Anomalous magnetic properties of Bi-containing manganites

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We have investigated the magnetic properties of $BiMnO_3$ in which the Bi^{3+} ion is replaced by La^{3+}, Pb^{2+}, Ca^{2+}, while the Mn^{3+} ion is replaced by Mg^{2+}, Co^{2+}, and Nb^{5+}. We show that, independent of the type of replacement ion, even negligible replacements give rise to destruction of the ferromagnetic order, although the distortion of the crystal structure may be very small. Our results are explained in terms of a model according to which $BiMnO_3$ is subject to antiferrodistortive ordering involving the $d_{x^2-y^2}$ orbitals of 50% of the manganese ions and the d_{z^2} orbitals of the remaining 50% of these ions.

1. INTRODUCTION

It is known that manganites with the formula $AMnO_3$ (where A is La, Y, or a rare earth ion) with the perovskite structure are antiferromagnets.[1] In $LaMnO_3$, $PrMnO_3$, and $NdMnO_3$, the magnetic structure has been identified as A-type by the method of neutron diffraction. A characteristic of this structure is the fact that the magnetic moments in the (a,b) planes are ordered parallel, with antiferromagnetic coupling between the planes.[1] In $TbMnO_3$ a spiral magnetic structure was observed by neutron diffraction.[2] The A-type magnetic structure is well explained by the orbital ordering of the d_{z^2} manganese orbitals, which is antiferrodistortive in nature.[3]

The magnetic properties of $BiMnO_3$ differ sharply from those of the other manganites with perovskite structure. In Refs. 4,5 it was shown that this compound is a magnetic material, with a spontaneous magnetic moment at 4.2 K close to the value expected for ferromagnetic ordering of the magnetic moments of the Mn^{3+} ions. The transition temperature to the paramagnetic state is about 100 K.

Whereas the rare-earth manganites are characterized by an O' orthorhombic structural distortion, the structure of $BiMnO_3$ exhibits a relatively large triclinic distortion. In Ref. 5 the ferromagnetism of $BiMnO_3$ was explained by assuming that there is no orbital ordering in this compound, and that the spontaneous magnetization is caused by dynamic correlations in the orbital positions. However, the reason why the cooperative Jahn–Teller effect is removed are not understood. In Ref. 6, the magnetic properties of $BiMnO_3$ were explained by analyzing the Mn–O–Mn angles; the authors concluded that $BiMnO_3$ should be ferromagnetic, independent of the type of orbital ordering. However, the correctness of the calculations given in Ref. 6, which were carried out without knowing the ion coordinates, is doubtful; furthermore, the almost cubic compound $Bi_{0.6}Pb_{0.4}MnO_{2.8}$ has properties close to those of spin glasses, although according to Ref. 6 this compound should also be ferromagnetic.

Therefore, we have undertaken a detailed study of these compounds, with a goal of better understanding the properties of Bi-containing manganites.

2. EXPERIMENTAL METHOD

We synthesized the compounds $BiMnO_3$, $(Bi_{1-x}Pb_x)MnO_{3-\lambda}$ $(x \leqslant 0.5)$, $Bi_{0.9}Ca_{0.1}MnO_{2.95}$, $Bi(Mn_{0.9}B^{2+}_{0.1})O_{2.95}$ (where $B=Mg^{2+}$, Ni^{2+}, Co^{2+}), and $Bi(Mn^{3+}_{0.9}Nb^{5+}_{0.1})O_{3.1}$, under high pressures ($P=5$ GPa) and temperatures 800–900 °C; the system $Bi_{1-x}La_xMnO_3$ $(0.3 \leqslant x \leqslant 1)$ was obtained at ordinary pressures. As the bismuth content increases, the calcination temperature decreases from 1300 °C ($x=1$) to 1100 °C ($x=0.3$). $Bi_{0.7}Sr_{0.3}(Mn^{3+}_{0.7}Mn^{4+}_{0.3})O_3$ was obtained by calcination in air at $T=1150$ °C.

X-ray structural analysis was carried out using a DRON-3 diffractometer based on the K_α line of Fe. We selected single-phase samples (no more than 4% impurities) for the magnetic and electrical measurements. The magnetization was measured with a vibrating magnetometer, the *ac* susceptibility with a mutual inductance bridge. Contacts were obtained by rubbing on an indium–gallium eutectic.

3. RESULTS OF X-RAY STRUCTURAL ANALYSIS

According to our investigations, $BiMnO_3$ is characterized by a triclinically distorted unit cell; like the authors of Ref. 7, we observed superstructure lines, indicating an increase in the length of the unit cell edges by a factor of two. The unit cell parameters were: $a=c=7.86$ Å, $b=7.98$ Å, $\alpha=91°20'$, and $\beta=90°35'$, with $V/8=61.59$ Å^3. It is interesting to note that the unit cell volume of $LaMnO_3$ is $V=61.06$ Å^3, i.e., smaller than that of bismuth manganite, although it is well known that the ionic radius of La^{3+} is larger than that of Bi^{3+}.

In Table I we list the results of our x-ray structural investigations of samples in which Bi ions are replaced by Pb^{2+}. All the samples were obtained at $P=5$ GPa and $T=800$ °C, but from different batches. The samples were placed either directly onto the graphite heater, or inside a nickel capsule which protected them from reduction of the manganese by graphite.

It is clear from this table that the replacement causes an abrupt decrease in the magnitude of the distortion. This was especially noticeable when samples of $Bi_{0.7}Pb_{0.3}MnO_{2.85}$ containing oxygen vacancies were syn-

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TABLE I. Unit cell parameters of the compounds $Bi_{1-x}Pb_xMnO_{3-\lambda}$.

composition	batch	medium	symmetry	parameters
$BiMnO_3$	$Bi_2O_3+Mn_2O_3$	nickel	Tr	$a = c = 7.86$ Å, $b = 7.98$ Å $\alpha = 91°20'$, $\beta = 90°35'$ $V/8 = 61.59$ Å^3
$Bi_{0.8}Pb_{0.2}MnO_3$	$0.4Bi_2O_3 + 0.2PbO+$ $+0.4Mn_2O_3 + 0.2MnO_2$	graphite	R	$a = 3.927$ Å, $\alpha = 90°20'$ $V = 60.54$ Å^3
$Bi_{0.7}Pb_{0.3}MnO_{2.85}$	$0.35Bi_2O_3 + 0.3PbO+$ $+0.15Mn_2O_3$	nickel	K	$a = 3.91$ Å $V = 59.96$ Å^3
$Bi_{0.6}Pb_{0.4}MnO_3$	$0.3Bi_2O_3 + 0.4PbO+$ $+0.3Mn_2O_3 + 0.4MnO_2$	nickel	T	$a = 3.928$ Å, $c = 3.853$ Å $V = 59.45$ Å^3
$Bi_{0.6}Pb_{0.4}MnO_{3-\lambda}$	— // —	graphite	T	$a = 3.929$ Å, $c = 3.859$ Å $V = 59.50$ Å^3
$Bi_{0.5}Pb_{0.5}MnO_{3-\lambda}$	$0.5Bi_2O_3 + 0.5PbO+$ $+0.5Mn_2O_3 + 0.5MnO_2$	graphite	T	$a = 3.93$ Å, $c = 3.79$ Å $V = 58.54$ Å^3
$Bi_{0.5}Pb_{0.5}MnO_3$	— // —	nickel	T	$a = 3.935$ Å, $c = 3.78$ Å $V = 58.53$ Å^3

thesized started from batches containing only Mn_2O_3. For such samples, we were unable to identify any splitting of the reflections, although it is noteworthy that the lines are somewhat broadened. Samples with a high lead content were tetragonally distorted, with $c<a$. Usually $c>a$ holds in ferroelectrics based on $BaTiO_3$.

In Table II we show the results of our investigations of the system $(Bi_{1-x}La_x)MnO_{3-\lambda}$. We were unable to obtain samples in the interval $0<x<0.3$ by synthesis in air. All the samples of this system obtained in air were characterized by very small distortions of the unit cell. As the bismuth content increased, the tetragonal distortions $(c<a)$ were replaced by rhombohedral distortions. It is noteworthy that the samples with Bi content less than 0.5 are apparently nonstoichiometric with respect to oxygen. This follows from the fact that samples of $La_{0.75}Bi_{0.25}MnO_3$ obtained at a pressure of 5 GPa and $T=1000$ °C had a strongly distorted O' type unit cell, as in stoichiometric $LaMnO_3$.

Our x-ray structural analysis indicates that $Bi_{0.7}Sr_{0.3}(Mn^{3+}_{0.7}Mn^{4+}_{0.3})O_3$ has an almost cubic unit cell with $a=7.86$ Å. The tetragonal distortion $(c<a)$ is very small, as is indicated by the negligible asymmetry of certain reflections.

The samples of $Bi_{0.9}Ca_{0.1}MnO_{2.95}$, $Bi(Mn_{0.9}Mg_{0.1})O_{2.95}$, and $Bi(Mn^{3+}_{0.9}Nb^{5+}_{0.1})O_{3.1}$ were characterized by negligible triclinic distortions. For this reason we were unable to compute the unit cell parameters with sufficient reliability, and we will not give the computed results here.

4. MAGNETIC AND ELECTRIC PROPERTIES

The compound $BiMnO_3$ is characterized by a spontaneous magnetization $\sigma_s=40$ A·m^2/kg at 77 K and 56

TABLE II. Unit cell parameters of the compounds $Bi_{1-x}La_xMnO_{3-\lambda}$.

composition	medium	symmetry	parameters
$Bi_{0.7}La_{0.3}MnO_3$	air	T	$a = 3.908$ Å, $c = 3.880$ Å $V = 59.26$ Å^3
$La_{0.5}Bi_{0.5}MnO_3$	air	R	$a = 3.897$ Å, $\alpha = 90°13'$ $V = 59.185$ Å^3
$La_{0.6}Bi_{0.4}MnO_{3-\lambda}$	air	R	$a = 3.895$ Å, $\alpha = 90°14'$ $V = 59.09$ Å^3
$La_{0.75}Bi_{0.25}MnO_{3-\lambda}$	air	R	$a = 3.887$ Å, $\alpha = 90°20'$ $V = 58.71$ Å^3
$La(Mn^{3+}_{0.72}Mn^{4+}_{0.28})O_{3.14}$	air	R	$a = 3.880$ Å, $\alpha = 90°14'$ $V = 58.88$ Å^3
$LaMnO_3$	vacuum	O'	$a = 5.537$ Å, $b = 7.743$ Å $c = 7.695$ Å

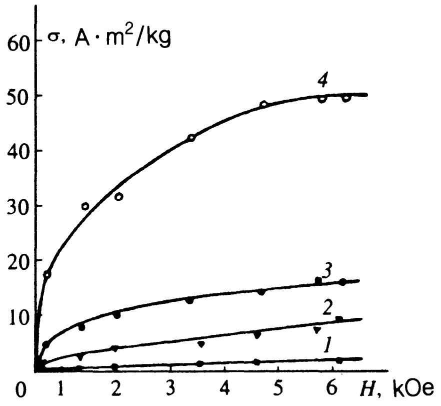

FIG. 1. Dependence of magnetization on field at 77 K for samples of $Bi_{1-x}La_xMnO_3$ when $x=0.3$ (1), $x=0.4$ (2), $x=0.5$ (3), and $x=0.75$ (4).

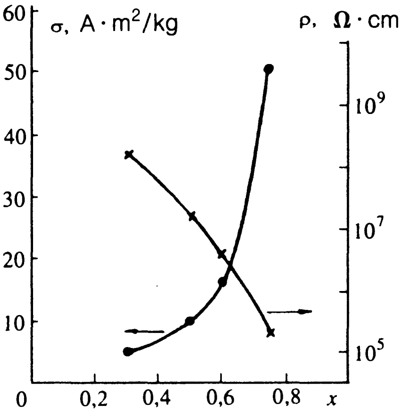

FIG. 2. Dependence of spontaneous magnetization and specific resistivity on composition for the system $Bi_{1-x}La_xMnO_3$ at $T=77$ K.

$A \cdot m^2/kg$ at 4.2 K. All the compounds in which bismuth ions were replaced by lead showed no spontaneous magnetic moment at 77 K. There also was no spontaneous magnetization at 77 K in the almost cubic compound $Bi_{0.7}Sr_{0.3}(Mn_{0.7}^{3+}Mn_{0.3}^{4+})O_3$.

The specific resistivity of the compound $BiMnO_3$ has the rather high value of $10^3\ \Omega \cdot cm$ at room temperature. The O'-orthorhombic compound $LaMnO_3$ is also characterized by approximately this value of the resistivity. This indicates that there are very few different-valence manganese ions in $BiMnO_3$. The replacement of Bi^{3+} ions by Pb^{2+} and Sr^{2+} leads to the appearance of Mn^{4+} ions and to an abrupt increase in the conductivity; however, a transition to metallic conductivity is not observed when $BiMnO_3$ is doped with Pb^{2+} and Sr^{2+}. The specific resistivity of $Bi_{0.7}Sr_{0.3}MnO_3$ at room temperature is of order 1 $\Omega \cdot cm$, and increases considerably as the temperature falls to 77 K.

For samples of the system $Bi_{1-x}La_xMnO_3$ with $0.3 \leqslant x \leqslant 0.4$, the functions $\sigma(H)$ reveal that there is no spontaneous magnetization at 77 K (Fig.1.). When the content of lanthanum ions is increased to $x=0.5$, a spontaneous magnetic moment appears, which increases with increasing lanthanum content (Figs. 1. and 2). The temperature at which the magnetic moment appears depends rather weakly on composition in the interval $0.5 < x \leqslant 0.8$. This follows from the results of differential susceptibility measurements (Fig. 3). As the La ion content increases, the electrical conductivity increases as well, which points to the appearance of Mn^{4+} ions and a departure from stoichiometry.

It is noteworthy that our stoichiometric samples of $La_{0.75}Bi_{0.25}MnO_3$ obtained under high pressure do not exhibit spontaneous magnetization above 77 K. This says that the ferromagnetism of $Bi_{1-x}La_xMnO_3$ with high La content is caused by deviations from stoichiometry.

Replacement of ions of manganese by the ions Mg^{2+} and Nb^{5+} also leads to a rather abrupt decrease in the spontaneous magnetization (Fig. 4). When insignificant replacements of Bi^{3+} ions by Ca^{2+} are made in $Bi_{0.9}^{3+}Ca_{0.1}^{2+}MnO_{2.95}$ (Fig. 4), the decrease in magnetization is considerably weaker. The Curie temperatures of this group of samples were all of order 100 K.

5. DISCUSSION OF RESULTS

We begin by noting that the exchange interaction Mn^{3+}–Bi^{3+}–$Mn^{3+}(Mn^{4+})$ does not play an important role in creating the magnetic properties of $AMnO_3$. The addition of Bi ions to $La(Mn_{0.72}^{3+}Mn_{0.28}^{4+})O_{3.14}$, which is a ferromagnet with $T_c=160$ K, causes its ferromagnetic properties to gradually disappear (Fig. 1 and Fig. 2). The compounds $Bi_{1-x}Pb_xMnO_3$ and $Bi_{0.7}Sr_{0.3}(Mn_{0.7}^{3+}Mn_{0.3}^{4+})O_3$ are also nonferromagnetic. Note that $Bi_{0.7}Pb_{0.3}MnO_{2.85}$ and $Bi_{0.7}Sr_{0.3}(Mn_{0.7}^{3+}Mn_{0.3}^{4+})O_3$ are almost cubic, which according to Refs. 3,8 should lead to ferromagnetism. Hence, criteria for a ferromagnetic state formulated for the rare-earth and lanthanum manganites are not applicable to the Bi-containing manganites. For example, the cubic $Bi_{0.7}Pb_{0.3}MnO_{2.85}$ is an insulator with $\rho=10^5\ \Omega \cdot cm$ at 293

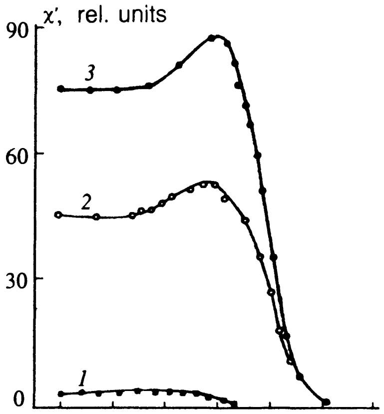

FIG. 3. Differential magnetic susceptibility of $Bi_{1-x}La_xMnO_3$ for $x=0.5$ (1), $x=0.6$ (2), and $x=0.75$ (3).

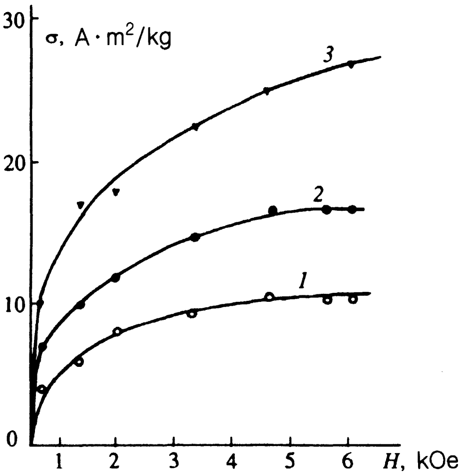

FIG. 4. Field dependence of magnetization for samples of $Bi(Mn_{0.9}Mg_{0.1})O_{2.95}$ (1), $Bi(Mn_{0.9}Nb_{0.1})O_{3.1}$ (2), and $Bi_{0.9}Ca_{0.1}MnO_{2.95}$ (3) at $T=77$ K.

K, whereas $Bi_{0.7}Sr_{0.3}(Mn^{3+}_{0.7}Mn^{4+}_{0.3})O_3$ is a rather good conductor. Neither of these compounds possess ferromagnetic properties.

The ferromagnetic state appears in the Bi-containing manganites at fairly high concentration of Bi ions, i.e., no less than 80 percent of the overall number of A-sites in $AMnO_3$. In this case a triclinic distortion of the crystal lattice should occur.

We will argue that these results can be explained only on the basis of a model which predicts antiferrodistortive ordering of the d_{z^2} and $d_{x^2-y^2}$ orbitals of the manganese ions in the (a,c) planes of $BiMnO_3$. The Mn^{3+} ions with ordered d_{z^2} orbitals and ordered $d_{x^2-y^2}$ orbitals are positioned in a chessboard pattern, and the axes of the d_{z^2} orbitals are oriented along the b-axis. Orbitals in neighboring (a,c) planes are oriented in such a way that there is overlap of the half-filled and empty e_g-orbitals of the Mn^{3+} ions along all the Mn–O–Mn directions. In this case, at each Mn^{3+} ion conditions are satisfied for the ferromagnetic Mn^{3+}–O–Mn^{3+} exchange interaction. The relatively low Curie temperature is apparently due to the considerable lattice distortion; this also explains why the Mn–O–Mn angle deviates from its optimum angle of 180°. The compounds $LaMnO_3$ and $NdMnO_3$ have approximately the same Néel temperatures—140 K and 90 K, respectively.

Apparently the Bi ions are also rather effective in stabilizing the local distortions of the MnO_6 octahedra (the orbital states are "frozen") for concentrations of the A-sites smaller than 80%. However, in these compounds the orbital ordering is not cooperative in nature, and therefore should manifest itself through properties that are characteristic of spin glasses. We have observed such properties in $Bi_{0.6}Pb_{0.4}MnO_{2.8}$.[5]

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