Anomalously high charge/orbital ordering temperature in Bi$_{0.5}$Sr$_{0.5}$MnO$_3$

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Abstract. Neutron/synchrotron diffraction data and magnetic measurements provide direct evidence of charge/orbital ordering at anomalously high temperatures in Bi$_{0.5}$Sr$_{0.5}$MnO$_3$, as well as in other (Bi, Sr)MnO$_3$ manganites. We report on the electronic and magnetic transitions of these oxides. The origin of the high value of the charge/orbital ordering temperature is discussed.

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Charge-ordering (CO) is a fascinating phenomenon in transition metal oxides with important implications in the ‘colossal’ magnetoresistance (CMR) of manganese perovskites. The discovery of CMR, in Ln$_{1−x}$M$_x$MnO$_3$ manganites (Ln = trivalent lanthanide, M = Ca, Sr, Ba) has led to an explosion of interest in the tendency displayed by many of these manganites to form nanoscopic inhomogeneous states: electronic phase separation and CO phenomena. The stability of CO is determined by the Coulomb repulsion between charges and the elastic energy from the static Jahn-Teller (JT) deformations that accommodate the associated orbital ordering (OO). Although covalency effects can be significant, the ionic picture describes the CO as a real orbital ordering (OO). Although covalency effects can be significant, the ionic picture describes the CO as a real orbital ordering (OO).

1 Experimental details

Details about the synthesis of polycrystalline Bi$_{1−x}$Sr$_x$MnO$_3$ oxides are given elsewhere [2, 3]. Neutron (NPD) and synchrotron (SXRPD) diffraction data were collected at the ILL (D2B) and the ESRF (BM16) in Grenoble in the temperature range 1.5−700 K. Moreover, X-ray laboratory thermomodificractometry, magnetotransport up to 8 T, and magnetization measurements up to 700 K were also carried out. High magnetic fields were performed at the facilities of the LVSM (Leuven). Using the discharge of a bank capacitor in the coil, pulsed fields up to 50 T with a duration time of 20 ms were used.

2 Results and discussion

First indications for the presence of CO at high temperatures were seen in the susceptibility data. Figure 1 presents the inverse of the susceptibility of Bi$_{0.5}$Ca$_{0.5}$MnO$_3$ and Bi$_{0.5}$Sr$_{0.5}$MnO$_3$ measured under 1 T of applied field up to 800 K. CO/ OO transition produces a peak in $\chi^{-1}(T)$ curves. This is due to the change from ferromagnetic (FM), $T > T_{CO}$, to antiferromagnetic (AFM), $T < T_{CO}$, of the fluctuating (paramagnetic) moments produced by the OO. It can be clearly appreciated that the anomaly in the $\chi^{-1}(T)$ curve of Bi$_{0.5}$Sr$_{0.5}$MnO$_3$ takes place (≈ 525 K) well above that of Bi$_{0.5}$Ca$_{0.5}$MnO$_3$ (≈ 320 K). Such a high temperature transition can also be identified in Bi$_{0.3}$Sr$_{0.7}$MnO$_3$ (≈ 475 K) compound (inset of Fig. 1). Based on high temperature NPD and SXRPD data, we observed the appearance, below the high temperature transition, of $q = 1/2b^*$ structural modulations in the Bi$_{0.5}$Sr$_{0.5}$MnO$_3$ sample. These modulations are associated to the periodic ordering concomitant with the OO/CO phase. To illustrate this, the inset of Fig. 2 shows, as a function of temperature, in the integrated intensity of the (1 ½ 0) superlattice peak (SXRPD, $\lambda = 0.45023$ Å) as measured for Bi$_{0.5}$Sr$_{0.5}$MnO$_3$ on heating. Its evolution confirms that the $q = 1/2b^*$ structural modulation induced by the periodic OO disappears at $T_{CO} \approx 500$ K. Above $T_{CO}$, neutron data was consistent with a single-phase diffraction.
pattern (Pbnm). However, the sample actually splits into two macroscopic phases with slightly different lattice parameters when cooled below $T_{CO}$. Figure 2 illustrates the evolution of the refined lattice parameters for, hereafter, Orth1 (55 wt.%, $q = 1/2b^*$) and Orth2 (45 wt.%, $q = 0$) phases, as obtained from laboratory X-ray data. Those phases present different JT deformation parameter $\sigma_{JT} \equiv \sqrt{\sum_i (d_{Mn-O_i} - \langle d_{Mn-O} \rangle)^2}$: $\sigma_{JT} = 0.023$ and 0.016 at RT and $\sigma_{JT} = 0.030$ and 0.017 at $T = 1.5$ K for Orth1 and Orth2 phases respectively.

NPD data have confirmed that Orth1 and Orth2 phases present different magnetic structures below $T_N \approx 110$ K [4]. The $q = 1/2b^*$ modulated phase (Orth1) adopts the AFM CE type structure while Orth2 orders with the AFM A-type structure [refined ordered moment, 2.7(1)$\mu_B$/Mn]. Macroscopic phase separation is commonly observed in samples with even very small compositional fluctuations as the CE and A type phases have very similar energies [5]. Actually, magnetic intensities for Orth1 indicate the simultaneous presence of CE and pseudo-CE magnetic peaks. These two sets can be satisfactorily reproduced by assuming that $m_x$ and $m_y$ components of the magnetic moment display CE-type ordering, while the component along the [001] direction ($m_z$) presents a pseudo-CE-like order [6] [refined ordered moments, 2.5(1) and 2.3(1)$\mu_B$/Mn at the two Mn sites of CE structure]. The corresponding magnetic structures are shown in Fig. 3. The gray arrows in Fig. 3a are projections of the moments at the $z = 0$ plane to illustrate the angle between the moments of neighboring Mn ions.

Furthermore, we want to emphasize some interesting features of the Orth2 phase (A-type). We believe that the current picture for manganites with $x \approx 0.5$ and A-type magnetic ordering (the “metallic antiferromagnetic” picture having conducting FM planes) is not valid in the present case. The reasons are: first, the very high resistivity and the absence of magnetoresistance (at $\mu_0H = 8$ T) displayed by this phase, as shown in Fig. 4a (it must be taken in to account that the amount of Orth2 phase found, 45 wt.%, ensures that it percolates the sample). Second, the much higher values of $T_{OO}$ compared to previous OO manganites presenting A-type magnetic ordering, which evidences a very high stability of this phase. As reported in [3], the weakly screened $6s^2$ Bi electrons in Bi-Sr-Mn-O perovskites makes the charges to be much more localized than,
for instance, in Pr$_{0.5}$Sr$_{0.5}$MnO$_3$ or Nd$_{0.5}$Sr$_{0.5}$MnO$_3$ (for which the resistivity at low temperature is $\sim 10^4$ times lower). The lone pair effect is, due to this charge localization, responsible of the high $T_{CO}$ in Bi$_{0.5}$Sr$_{0.5}$MnO$_3$. Such localization, thus, evidences that the FM planes cannot be conducting or metallic in the present Orth2 A-type phase. In addition, the lattice strain energy due to Jahn-Teller distortions and the Coulomb repulsion favor the ordered pattern of $e_g$ electrons, instead of them being randomly placed. In the last case, we would expect a higher magnetic disorder. Therefore, we are led to conclude that the presence of CO of the type pointed out theoretically in [7] (with $q = 0$) is very probably the ground state of the present Orth2 A-type phase.

The isothermal $M(H)$ curve and its derivative $\frac{dM}{d\mu_0 H}$ of Bi$_{0.5}$Sr$_{0.5}$MnO$_3$ (Fig. 4b) at $T = 4.2$ K indicates that a field induced transition is only achieved at $\mu_0 H \approx 37$ T. Moreover, a magnetic field $\mu_0 H = 48$ T is not enough to saturate the magnetic moment of the Mn ions (3.5 $\mu_B$/Mn). This evidences that the OO of the A-type phase, and the CO of the CE-type phase are much more stable than in other rare-earth based manganites like Pr$_{0.5}$Sr$_{0.5}$MnO$_3$ or Nd$_{0.5}$Sr$_{0.5}$MnO$_3$ and is in agreement with the very high $T_{CO}$ reported for this compound.

Phase coexistence below $T_{CO}$ has been also observed in the Bi$_{0.33}$Sr$_{0.67}$MnO$_3$ sample, one phase being pseudotrangular (45 wt. %) and the other orthorhombic (55 wt. %) and presenting a $q = 1/3b^*$ structural modulation. Below $T_N \approx 200$ K, the latter exhibits a magnetic ordering similar to that reported for the CO phase of La$_{0.33}$Ce$_{0.67}$MnO$_3$ [8]. The former (having $q = 0$), exhibits a pseudo-A-type magnetic structure with the magnetic moments displaying partial misalignment probably due to the presence of defects and/or inhomogeneities.

3 Conclusions

To conclude, the reported CO/OO transitions occur some $\approx 450$ K above the expected temperature in the current scenario (bandwidth tuning mechanism) for (Ln, Ca, Sr)MnO$_3$ manganites. The possibility that Bi and Sr form some kind of ordering was examined and has to be ruled out in these oxides. According to the discussion given in [3] the 6$s^2$ lone pair character is probably strongly screened in (Bi, Ca)MnO$_3$ compounds but not in those doped with Sr. This pushes $T_{CO}$ up to 525 K and makes that Orth2 A-type phase probably presents CO.

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References