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Abstract. The magnetic properties of solid solutions based on lanthanum and bismuth manganites were investigated. It is established that the substitution of La^{3+} ions by Bi^{3+} ones causes the transition from the ferromagnetic to the antiferromagnetic state while $BiMnO_3$ is a ferromagnet. The results are explained in terms of the superexchange interaction via anions and local distortions of the crystal structure.

1. Introduction

The perovskites $La_{1-x}Sr_x(Mn^{3+}_{1-x}Mn^{4+}_x)O_3$ (for $x \geqslant 0.15$) have been of great interest for many years since they exhibit various antiferromagnet–ferromagnet and insulator–metal transitions [1]. In recent times there has been a renewed interest in this area following the discovery of a colossal magnetoresistive effect in these compounds [2]. In order to explain the correlation between electrical and magnetic properties Zener introduced a special form of exchange interactions via carriers—double exchange [3]. Further Goodenough has suggested that the ferromagnetism in this material is governed not only by strong double exchange but also by the orbital ordering in the system of the Jahn–Teller Mn^{3+} ions [4]. It has been shown that magnetic properties are correlated with the distance between the manganese ions [5]. In [6] and [7] arguments are presented in favour of the fact that the sign of the exchange interactions is determined by the magnitude of the Mn–O–Mn angle. There is no general agreement concerning the exchange interaction mechanism in orthomanganites.

It is well known that manganites with the formula $AMnO_3$ (where A is La or a rare earth ion) are antiferromagnets. The magnetic properties of $BiMnO_3$ perovskite differ sharply from those of the other orthomanganites. It is demonstrated that this compound is a soft magnetic material, with a spontaneous magnetic moment at 4.2 K close to the value expected for the ferromagnetic ordering of magnetic moments of the Mn^{3+} ions. The temperature of transition to the paramagnetic state is 98 K. In [8] it was reported that the replacement of Bi ions by Pb^{2+} in $Bi_{1-x}Pb_xMnO_3$ gives rise to the destruction of the ferromagnetic order accompanied by the crystal structure transforming from triclinic to cubic or tetragonal. The magnetic behaviour of the Bi-containing manganite is not clearly understood at the moment.

It is well known that the magnetic properties of $LaMnO_3$ depend on the oxygen content. In recent times it has been shown that nonstoichiometry might arise due to a lanthanum

deficit [9]. -Magnetic properties of manganites with such a type of nonstoichiometry had not been studied.

We have made a magnetic study of the $La_{1-x}MnO_{3+y}$, $La_{1-x}Bi_xMnO_3$, $La_{0.8-x}Bi_xMnO_3$ and $La_{2/3-x}Bi_xSr_{1/3}MnO_3$ compounds with the goal of better understanding of the magnetic properties of manganese-containing compounds with perovskite structure. It is shown that the replacement of Mn^{3+} ions by Mn^{4+} in $La_{1-x}MnO_{3+y}$ leads to the antiferromagnet–ferromagnet transition while a similar process for $BiMnO_3$ gives rise to the collapse of the ferromagnetic state.

2. Experimental method

The $La_{1-x}MnO_{3+y}$, $La_{1-x}Bi_xMnO_3$, $La_{0.8-x}Bi_xMnO_3$ and $La_{2/3-x}Bi_xSr_{1/3}MnO_3$ samples were prepared from high-purity oxides or carbonates La_2O_3, Bi_2O_3, Mn_2O_3 and $SrCO_3$ using conventional ceramic technology. As the bismuth content in the solid solution increases the calcination temperature decreases from 1400 °C ($x = 0$) to 900 °C. The Bi-containing samples were slowly cooled (150° h^{-1}) in a furnace. The $LaMnO_{3+y}$ and $La_{1-x}MnO_{3+y}$ samples were annealed in air at 900 °C or in vacuum at up to 10^{-8} Pa. The $BiMnO_3$ sample was prepared under high-pressure conditions ($P = 5$ GPa, $T = 900$ °C).

The overall Mn^{4+} content for the $La_{1-x}MnO_{3+y}$ series was determined by standard wet-chemical chromatometric titration. Chemical analyses of the Bi-containing samples were not performed, therefore the denoted compositions are the nominal ones.

X-ray structural analysis was performed on a DRON-3 diffractometer in Cr-Kα radiation. Single-phase samples were selected for magnetic measurements. The magnetization was measured with a vibrating sample magnetometer in steady fields up to 120 kOe. Ac magnetic susceptibility was measured using a mutual inductance bridge.

3. Results

The x-ray patterns show the O^I orthorhombic structure of the $LaMnO_{3+y}$ system at $y < 0.05$ ($c/\sqrt{2} < a < b$, orbital ordered phase), the O orthorhombic structure at $0.07 < y < 0.11$ ($a < c/\sqrt{2} < b$, orbital disordered phase) and the rhombohedral one at $y \geqslant 0.11$. The samples of $La_{0.85}MnO_{3+y}$ annealed at 1073 K in air for 20 h and cooled slowly from 1573 K have a rhombohedrally distorted unit cell in contrast to the specimens reduced in vacuum characterized by the O^I orthorhombic structure. According to the x-ray data the $LaMnO_{3.13}$ and $La_{0.85}MnO_{2.95}$ compounds are rhombohedral. The unit cell parameters are listed in table 1.

The specimens of $LaMnO_{3+y}$ ($0.08 \leqslant y \leqslant 0.2$) show weak spontaneous magnetization (σ_s) vanishing near 147 K (figure 1). It seems that the stoichiometric lanthanum manganite is a weak ferromagnet with $T_c = 147$ K and ($\sigma_s = 2.0$ emu g^{-1} at 4.2 K. The deficit of La^{3+} cations leads to an insignificant decrease in T_c (figure 1). The $La_{1-x}MnO_{3+y}$ samples reduced in vacuum are hard magnetic materials. The coercive field value reaches 16 kOe (figure 2(a)). The samples $La_{1-x}MnO_{3+y}$ with a high concentration of Mn^{4+} ions are ferromagnets with low coercive field (figure 2(b)). In accordance with ac-susceptibility and magnetization measurements $LaMnO_{3.13}$ and $La_{0.85}MnO_{2.95}$ are ferromagnets with Curie temperatures of 150 and 240 K respectively (figure 3).

The cubic symmetry distortion of $La_{1-x}Bi_xMnO_3$ and $La_{0.8-x}Bi_xMnO_{3+y}$ in the range $0.4 \leqslant x \leqslant 0.6$ and $0.2 \leqslant x \leqslant 0.6$, respectively, is so small that the x-ray diffraction lines are indexed based on a cubic perovskite pseudocell containing one formula unit. On

Table 1. The symmetry (S), unit cell parameters (a, b, c, β), magnetic state (wF, weak ferromagnet; F, ferromagnet; AS, antiferromagnet with ferromagnetic cluster inclusions), spontaneous magnetization (σ_s) and characteristic temperature (T_c) for some investigated compounds.

| Formula	S	a (Å)	b (Å)	c (Å)	α (°)	β (°)	Magnetic state	σ_s (emu g^{-1})	T_c (K)
$LaMnO_{2.99}$	O^I	5.530	7.770	5.730			wF	2.0	147
$LaMnO_{3.13}$	R	3.893				89.40	F	80	150
$La_{0.85}MnO_{2.80}$	O^I	5.520	7.770	5.710			wF	2.7	138
$La_{0.85}MnO_{2.95}$	R	3.887				89.50	F	82	240
$La_{0.4}Bi_{0.6}MnO_3$	C	3.906					AS	12	70
$La_{0.4}Bi_{0.4}MnO_3$	C	3.911					F	46	90
$La_{0.2}Bi_{0.6}MnO_3$	C	3.918	3.880				AS	14	60
$BiMnO_3$	Tr	7.860	7.980	7.860	91.20	90.35	F	56	98
$La_{2/3}Sr_{1/3}MnO_3$	C	3.865					F	94	375
$La_{0.22}Bi_{0.44}Sr_{0.34}MnO_3$	C	3.910					AS	15	320
$Bi_{2/3}Sr_{1/3}MnO_3$	T	3.906		3.880			AS	—	50
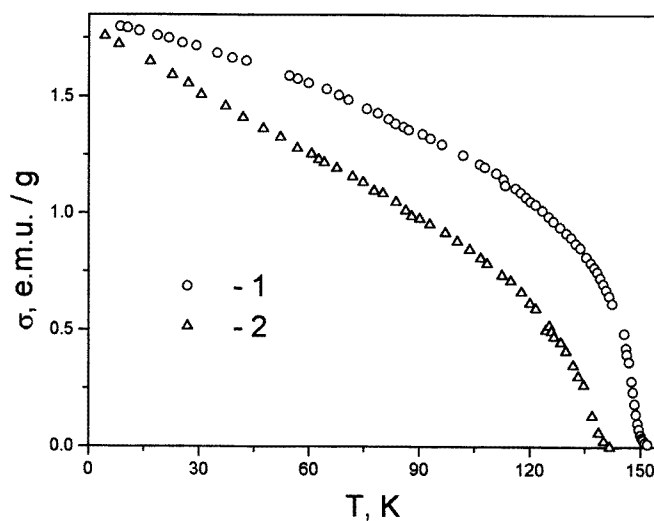
Figure 1. The temperature behaviour of residual magnetization for $LaMnO_{2.99}$ (1) and $La_{0.85}MnO_{2.80}$ (2).

substituting La^{3+} by Bi^{3+} in $La_{0.8-x}Bi_xMnO_3$ solid solutions the cubic unit cell parameter increases gradually (table 1). It is interesting to note that the unit cell volume of $LaMnO_3$ and $La_{2/3}Sr_{1/3}MnO_3$ is less than that of Bi-containing manganites, although it is known that the replacement of La^{3+} by Bi^{3+} in $La_{1-x}Bi_xFeO_3$ perovskites leads to the decrease of the unit-cell volume. Such a behaviour arises, apparently, due to local crystal structure distortions around the Bi ions in manganites.

The size of the Bi^{3+} ion depends on the degree of $6s^2$ lone-pair character of the chemical bond. When Bi is forced into high symmetry the size of Bi^{3+} is less than that of La3+, but when the lone-pair character is dominant the Bi^{3+} compound is distorted and its volume may be more than that of the La^{3+} compounds.

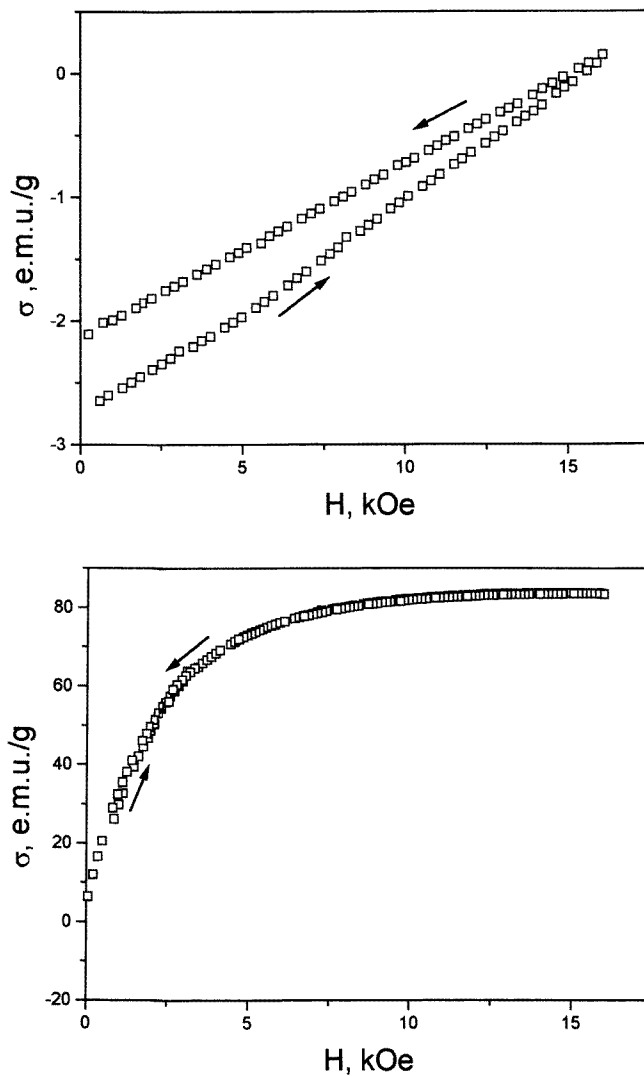The magnetization and Curie temperature decrease with increasing bismuth content in

Figure 2. The dependence of magnetization on magnetic field at 4.2 K for field cooled samples of (*a*) $La_{0.85}MnO_{2.80}$ and (*b*) $La_{0.85}MnO_{2.95}$.

$La_{0.8-x}Bi_xMnO_3$ solid solutions. Magnetization of $La_{0.4}Bi_{0.4}MnO_3$ depends on the magnetic history of the sample. Figure 4 represents the magnetization behaviour of $La_{0.4}Bi_{0.4}MnO_3$ after cooling in zero magnetic field (ZFC) and in the measurement field (FC). Below 90 K the FC magnetization is larger than the ZFC values. The magnetization isotherm of $La_{0.4}Bi_{0.4}MnO_3$ at 4.2 K is characterized by a significant paraprocess (figure 5). The spontaneous magnetic moment per formula unit is less than 3 μ_B. The $La_{0.4}Bi_{0.4}MnO_3$ perovskite is probably an inhomogeneous ferromagnet with antiferromagnetic cluster inclusions. The $La_{0.2}Bi_{0.6}MnO_3$ sample is characterized by the presence of a sharp maximum at $T = 40$ K in the temperature dependence of ZFC magnetization (figure 4(b)). Below 60 K the ZFC and FC magnetizations do not coincide. Replacement of La^{3+} ions by Bi^{3+}
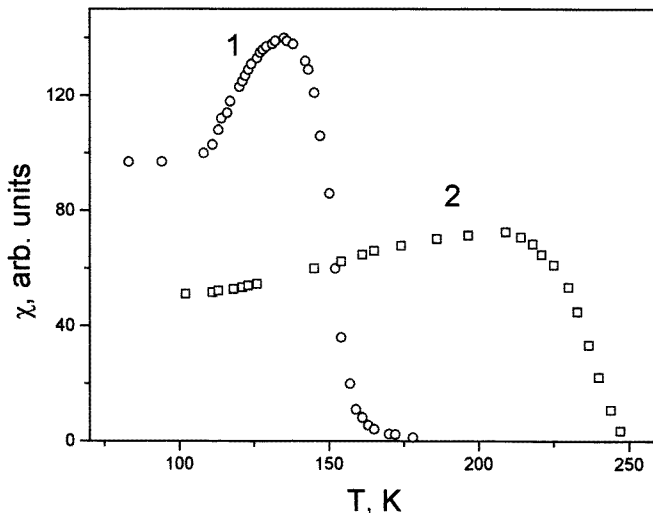
Figure 3. Ac susceptibilities against temperature for LaMnO$_{3.13}$ (1) and La$_{0.85}$MnO$_{2.95}$ (2).

up to $x = 0.6$ leads to an abrupt decrease in the spontaneous magnetization and increase of the paraprocess (figure 5). Similar behaviour is characteristic of inhomogeneous magnetics consisting of a mixture of both antiferromagnetic and ferromagnetic clusters. The magnetic behaviour La$_{1-x}$Bi$_x$MnO$_3$ series is analogous to that for La$_{0.8-x}$Bi$_x$MnO$_3$. The long-range ferromagnetic order vanishes at $x = 0.5$.

The magnetization measurements indicate that La$_{2/3}$Sr$_{1/3}$MnO$_3$ is a ferromagnet with the highest Curie temperature ($T_C = 375$ K) among orthomanganites with the perovskite structure. The spontaneous magnetic moment per formula unit is 3.6 μ_B at 4.2 K. The substitution of La^{3+} by Bi^{3+} in La$_{2/3-x}$Bi$_x$Sr$_{1/3}$MnO$_3$ leads to a decrease of magnetization; however the Curie temperature changes insignificantly. The magnetization measurements for $x = 0.54$ show small spontaneous magnetization at room temperature. The percolation threshold for this series is $x \approx 0.4$. No sharp anomalies have been observed in the temperature dependence of the magnetization for Bi$_{2/3}$Sr$_{1/3}$MnO$_3$ (figure 6). Both the ZFC and FC magnetizations decrease gradually with increasing temperature. Below 50 K the FC magnetization is higher than the ZFC one. For Bi$_{2/3}$Sr$_{1/3}$MnO$_3$ the magnetization–field ($\sigma(H)$) dependence reveals no spontaneous magnetization at 4.2 K (figure 5). However the magnetization in high magnetic field is relatively large. It is apparent that the magnetization is caused by the short-range ferromagnetic ordering.

With increasing bismuth concentration in La$_{1-x}$Bi$_x$MnO$_3$ and La$_{0.8-x}$Bi$_x$MnO$_3$ solid solutions the resistivity decreases insignificantly at room temperature. The ferromagnet–paramagnet transition in these materials is not accompanied by the metal–insulator transition. Such a behaviour of electrical conductivity is in contrast with that of La$_{1-x}$Sr$_x$MnO$_3$ where strong correlation between the electrical and magnetic properties was found [1]. BiMnO$_3$ is an insulator with resistivity $\rho \approx 10^3$ Ω cm at room temperature. With decreasing temperature down to 77 K the resistivity increases by a factor of 10^3. The substitution of Bi^{3+} by Sr^{2+} in Bi$_{1-x}$Sr$_x$MnO$_3$ solid solutions leads to a strong increase of electrical conductivity, however, Bi$_{2/3}$Sr$_{1/3}$MnO$_3$ is a semiconductor below 700 K. Above 700 K the activation energy vanishes gradually and conductivity decreases with increasing temperature as for a metal.
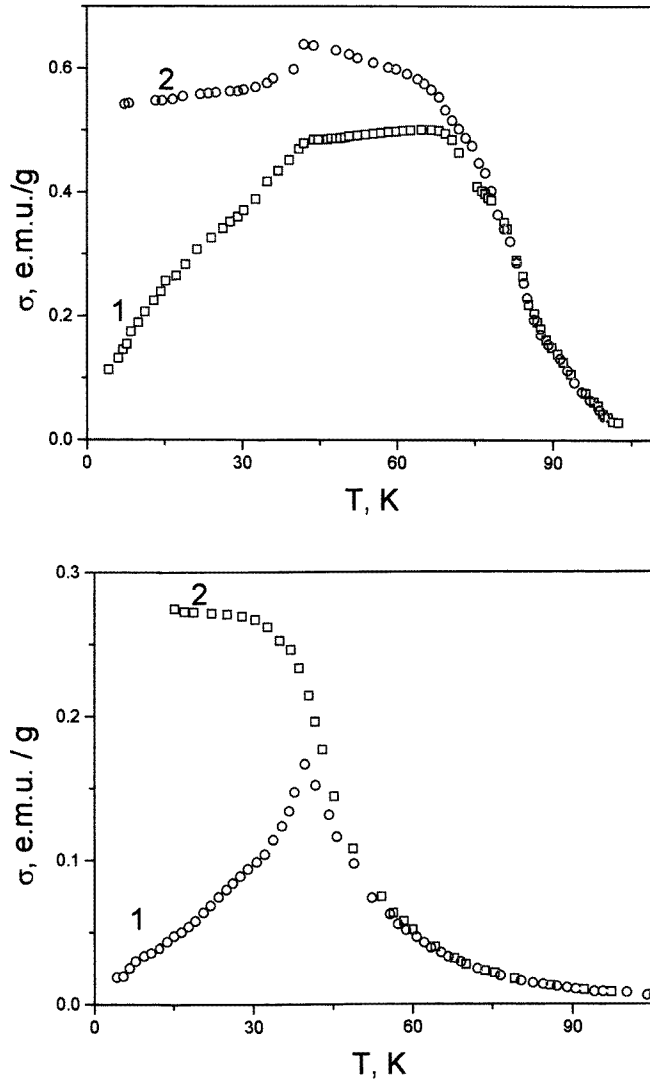
Figure 4. ZFC (1) and FC (2) magnetization against temperature for (*a*) $La_{0.4}Bi_{0.4}MnO_3$ and (*b*) $La_{0.2}Bi_{0.6}MnO_3$ at $H = 15$ Oe.

The mechanism of exchange interactions connected with the exchange via charge carriers does not play an important role in the magnetism of Bi-containing manganites. The reason is that the appearance of ferromagnetism in the $Bi_{1-x}Sr_xMnO_3$ system is accompanied by a decrease of conductivity in contrast with the behaviour of $La_{1-x}Sr_xMnO_3$ system. We think that the the exchange via Bi^{3+} ions is insignificant because the addition of Bi ions to the lanthanum manganite leads to the disappearance of ferromagnetism while $BiMnO_3$ is a ferromagnet (figure 5).

The most adequate interpretation of magnetic properties could be obtained within the model of exchange interactions via anions. The local crystal structure distortions should be taken into account. The ferromagnetic fraction of the exchange is determined by electron
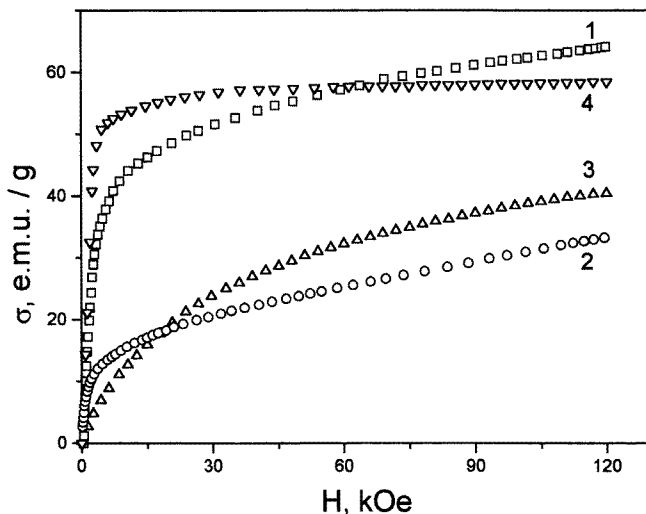
Figure 5. The field dependences of magnetization at 4.2 K for $La_{0.4}Bi_{0.4}MnO_3$ (1), $La_{0.2}Bi_{0.6}MnO_3$(2), $Bi_{2/3}Sr_{1/3}MnO_3$ (3) and $BiMnO_3$ (4).

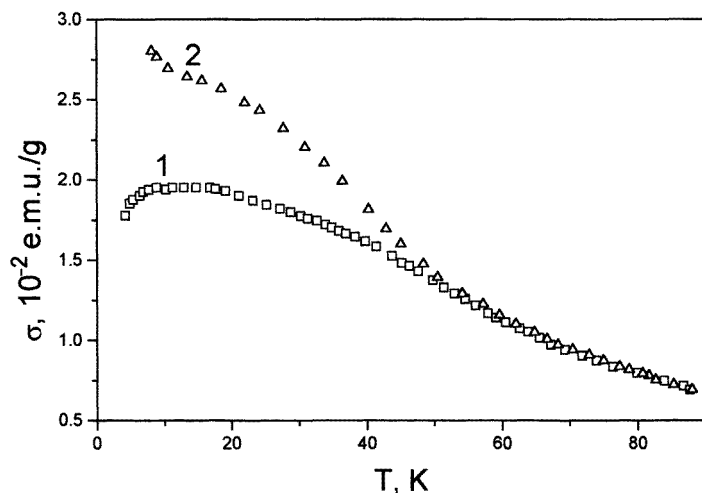**Figure 6.** ZFC (1) and FC (2) magnetization against temperature for $Bi_{2/3}Sr_{1/3}MnO_3$ at $H = 15$ Oe.

transfer from the half-filled orbitals into an unoccupied orbital of the nearest manganese ions. The antiferromagnetic part of the exchange is determined by transitions between half-filled orbitals. In the case of the relatively broad 3d band (the Mn–O–Mn angle is close to 180°) the contribution of the first type of transfer is dominant, thus leading to ferromagnetism [7].

The replacement of La^{3+} by Bi^{3+} leads to the increase of the Mn–Mn distance and stabilizes the cubic or tetragonal structure (table 1). Despite a small crystal structure distortion the long-range ferromagnetic order is collapsed.

We believe that the replacement of La^{3+} by Bi^{3+} ions results in the creation of microdomains with local crystal structure distortions. Their size is of the order of the

unit cell. The reason for local structure distortions is the $6s^2$ lone-pair character of the Bi^{3+}–O^{2-} chemical bond.

The long-range ordering of the distortions is caused by the lowering macroscopic lattice symmetry to triclinic as observed for $BiMnO_3$. Supposing that local distortions are distributed statistically, the macroscopic cubic symmetry is preserved. The cluster spin glass properties of the Bi-containing cubic perovskites are apparently due to the considerably non-correlated local lattice distortions. It is worthwhile to note that the lattice distortions could provoke the orbital ordering. It is possible that the ferromagnetic state in $BiMnO_3$ is specified by the complex ordering of $d_{x^2-y^2}$ and d_{z^2} orbitals of the Mn^{3+} ions.

Acknowledgment

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