Investigating ferromagnetism and charge order in $Bi_{1-x}Sr_xMnO_3$ (x<0.3) ceramic oxides

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The possible coexistence of ferromagnetism and charge/orbital order in $Bi_{3/4}Sr_{1/4}MnO_3$ has been investigated. The manganite $Bi_{0.75}Sr_{0.25}MnO_3$, with commensurate charge balance, undergoes an electronic transition at T_{CO}~600 K that produces a long-range modulation with double periodicity along a and c axis, and unusual anisotropic evolution of the lattice parameters. The previously proposed ferromagnetic properties of this new ordered phase were studied by magnetometry and diffraction techniques. In zero field the magnetic structure is globally antiferromagnetic, ruling out the apparition of spontaneous ferromagnetism. However, the application of magnetic fields produces a continuous progressive canting of the moments, inducing a ferromagnetic phase even for relatively small fields (H<<1 T). Application of pulsed high fields produces a remarkable and reversible spin polarization (under 30 T, the ferromagnetic moment is ~3 μ_B/Mn, without any sign of charge order melting). The coexistence of ferromagnetism and charge order at low and very-high fields is a remarkable property of this system.

Keywords: Manganites, Charge order, Ferromagnetic oxides, Multiferroic.

Estudio de la posible coexistencia de ferromagnetismo y orden de carga en oxidos ceramicos $Bi_{1-x}Sr_xMnO_3$ (x<0.3)

Se ha estudiado la coexistencia de ferromagnetismo y orden de carga en óxidos cerámicos del tipo $Bi_{1-x}Sr_xMnO_3$ con x<<0.5. $Bi_{0.75}Sr_{0.25}MnO_3$ (x =2/8) presenta una transición estructural y electrónica a T_{CO}~600 K que da lugar a nueva fase de orden de carga con simetría promedio Ibmm y una supercelda que dobla los ejes a y c . $BiMnO_3$ (multiferroico) es ferromagnético por debajo de T_C=105 K. Se han utilizado técnicas magnéticas y de difracción para investigar si la persistencia de ferromagnetismo en las medidas magnéticas hasta x≤0.4 puede ser el resultado de una dilución progresiva de la fase ferromagnètica del compuesto monoclínico puro. La estructura magnética en $Bi_{0.75}Sr_{0.25}MnO_3$ es globalmente antiferromagnètica, descartando la aparición de ferromagnetismo espontáneo. Sin embargo, la respuesta al campo magnético es inusual: se observa un canting continuado y progresivo de los momentos desde campos muy pequeños hasta la saturación ferromagnètica, sin signos de la fusión del orden de carga con campos de hasta 30 Teslas. La coexistencia de ferromagnetismo y orden de carga es una propiedad remarcable de estos óxidos.

Palabras clave: orden de carga, manganitas, ferromagnetismo multiferróico.

1. INTRODUCTION

In mixed-valence metal oxides the electronic-type transitions related with charge localization, orbital ordering (OO) assisted by the Jahn-Teller effect, and charge ordering (CO) are currently the object of intense investigations. The Bi-Sr-Mn-O system is receiving great attention due to the observation of some singularities that differ from the general behaviour of previously studied manganites (1-8). One is the great tendency of Bi-Sr manganites to present charge-order (CO) at very high temperatures (1-3). Another one is the presence in the electron microscopy images at atomic resolution of internal periodic structures consistent with double stripes of MnO_6 octahedra (3,6), which still don't have a convincing justification. Obtaining a detailed picture, at atomic level, of the magnetic and electronic features of the (so far unique) charge-order phase detected in $Bi_{3/4}Sr_{1/4}MnO_3$ is one of the best opportunities to discern between different microscopic models proposed in CO manganites

(9,10). Moreover, it represents a good occasion to build a comprehensible description of defective but commensurate CO compositions with x<4/8 : 1/8, 2/8 or 3/8.

$BiMnO_3$, a ferromagnetic insulator (T_C=105 K), crystallizes at high pressure in a highly distorted perovskite structure (11-12). The lone pair of Bi drives the off-center distortion in $BiMnO_3$ producing its multiferroic behavior. $BiMnO_3$ is a prototypical magnetic ferroelectric, with a Curie temperature of around 450 K, remaining ferroelectric down to low temperatures through the ferromagnetic transition at 105 K (11-14). It is thus one of the very few monophasic materials exhibiting magnetoferroelectricity, although the origin of ferromagnetism in pure $BiMnO_3$ is not yet well understood. Moreover, the dependence of the properties of $Bi_{1-x}Sr_xMnO_3$ compounds on the Sr content is still an open issue. The composition $Bi_{0.75}Sr_{0.25}MnO_3$ is particularly appealing due to its commensurability (x=1/4=1/8+1/8). With this particularity

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in mind we performed a high-temperature neutron and synchrotron powder diffraction study (5,8) revealing that $Bi_{0.75}Sr_{0.25}MnO_3$ undergoes a charge-order transition at T_{CO}=600 K, well above the ordering temperature in half doped $Bi_{0.5}Sr_{0.5}MnO_3$ (T_{CO}=525 K). A structural study of $Bi_{3/4}Sr_{1/4}MnO_3$ between RT and 750 K was reported in Ref. 8. The existence of a new type of charge ordered phase in this compound was concluded. The new type of superstructure has also been confirmed for x~0.25-0.33 (6,8). The average structure changes from Ibmm (below T_{CO}) to Pbnm (above T_{CO}) (8). The symmetry change in this transformation is also very intriguing and different from the usual behavior in modulated manganites. In this paper we have extended our previous investigations in $Bi_{1-x}Sr_xMnO_3$, trying to clarify the origin and nature of the ferromagnetic behavior in the magnetic measurements of samples with x values up to x≈0.4. For this we have mainly focused on the magnetic properties of the system $Bi_{3/4}Sr_{1/4}MnO_3$.

2. EXPERIMENTAL DETAILS

Polycrystalline $Bi_{1-x}Sr_xMnO_3$ ceramics (0.25≤x≤0.50) were prepared following a sol-gel route and standard solid-state reaction methods, depending on the Bi content. $Bi_{0.75}Sr_{0.25}MnO_3$ was prepared following a sol-gel route, starting from stoichiometric quantities of Bi_2O_3 (99.9%), MnO_2 (99.99%), and $SrCO_3$ (99.99%). They were dissolved in concentrated nitric acid, the solution jellified according to the acrylamide polymerization method, and then subjected to self-ignition. The corresponding powders were heated at 700 ºC for 12 h and then to 950 ºC for 12 h in flowing oxygen. Sol-gel synthesis was chosen with the purpose of obtaining a single-phase material and to minimize a possible Bi deficiency due to evaporation. The electron diffraction (ED) study was carried out using a JEOL 200 CX microscope fitted with a eucentric goniometer (±60°), and equipped with an energy dispersive spectroscopy (EDS) analyser. Magnetic measurements over the range 5<T<700 K were done using a SQUID magnetometer. Magnetotransport characterization was performed by the four-probe method, using a commercial PPMS system (Quantum Design) in the temperature range 5<T<350 K. High-magnetic-field M(H) curves were measured at the facilities of the LNCMP in Toulouse (France). Neutron powder diffraction (NPD) patterns were collected at the Institut Laue-Langevin (Grenoble, France) in the temperature interval 1.5<T<750 K, using D2B (λ =1.594 Å, in its high flux mode) and D1B (λ =2.52 Å). Synchrotron X-ray powder diffraction (SPD) patterns were collected on BM16 (λ =0.540092 Å) diffractometer of ESRF (Grenoble, France). The FULLPROF program was used for diffraction data analysis (15).

3. RESULTS AND DISCUSSION

3.1 Electron microscopy.

The combined electron diffraction (ED)/cationic analysis (EDS) characterization of $Bi_{0.75}Sr_{0.25}MnO_3$ was carried out on about fifty grains. The sample exhibits a very good crystallinity and the average composition (calculated for one Mn per formula unit) is close to $Bi_{0.71\pm0.04}Sr_{0.29\pm0.04}Mn$. The grains are faceted and their average size is of the order of the micrometer (Fig.1(a)). A different habit is commonly

observed for other compositions obtained from the same sol gel synthesis process, as for example x=0.50 and x=0.55 (24) (small spherical crystallites, forming low density structures, and having an average diameter of the order of a few tens nanometers). At room temperature, the reconstruction of the reciprocal space showed that a large majority (more than 90%) of the crystals exhibit a superstructure with regard to $a_p\sqrt{2}$ x $a_p\sqrt{2}$ x $2a_p$ (a_p is for the ideal cubic perovskite). The same superstructure was observed in $Bi_{2/3}Sr_{1/3}MnO_3$, and presents a double modulation, $1/2\,a^*$ and $1/2\,c^*$, referred to the Ibmm-type subcell. The [001] ED pattern given in Fig.1(b) shows the satellites along a^*. The extra reflections generated by the modulation along c^* are visible in the [2$\bar{1}$0] ED patterns (see the white triangles in Fig. 1(c)). Hence, the observations confirm an orthorhombic supercell, with a P-type space group and the doubling of the a and c parameters ($2a_p\sqrt{2}$ x $a_p\sqrt{2}$ x $4a_p$). The crystallites of the minority phase (about 5%) are characterized by the absence of extra reflections, i.e. they exhibit the reflections of the Ibmm subcell. The corresponding EDS analysis evidenced a small but significant Mn deficiency with regard to the ideal perovskite composition. Small traces (~1%) of Mn_3O_4 were also detected.
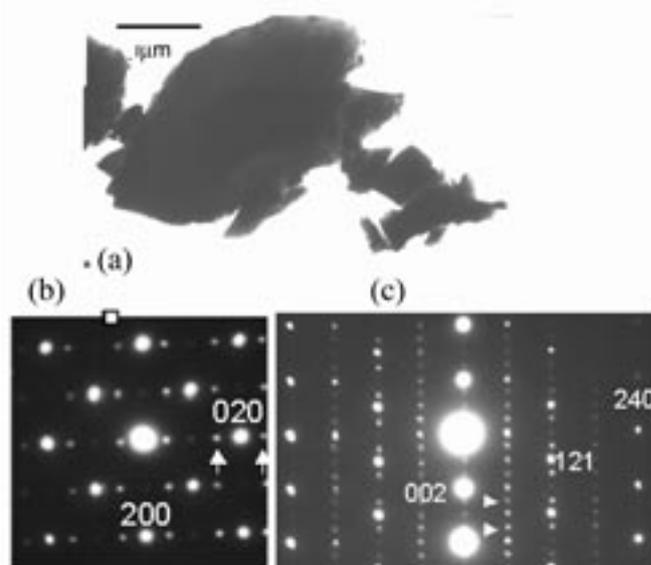

Fig. 1- (a) Overall bright field image of $Bi_{0.75}Sr_{0.25}MnO_3$ prepared by sol-gel. (b) [001] ED patterns recorded at RT. Arrows signal the satellites corresponding to the modulation along a*. (c) [2$\bar{1}$0] ED patterns showing the extra spots from the new periodicity along the c-axis. (Indexation is referred to the Ibmm subcell).

3.2 Magnetic, high magnetic field and magnetotransport measurements

The inverse DC magnetic susceptibility of $Bi_{0.75}Sr_{0.25}MnO_3$ is shown in the inset of Fig. 2(a) in the high temperature range up to 700 K. The magnetic susceptibility shows an anomaly at the transition temperature that is accompanied by a change of the effective paramagnetic moment (from 4.68(4)μ_B/Mn to 5.26(2) μ_B/Mn in $Bi_{0.75}Sr_{0.25}MnO_3$). Notice that the effective moment found below T_{CO} does not agree with the ordering of ionic Mn^{3+} and Mn^{4+} species, as discussed in Ref. 8. Although such an enhancement of μ_{eff} has been recently attributed to the formation of Zener polarons, other explanations should not be

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ruled out (16). Figure 2(a) suggests a magnetic transition from paramagnetic to a ferro or ferrimagnetic phase (note that these measurements were performed under 1 T of applied field). Magnetotransport measurements confirmed that these oxides do not present significant magnetoresistance and the onset of long range magnetic order does not produce changes in the thermal evolution of ρ(T,H) (8).
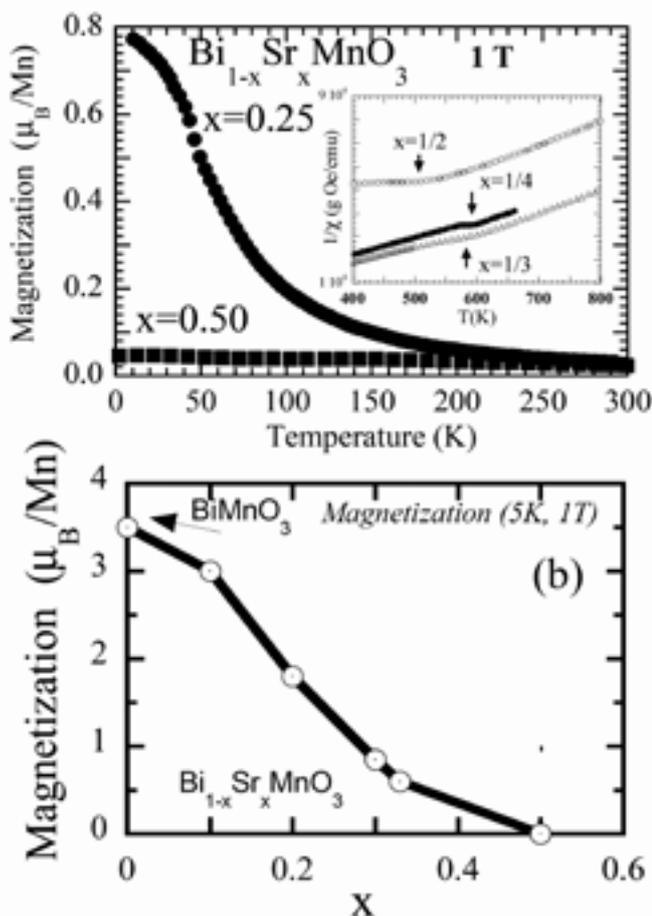

Fig. 2- (a) Comparison of the magnetization (FC, 1 T) of Bi$_{0.75}$Sr$_{0.25}$MnO$_3$ and Bi$_{0.50}$Sr$_{0.50}$MnO$_3$ below RT. Inset: Inverse susceptibility showing the electronic transition in Bi$_{1-x}$Sr$_x$MnO$_3$ oxides (x≤0.50) (H=1T, curves have been shifted for the sake of clarity). (b) Evolution with the Sr content x of the magnetization M(1T,5K) of Bi$_{1-x}$Sr$_x$MnO$_3$. (Data taken from Ref. 17.)

It is noteworthy that the evolution of M(T) of Bi$_{0.75}$Sr$_{0.25}$MnO$_3$ shows a ferromagnetic component below the magnetic transition at low temperature. We observe that ferromagnetic moment is, at 5 K, 0.78 μ_B/Mn ion (1T). Of interest is thus the different M(T) evolution in the charge-ordered phase of composition x=1/4, with respect to the charge ordered phase of x=1/2 (Fig. 2(a)). The half doped material remains globally antiferromagnetic (AFM) below T$_N$ (≈110 K) (1). This is in contrast with the M(T) evolution of x=0.25 or x=0.33 specimens. This behavior was already found in Ref. (17), and one of the motivations of the present study was to investigate the astonishing coexistence of ferromagnetism and charge order in the system. At this point we recall that BiMnO$_3$ is ferromagnetic below T$_C$=105 K and the origin of ferromagnetism in pure BiMnO$_3$ is a long-standing open question (11-14). The saturation moment found in the pure perovskite is 3.6 μ_B/

Mn (11), a value slightly lower than expected for a perfect alignment of Mn^{3+} moments (4 μ_B/Mn). In a series of pioneer studies (11,17) Chiba et al prepared Bi$_{1-x}$Sr$_x$MnO$_3$ ceramic samples (using conventional and high-pressure synthesis techniques). Fig. 2(b) reproduces the ferromagnetic component reported by Chiba et al (17) as a function of the Sr content (from magnetization measurements). Ignoring the existence of charge-order in these compounds, they found that doping with Sr systematically decreases the ferromagnetic moment from the saturation value of 3.6 μ_B observed in the parent BiMnO$_3$ perovskite. Consequently, they concluded that a characteristic feature of the low-doped region of Bi$_{1-x}$Sr$_x$MnO$_3$ is the persistence of a ferromagnetic component, which only disappeared at doping levels x > 0.4 (17). In this context, one of the objectives of the present study has been to investigate the origin and nature of ferromagnetism in Bi$_{1-x}$Sr$_x$MnO$_3$ at moderate doping.

High-magnetic-field magnetization of Bi$_{1-x}$Sr$_x$MnO$_3$ samples, with x=0.33 and x=0.50 is shown in Fig. 3(a), as measured using pulsed fields at the facilities of the LNCMP in Toulouse (at 4.2 K after a ZF cooling process). We recall that the composition x=0.33 exhibits the same structural transition, modulation and CO phase than the compound with x=0.25 (6,8). Figure 3(b) displays the behavior of M(H) in Bi$_{0.75}$Sr$_{0.25}$MnO$_3$ during a hysteresis cycle at 5 K (up to 6 Teslas, M$_0$=0.067 μ_B/Mn, H$_c$= 665 Oe). An interesting result is that, in contrast with the M(T) curve of the Fig. 2(a) which suggests a net FM component, the evolution of M(H) at low fields evidences that the CO phase of Bi$_{0.75}$Sr$_{0.25}$MnO$_3$ and Bi$_{0.67}$Sr$_{0.33}$MnO$_3$ (as in Bi$_{0.50}$Sr$_{0.50}$MnO$_3$) is globally antiferromagnetic in zero field, and intrinsic spontaneous ferromagnetism was ruled out. To be emphasized is that the AFM ground state is an unexpected conclusion after the work of Chiba et al (17), which suggested spontaneous ferromagnetism. Nevertheless, it is interesting to note in Figure 3 that, in contrast with the linear M-H evolution of Bi$_{0.50}$Sr$_{0.50}$MnO$_3$, the magnetization curves for x=0.25 and 0.33 samples show a marked curvature in the M(H) isotherms confirming the induction of ferromagnetism by the external field. This effect is already visible even for very small fields (<< 1T). Moreover, it is worthwhile noticing that (i) there is no evidence of charge order melting up to 30 T; and (ii) at this field the ferromagnetic moment is very close to 3 μ_B/Mn ion.

III.3 Synchrotron, neutron diffraction and magnetic structure

We recall that the ferromagnetic ground state and the monoclinic C2 distortion of the pure oxide BiMnO$_3$ are related with the polarization of the Bi^{3+} lone-pair in the structure (11).

TABLE I. MAGNETIC STRUCTURE REFINED FROM NPD DATA AT LOW TEMPERATURE. SITES ARE REFERRED TO THE AVERAGE √2A$_P$X√2A$_P$X2A$_P$ CELL.

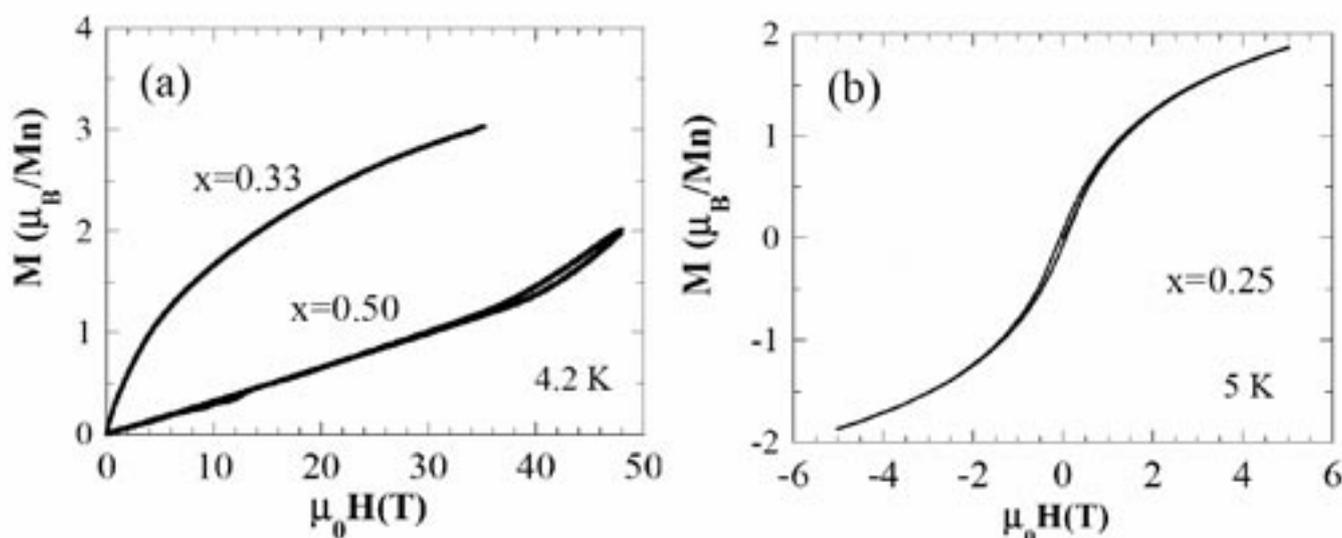| Mn-sites	m$_x$(μ_B)	m$_y$(μ_B)	m$_z$(μ_B)
(½ 0 0) (0 ½ 0) (½ 1 0) (1 -½ 0) (½ 0 ½) (0 ½ ½) (½ 1 ½) (1 -½ ½)	2.74(6)	0.42(9)	1.35(4)
(-½ 0 0) (0 -½ 0) (1 ½ 0) (-½ 1 0) (-½ 0 ½) (0 -½ ½) (1 ½ ½) (-½ 1 ½)	-2.74(6)	-0.42(9)	-1.35(4)

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Fig. 3- (a) Magnetization versus field curves for (a) x=0.33 and 0.50 obtained at 4.2 K. (b) M(H) for x=0.25 (ZFC, 5K) obtained during a hysteresis cycle.
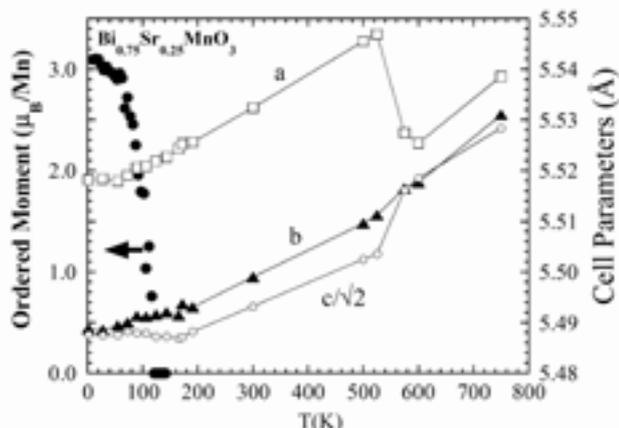

Fig. 4- $Bi_{0.75}Sr_{0.25}MnO_3$: Evolution of lattice parameters across the magnetic and electronic transitions (right axis). Ordered magnetic moment (from neutron data, left axis).
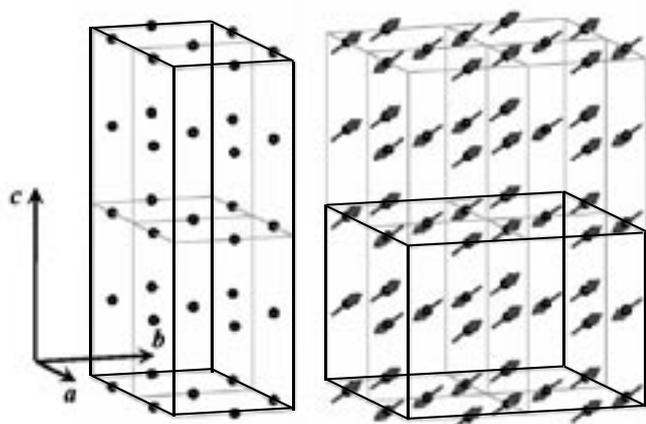

Fig. 5- Schematic view of the magnetic structure determined for $Bi_{0.75}Sr_{0.25}MnO_3$ (Table I). Comparison of the superstructure crystal (left) and magnetic (right) cells (thick lines).

The persistence of ferromagnetism with increasing x in the magnetization of $Bi_{1-x}Sr_xMnO_3$ (found to vanish only x>0.4), was interpreted as a progressive dilution of the ferromagnetic ground state of $BiMnO_3$ (17). Such scenario would require the persistence of regions in the material retaining the peculiar monoclinic structure of $BiMnO_3$. Microscopic regions of C2 symmetry were neither detected in our ultra-high-resolution synchrotron measurements, nor in TEM data of the x=0.25 compound. On the contrary, $Bi_{0.75}Sr_{0.25}MnO_3$ presents a new and well-crystallized charge modulation, very stable against temperature and compositional fluctuations. So, our current knowledge of this system suggests a robust ordered phase, which cannot be seen as the result of a progressive disordered dilution of the $BiMnO_3$ structure by Sr substitution.

The structural study reported in Ref. 8 was based on diffraction data taken between RT and 750 K. The evolution of the lattice parameters in the temperature interval 3K-750 K is shown in Fig. 4. A neutron diffraction study of the magnetic order below T_N=120 K was performed, which established an AFM order. All the details can be found in (18). The best solution was obtained with the same value of the magnetic moment in all Mn sites, and it is summarized in Table I. It corresponds to a pseudo-CE type magnetic order but the spin orientation presents no-null projections along the three directions of the crystallographic cell. Referred to the average Ibmm cell, ordered moments in the AFM collinear structure align according to m=(m_x=2.74(6),m_y=0.42(9),m_z=1.35(4)) μ_B (Fig. 8). A schematic view of the magnetic ordering proposed for $Bi_{0.75}Sr_{0.25}MnO_3$ is shown in Fig. 5. A derivation or variation of the "average" pseudo-CE magnetic structure is not excluded if a much larger number of magnetic reflections were collected from a single crystal. A key issue is to know how extra e_g electrons are distributed randomly or in ordered manner. A more detailed picture of this novel orbital order structure requires single crystal neutron diffraction experiments, in order to solve completely the superstructure.

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4. CONCLUSIONS

After the pioneer studies of Chiba et al (17) in this work we have studied the origin and nature of ferromagnetism in Bi$_{1-x}$Sr$_x$MnO$_3$ at moderate doping, and the possible coexistence of ferromagnetism and charge/orbital order in Bi$_{3/4}$Sr$_{1/4}$MnO$_3$. Multi-phase segregation tendencies were not observed in the present ordered phase. Microphase separation into ferromagnetic and antiferromagnetic regions was not detected and is unlikely in Bi$_{3/4}$Sr$_{1/4}$MnO$_3$. This oxide exhibits a well-crystallized modulation, very robust against temperature and compositional fluctuations. The periodicity of the magnetic structure (2a$\times$2b$\times$c magnetic cell) differs from the dimensions of the superstructure cell (2a$_p\sqrt{2}$ $\times$ a$_p\sqrt{2}$ $\times$ 4a$_p$). The net ferromagnetic moment detected in previous works is not related to the persistence of the peculiar ferromagnetic structure of the pure BiMnO$_3$ phase. In zero field the magnetic structure is antiferromagnetic, ruling out the apparition of spontaneous ferromagnetism. However, the application of magnetic fields produces a continuous progressive canting of the moments, clearly visible even for relatively small fields (H<<1 T), but no appreciable changes in the resistivity. Application of high fields produces a remarkable and reversible spin polarization (under 30 T, the ferromagnetic moment is ~3 μ_B/Mn), without any sign of charge or orbital order melting. The coexistence of ferromagnetism and charge order at low and very-high fields is a remarkable property of this system.

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REFERENCES

1. C. Frontera, J. L. García-Muñoz, A. Llobet, C. Ritter, J.A. Alonso, and J. Rodríguez-Cavajal, "Dependence of the physical properties of Nd$_{0.5}$Ca$_{0.5}$MnO$_{3+\delta}$ on the oxidation state of Mn", Phys. Rev. B 62, 3002 (2000).
2. J.L. García-Muñoz, C. Frontera, M.A. García-Aranda, A. Llobet and C. Ritter, "High temperature charge and orbital ordering in Bi$_{1/2}$Sr$_{1/2}$MnO$_3$", Phys. Rev. B 63, 064415 (2001).
3. M. Hervieu, A. Maignan, C. Martin, N. Nguyen, and B. Raveau, "Double Mn³⁺ stripes in Bi$_{1-x}$Sr$_x$MnO$_3$: New type of charge ordering at room temperature", Chem. Mater. 13, 1356 (2001).
4. P. Beran, S. Malo, C. Martin, A. Maignan, M. Nevrîva, M. Hervieu, and B. Raveau, Solid "Bi$_{0.5}$Sr$_{0.5-x}$Ca$_x$MnO$_3$ phase diagram: a discontinuous evolution", State Sci. 4, 917 (2002).
5. C. Frontera, J. L. García-Muñoz, C. Ritter, L. Mañosa, X. Capdevila, and A. Calleja, "Enhanced stability of charge-order in underdoped Bi$_{3/4}$Sr$_{1/4}$MnO$_3$", Solid State Commun. 125, 277 (2003).
6. M. Hervieu, S. Malo, O. Perez, P. Beran, C. Martin, and B. Raveau, "New Type of Charge/Orbital Ordering above Room Temperature in the Perovskite Bi$_{2/3}$Sr$_{1/3}$MnO$_3$", Chem. Mater. 15, 523 (2003).
7. J.L García-Muñoz, C. Frontera, M.A.G. Aranda, C. Ritter, A. Llobet, M. Respaud, M. Goiran, H. Rakoto, O. Masson, J. Vanacken and J.M. Broto, "Charge and Orbital Order in Rare-Earth and Bi Manganites: a Comparison", J. of Solid State Chem. 171, 84 (2003).
8. C. Frontera, J. L. García-Muñoz, M. Hervieu, M.A.G. Aranda, C. Ritter, Ll. Mañosa, X. G. Capdevila and A. Calleja, "New charge and Zener polaron ordered phase in Bi$_{3/4}$Sr$_{1/4}$MnO$_3$", Phys. Rev. B 68, 0134408 (2003).
9. R. J. Goff and J. P. Attfield, "Charge ordering in half-doped manganites", Phys. Rev. B 70, 140404 (2004)
10. Larochelle, Mehta, Kaneko, K. Mang, AF. Panchula, L. Zhou, J. Arthur, and M. Grevenet, "Nature of e$_g$ Electron Order in La$_{1-x}$Sr$_{1+x}$MnO$_4$", Phys. Rev. Lett. 87, 95502 (2001).
11. T. Atou, H. Chiba, K. Ohoyama, Y. Yamaguchi, and Y. Syono, "Structure Determination of Ferromagnetic Perovskite BiMnO$_3$", J. Solid State Chem. 145, 639 (1999).
12. N.A. Hill and K.M. Rabe, "First-principles investigation of ferromagnetism and ferroelectricity in bismuth manganite", Phys. Rev. B 59, 8759 (1999).
13. A. Moreira dos Santos, S. Parashar, A. R. Raju, Y. S. Zhao, A. K. Cheetham and C. N. R. Rao, "Evidence for the likely occurrence of magnetoferroelectricity in the simple perovskite, BiMnO$_3$", Sol. Stat. Comm.122 ,49 (2002).
14. R. Seshadri, N.A. Hill, "Visualizing the role of Bi 6s lone-pairs in the off-center distortion in ferromagnetic BiMnO$_3$", Chem. Mater. 13, 2892 (2001).
15. J. Rodríguez-Carvajal, Physica B 192, 55 (1993).
16. G. Subías, J. García, P. Beran, Miloš Neviva, J. L. García-Muñoz and M. C. Sánchez, "The checkerboard ordered pattern of Bi$_{0.5}$Sr$_{0.5}$MnO$_3$ low temperature phase probed by x-ray resonant scattering", Phys. Rev. B, in press.
17. H. Chiba, T. Atou, and Y. Syono, "Magnetic and Electrical Properties of Bi$_{1-x}$Sr$_x$MnO$_3$: Hole-Doping Effect on Ferromagnetic Perovskite BiMnO$_3$", J. Solid State Chem. 132, 139 (1997).
18. J. L. García-Muñoz, C. Frontera, M. Respaud, M. Giot, C. Ritter, X.G. Capdevila, "Unconventional magnetic properties of Bi$_{0.75}$Sr$_{0.25}$MnO$_3$ (x≈2/8, T$_{CO}$=600 K): ferromagnetism and charge order", Phys. Rev. B 72, 054432 (2005).

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