fe^{3+} ions in different occupational sites associated with oxygen vacancies and to the exchange coupling of Fe ions with mixed valence, Fe^{3+} and Fe^{4+}. There is a multiferroic region which depends strongly on the Fe-doping concentration. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4807412]

I. INTRODUCTION

Multiferroics are materials which exhibit simultaneously ferroelectricity and magnetic order in a certain temperature region.[1] They have the property that the magnetic and dielectric order parameters are coupled, so that the ferroelectricity can be controlled by magnetism and vice versa. However, it is a very rare case in nature that both magnetic and electric polarizations coexist in one substance. Ferroelectricity is usually generated by transition metal compounds with empty *d*-shells (d^0). On the other hand, ferromagnetism usually requires a transition metal with a partially filled *d*-shell. Therefore, alternative mechanisms are required to combine these two properties. At present, much interest is being focused on the realization of ferromagnetism in the ferroelectric (FE) material $BaTiO_3$ (BTO) by impurity doping.[2–11] So far, ferromagnetic ordering has been reported for Co-,[2,3] Mn-,[2,4] and Fe-doped[5–11] BTO systems. Unfortunately, the obtained results about the effects of Fe-doping on the magnetic properties in BTO (BFTO) are controversial. Rajamani *et al.*[5] and Guo *et al.*[10] reported an increase, whereas Lin *et al.*[7] reported a decrease of the saturation magnetization M_s with the Fe-doping concentration x. The observed M_s by Qiu *et al.*[8] increased with x to reach a maximum value at about 4%, followed by a decrease, and then increased again. The temperature dependence of the magnetization is controlled by disorder in the samples and any shape from concave to linear to convex is possible as shown theoretically by Berciu and Bhatt.[12] This is confirmed also experimentally.[2,5,10] Rajamani *et al.*[5] and Lin *et al.*[6] have found that the magnetic properties were also sensitive to preparation atmosphere. BTO grown in vacuum and oxygen were both ferromagnetic but the latter showed significantly lower magnetization than the former. Lin *et al.*[6] have discussed the origin of the room temperature ferromagnetism in ceramics prepared by solid-state reaction and post-annealed in vacuum and oxygen, respectively. For the as-prepared sample, the super-exchange interactions of Fe^{3+} in different occupational sites (pentahedral and octahedral sites) are expected to produce the ferromagnetism observed. After annealing in vacuum, the magnetization is reduced while the exchange mechanism remains unchanged. On the contrary, O_2 annealing can effectively enhance the magnetization due to the presence of Fe^{4+}. The exchange coupling of Fe ions with mixed valence (Fe^{3+} and Fe^{4+}) determines the magnetic behavior. Magnetic properties are also observed experimentally in Co-,[13–16] Mn-,[17–20] Cr-,[13] and Fe-doped[13,21–23] BTO thin films and nanoparticles.

There are not so many theoretical investigations about the origin of the ferromagnetism in ion doped BTO. Nakayama and Katayama-Yoshida[24] have performed *ab-initio* total energy calculations for the system of BTO doped with 3d transition metal (from Sc to Cu), within the framework of the local spin-density approximation (LSDA). The results predict that the Cr-, Mn-, and Fe-doped BTO are candidates for ferromagnetic fabrication. Xu *et al.*[25] reported the ferroelectricity and ferromagnetism coexistence in the Fe-doped BTO. Their first-principles calculation based on the density-functional theory predicted a ferromagnetic coupling among the magnetic moments of the Fe dopants by using LSDA + U method. The theoretical prediction was confirmed experimentally.

In our previous papers,[26,27] we have proposed a model for pure perovskite ferroelectric BTO and ABO_3 nanoparticles, respectively, which allows finding out the multiferroic properties in these nanostructures. We have shown that the unexpected ferromagnetic properties observed recently at room temperatures can be explained by considering oxygen vacancies at the surface of the nanocrystalline materials. The aim of the present paper is using a microscopic model and the Green's function technique to extend these studies in order to explain the origin of ferromagnetism in bulk BTO doped with transition metal ions, for example, Fe.

II. THE MODEL AND THE GREEN'S FUNCTION

In principle, the Hamiltonian which describes the ferroelectric properties of BTO is the transverse Ising model (TIM)

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$$H^e = -\Omega\sum_i B_i^x - \frac{1}{2}\sum_{ij} J'_{ij} B_i^z B_j^z, \tag{1}$$

where B_i^x, B_i^z are the spin-1/2 operators of the pseudo-spins, J'_{ij} denotes the nearest-neighbor pseudo-spin interaction, Ω is the tunneling frequency. Blinc and de Gennes[28] proposed the TIM for the description of order-disorder KDP(KH_2PO_4)-type FE. Further, the TIM is applied to displacive type FE such as BTO[29,30] too.

In usual perovskite-based ferroelectrics like BTO, the ferroelectric distortion occurs due to the displacement of B-site cation (Ti^{4+}) with respect to the oxygen octahedral cage. Here, the transition metal ion (Ti^{4+} in BTO) requires an empty *d* shell since the ferroelectric displacement occurs due to the hopping of electrons between Ti *d* and O *p* atoms. This normally excludes any net magnetic moment because magnetism requires partially filled *d* shells of a transition metal. Practically, all ferroelectric perovskites contain transition metal ions with an empty *d* shell, such as Ti^{4+}, Ta^{5+}, W^{6+}. But the situation is changed after doping of the ferroelectric BTO with transition metal ions, for example, Fe. It is known that perovskite oxides, ABO_3, are subject to indirect superexchange magnetic interactions. Besides, ferromagnetic behavior in oxides is also explained commonly within the framework of the double exchange interaction. The Moessbauer spectra clearly suggest the presence of a second valence for iron, Fe^{4+} besides the usual one, Fe^{3+}. Thus, the simultaneous presence of Fe^{3+} and Fe^{4+} allows new exchange mechanism responsible for the ferromagnetic interaction. Not only the super-exchange Fe^{4+}-O^{2-}-Fe^{4+} interaction but also the double exchange Fe^{3+}-O^{2-}-Fe^{4+} interaction is expected to determine the magnetic behavior. It is generally suggested that the Fe^{4+}-O^{2-}-Fe^{4+} interaction is ferromagnetic, while the Fe^{3+}-O^{2-}-Fe^{4+} and Fe^{3+}-O^{2-}-Fe^{3+}(octahedral-octahedral) interactions are anti-ferromagnetic.[21,31] The ferromagnetic Fe^{4+}-O^{2-}-Fe^{4+} interaction dominates over the antiferromagnetic Fe^{3+}-O^{2-}-Fe^{4+} and Fe^{3+}-O^{2-}-Fe^{3+} interactions, producing the remarkably enhanced magnetization.

We have calculated the magnetic properties of Fe doped BTO based on the Heisenberg model

$$\begin{aligned} H^m = &-\frac{1}{2}\sum_{ij} J_{ij}^{AA}\mathbf{S}_i^A.\mathbf{S}_j^A - \frac{1}{2}\sum_{ij} J_{ij}^{BB}\mathbf{S}_i^B.\mathbf{S}_j^B \\ &-\frac{1}{2}\sum_{ij} J_{ij}^{AB}\mathbf{S}_i^A.\mathbf{S}_j^B - g\mu_B H\sum_i B_i^z, \end{aligned} \tag{2}$$

where $\mathbf{S}_i^{A,B}$ is the Heisenberg spin operator at the site *i*, *A* stays for Fe^{4+}, and *B* for Fe^{3+}. *J* is the exchange integral between the Fe-ions, where $J^{AA} > 0$, $J^{BB} < 0$, $J^{AB} = J^{BA} < 0$. *H* is an external magnetic field.

For the retarded spin Green's function, we have the 2×2 matrix

$$G_{ij}(t) = \langle\langle T_i(t); T_j^+\rangle\rangle. \tag{3}$$

The operator T_i stands symbolically for the set of the operators S_i^A, S_i^B. Using the Green's function method, we have calculated from the poles of the Green's function (3) the spin-wave energy to

$$E_{ij}^{1,2} = 0.5(E_{ij}^{AA} - E_{ij}^{BB}) \pm [(E_{ij}^{AA} - E_{ij}^{BB})^2 + 4E_{ij}^{BA}E_{ij}^{AB}]^{1/2} \tag{4}$$

with

$$\begin{aligned} E_{ij}^{AA} &= \frac{2}{N}\sum_k J_{ik}^{AA}\langle S_k^{Az}\rangle\delta_{ij} - 2J_{ij}^{AA}\langle S_i^{Az}\rangle - \frac{2}{N}\sum_k J_{ik}^{AB}\langle S_k^{Bz}\rangle\delta_{ij} \\ &\quad + g\mu_B H\delta_{ij}, \\ E_{ij}^{BB} &= \frac{2}{N}\sum_k J_{ik}^{BB}\langle S_k^{Bz}\rangle\delta_{ij} - 2J_{ij}^{BB}\langle S_i^{Bz}\rangle - \frac{2}{N}\sum_k J_{ik}^{AB}\langle S_k^{Az}\rangle\delta_{ij} \\ &\quad + g\mu_B H\delta_{ij}, \\ E_{ij}^{AB} &= 2J_{ij}^{AB}\langle S_i^{Az}\rangle\delta_{ij}, \quad E_{ij}^{BA} = 2J_{ij}^{AB}\langle S_i^{Bz}\rangle\delta_{ij}. \end{aligned}$$

The magnetization of the system is given by

$$M^z = |M^{Az} - M^{Bz}| = \left|\sum_i \langle S_i^{Az}\rangle - \langle S_i^{Bz}\rangle\right|. \tag{5}$$

III. NUMERICAL RESULTS AND DISCUSSION

We will present and discuss now our numerical results. The numerical calculations are made with the programs in the computer language JAVA. It has been used self-consistent method iterations. As input data for the first iteration are used the model parameters given below. In any subsequent calculation of input data are taken the results of the previous calculation. Calculations continue until the difference between two consecutive iterations does not exceed a predetermined small enough value. We have calculated at first numerically the normalized magnetization $M/M(T=0)$ of Fe doped $BaTiO_3$, $Ba(Ti_{1-x}Fe_x)O$ for $x = 0.6$ in dependence on the temperature taking the following model parameters: $J' = 700\,K$, $\Omega = 10\,K$, $J^{AA} = 250\,K$, $J^{BB} = -175\,K$, $J^{AB} = -150\,K$, $S(Fe^{4+}) = 1$,[5] $S(Fe^{3+}) = 5/2$. The results are shown in Fig. 1. The *M–T* curve shows a ferromagnetic-paramagnetic transition. It can be seen that *M* decreases with increasing temperature *T*. BFTO exhibit ferromagnetism at room temperature. This behavior is in qualitative agreement with the experimental data of Rajamani *et al.*[5] and Guo *et al.*[10] in BFTO, and of Maier *et al.*[22] in BFTO thin films.

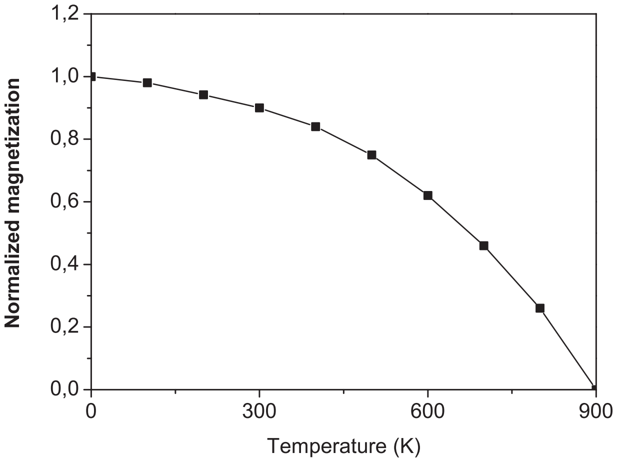

FIG. 1. Temperature dependence of the normalized magnetization $M/M(T=0)$ for $Ba(Ti_{1-x}Fe_x)O_3$, $x = 0.6$.

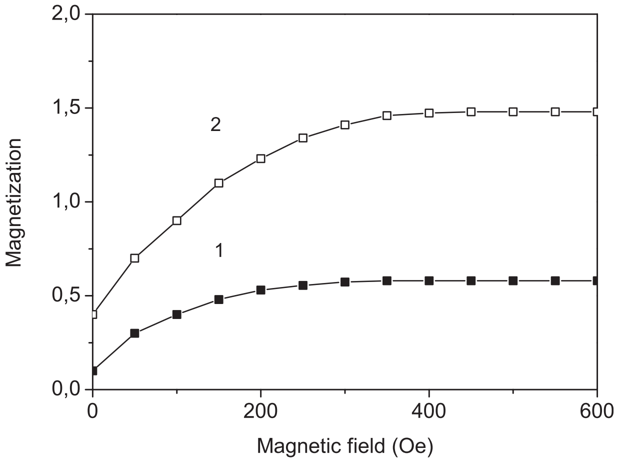

FIG. 2. Magnetic field dependence of the magnetization in Ba($Ti_{1-x}Fe_x$)O_3, (1) $x = 0.1$ and (2) $x = 0.5$.

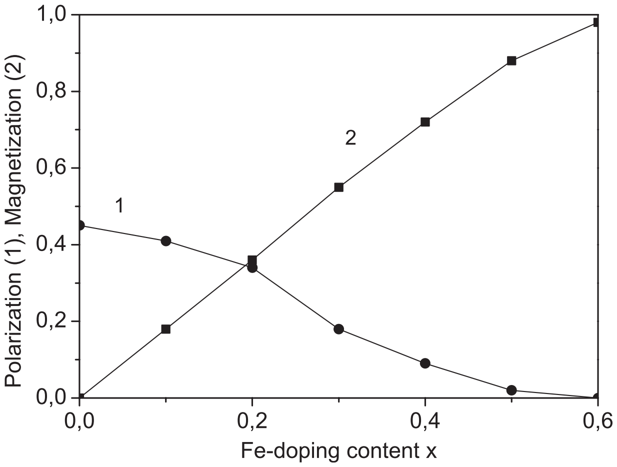

FIG. 4. Dependence of the polarization (1) and the magnetization (2) in Ba($Ti_{1-x}Fe_x$)O_3 on the Fe-doping content x for $T = 100$ K.

Fig. 2 demonstrates the magnetic field dependence of the magnetization M for different Fe-ion concentrations. M increases with increasing of H and with x, which is in agreement with the experimental data of Guo *et al.*[10] It must be noted that Fe^{3+} ions substituting for Ti^{4+} ions will introduce oxygen vacancies into $BaTiO_3$. Such oxygen vacancies may act as a kind of medium through which superexchange interactions between neighboring Fe^{3+} ions occur. This could explain the increasing behavior of the saturated magnetization with x. Similar increasing of M with x is reported also for Fe-doped $SrTiO_3$ thin films.[32] It must be mentioned that Lin *et al.*,[7] Wei *et al.*,[9] and Ray *et al.*[11] observed a decrease of M_s with x in BFTO ceramics. But this is something surprising, because the cubic perovskite $BaFeO_3$ is a pure ferromagnetic material, it shows no ferroelectric properties, $P = 0$. The specific ferromagnetism is attributed to the enhancement of O → Fe charge transfer that arises from deepening of the Fe^{4+} d levels. Therefore, the magnetization must be maximal for $x = 1$.

In Fig. 3 is presented the Fe-concentration dependence of the magnetic phase transition temperature T_C. T_C increases nearly linearly with the doping concentration x. Similar increasing of T_C is observed by Guo *et al.*[10] in BFTO and Maier *et al.*[22] in BFTO thin films. The Curie temperature T_C shifts to higher temperature as the doping level increases, for example, it is found by Guo *et al.*[10] around 770 K in BFTO ($x = 0.10$) samples, and increases to about 800 K as the doping level increases to $x = 0.40$, which is compatible with the result of $BaTi_{0.95}Fe_{0.05}O_3$ ($T_C = 680$ K) in literature.[25] Our results are $T_C = 700$ K for $x = 0.1$ and $T_C = 820$ K for $x = 0.4$.

Thus, we obtain that Fe-doped BTO shows a room temperature ferromagnetism, i.e., it shows multiferroic properties below the ferroelectric critical temperature. Whereas M and the magnetic transition temperature T_C increase with Fe-doping, we obtain that the polarization P and the ferroelectric T_C decrease (Fig. 4). $BaFeO_3$ is a pure magnetic material, it shows no ferroelectric properties, $P = 0$. Qiu *et al.*[8] observed also that the ferroelectricity decreases with the increase of Fe doping level. Guo[10] reported decreasing of the maximal value of the dielectric constant with increasing Fe concentration. Jana *et al.*[33] and Maso *et al.*[34] have shown that the ferroelectric-paraelectric phase transition temperature T_C strongly depends upon the Fe-dopant concentration in the BTO specimens. For the undoped specimen, the phase transition is observed at 125 °C and it is shifted to a lower temperature with a further increase of Fe-content. Recently, Maikhuri *et al.*[35] have reported also a suppressed ferroelectric behavior in Fe substituted BTO ceramics as compared to pure BTO.

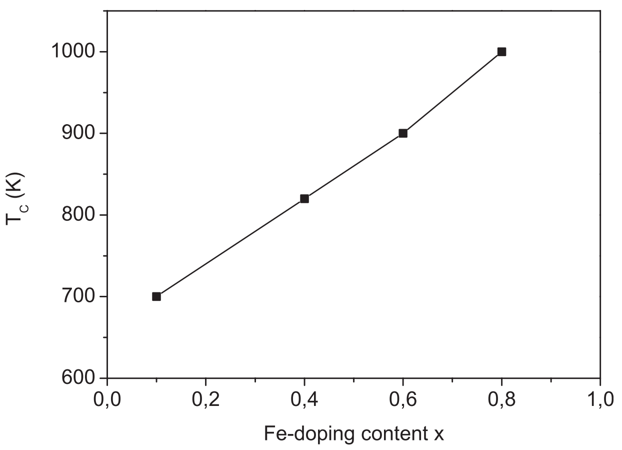

FIG. 3. Dependence of the magnetic phase transition temperature T_C in Ba($Ti_{1-x}Fe_x$)O_3 on the Fe-doping content x.

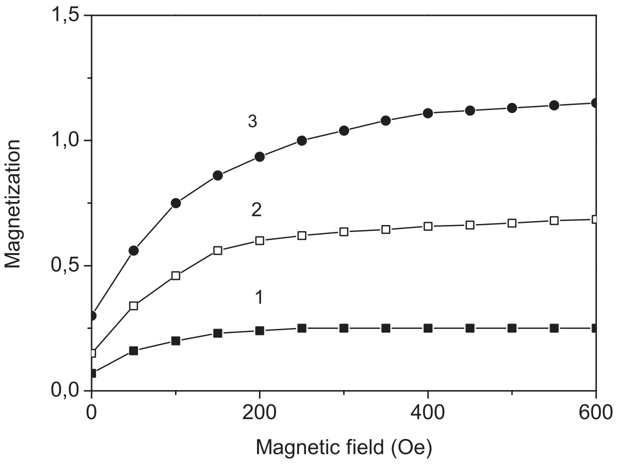

FIG. 5. Magnetic field dependence of the magnetization in Pb($Ti_{1-x}Mn_x$)O_3, (1) $x = 0.1$, (2) $x = 0.3$, and (3) $x = 0.6$.

Magnetization-magnetic field loops show ferromagnetic behavior in the Fe-doped BTO at room temperature.

We have investigated also Mn-doped BTO and $PbTiO_3$ (PTO), where Mn appears in the two valencies Mn^{2+} ($S=5/2$) and Mn^{4+} ($S=3/2$).[36] The results for Mn-doped PTO are shown in Fig. 5. It demonstrates the magnetic field dependence of the magnetization M for different Mn-ion concentrations x. M increases with increasing of H and with x. This is in agreement with the experimental data of Kumar andYadav[37] for $PbTi_{1-x}Mn_xO_3$ and Lin *et al.*[17] for Mn doped BTO. We obtain a similar behavior compared to that of Fe-doped BTO (Fig. 2), i.e., an increase of M with increasing of the Mn-ion concentration in PTO. In Co-doped BTO, we observed also a room temperature ferromagnetism. The magnetization M increases with increasing Co-concentration, as reported by Liu *et al.*[13] in Co-doped BTO nanoparticles.

As already mentioned in the Introduction, we have shown[26,27] that the unexpected ferromagnetic and multiferroic properties observed at room temperature in ferroelectric ABO_3, such as $BaTiO_3$, $SrTiO_3$, or $PbTiO_3$ nanoparticles can be due to the oxygen vacancies at the surface leading to the appearance of Ti^{3+} and/or Ti^{2+} ions with $S \neq 0$. Therefore, we assume that the transition metal ion doping effects in ABO_3 nanostructures would be stronger compared to the bulk case because to the magnetization due to the doping ions there is also the additive contribution of the surface effects. This will be discussed in a next paper.

IV. CONCLUSIONS

In conclusion, we have shown that ferromagnetic properties at room temperature, which lead to multiferroic properties in BTO, could be due to doping with transition metal ions, for example, Fe, i.e., to the super exchange interactions between Fe^{3+} ions in different occupational sites associated with oxygen vacancies and to the exchange coupling of Fe ions with mixed valence, Fe^{3+} and Fe^{4+}. Whereas the magnetization and the magnetic phase transition temperature increase with increasing of the Fe-ion concentration, the polarization and the ferroelectric critical temperature decrease. In order to show that our model and theory could be applied also to other transition metal ion doped ABO_3 materials, we have considered the magnetic field dependence of the magnetization M for Mn doped PTO where Mn appears in the two valencies Mn^{2+} and Mn^{4+}. M increases also with increasing of the Mn-ion concentration in PTO. The observed results are in good qualitative agreement with the experimental data. Therefore, we can conclude that the doping of perovskite ferroelectric ABO_3 materials with transition metal ions is the origin of the ferromagnetic, i.e., multiferroic properties observed recently at room temperatures.

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