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Magnetic and transport properties of $\text{Bi}_{0.5}\text{Ca}_{0.5}\text{Fe}_x\text{Mn}_{1-x}\text{O}_3$ ($0 \leq x \leq 0.6$)

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Abstract

A series of Fe-substituted manganites $\text{Bi}_{0.5}\text{Ca}_{0.5}\text{Fe}_x\text{Mn}_{1-x}\text{O}_3$ ($0 \leq x \leq 0.6$) was synthesized by ceramic technology. The crystal lattice parameters change monotonically with increasing Fe substitution for Mn as found from x-ray powder diffraction and neutron diffraction investigations at room temperature. Magnetic properties were studied between 5 and 1300 K in fields up to 16 kOe. All the compounds are antiferromagnetic below a certain temperature, which decreases with increasing Fe substitution, and for $x \geq 0.1$ the antiferromagnetism is accompanied by a weak ferromagnetism. The charge/orbital order exists in the pure form for the compounds without or with very low Fe substitution ($x = 0$ and 0.05). A new magnetic cluster state exists in the paramagnetic region of manganites with Fe substitution $x \geq 0.3$, but only in the presence of magnetic field.

The conductivity of compounds measured between 100 and 600 K is of semiconducting type, and there is no magnetoresistivity effect in fields up to 7 kOe.

1. Introduction

Recent research on colossal magnetoresistance manganites revealed a very complex nature of the interplay of the lattice, charge, and spin degrees of freedom. The crystal structure is perovskite-like with oxygen octahedra containing Mn^{4+} or the Jahn–Teller Mn^{3+} ion species. Even subtle changes in the $\text{Mn}^{3+}\text{–O–Mn}^{4+}$ network may substantially alter the magnetic and charge transport response. The manganite systems display a rich phase diagram and, in addition, orbital (OO) and charge ordering (CO) phenomena accompany the structural evolution under the influence of external factors such as temperature, magnetic

field, pressure. The investigations were mainly concentrated on the substituted $\text{RE}_{1-x}\text{A}_x\text{MnO}_3$ systems (RE = Y^{3+} , La^{3+} or another rare earth; A—divalent alkaline-earth ions such as Ca^{2+} , Ba^{2+} , Sr^{2+}).

The family of Bi-based manganites $\text{Bi}_{1-x}\text{A}_x\text{MnO}_3$ became of recent interest because of the physics that lies behind the unusually high temperature of charge ordering, T_{CO} . Early results of studies on structure–transport property relationships were reported long ago [1] but should now be reconsidered in the light of recent understanding of OO–CO effects. Among the manganites, half-doped $\text{Bi}_{0.5}(\text{Ca}, \text{Sr})_{0.5}\text{MnO}_3$ displays unusually high T_{CO} , far above room temperature. In particular, $\text{Bi}_{1-x}\text{Ca}_x\text{MnO}_3$ is insulating for $0.2 < x < 1.0$, with CO at and above room temperature (RT) for $0.4 \leq x \leq 0.6$ [2, 3]. Its CO temperature is $T_{\text{CO}} = 325$ K for $x = 0.5$, it peaks at 335 K for $x = 0.6$, and it drops to 210 K in the Mn^{4+} rich region for $x = 0.82$ [4]. This system is little understood compared to $\text{RE}_{1-x}\text{Ca}_x\text{MnO}_3$, in which e_g orbital order, charge order, and related effects were studied systematically. It was suggested that the two systems are much alike [3, 5], so for $x = 0.5$ one might expect a CE-type antiferromagnetic (AFM) order [6, 7] in $\text{Bi}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ (BCMO). CE-type antiferromagnetic structure can be considered as a checkerboard of two alternating blocks with different antiferromagnetic arrangements of Mn^{3+} and Mn^{4+} magnetic moments. By systematic investigations of structural, magnetic, and conductivity properties it was confirmed that $\text{RE}_{1-x}\text{Ca}_x\text{MnO}_3$ manganites are insulating and antiferromagnetic for $0.4 \leq x \leq 0.9$ [8]. However, for $0.74 \leq x \leq 0.82$, unlike the different AFM structures found in $\text{RE}_{1-x}\text{Ca}_x\text{MnO}_3$, only C-type order is found in $\text{Bi}_{1-x}\text{Ca}_x\text{MnO}_3$ [4]. Even more striking is half-doped $\text{Bi}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ for which charge ordering was observed by means of electron and neutron diffraction to occur at the highest temperature reported yet ($T_{\text{CO}} = 475$ K) for OO and CO in the manganites [2].

Here we note that the physical interpretation of the CO/OO ordering scheme has long been controversial, and only recently do phenomenological [9] and microscopic [10] theories seem to have resolved the main contradictions. There are two distinct structural models giving alternative superstructures of the CO phase in half-doped manganites. Both may produce the CE type of complex AFM arrangement at $T_{\text{N}} < T_{\text{CO}}$. The ordered Zener polaron (ZP) model [11] describes an electronic state in which the manganese ions have an intermediate valence of 3.5 throughout the structure. The conventional OO/CO ionic model [6, 12] assumes $\text{Mn}^{3.5+\delta}/\text{Mn}^{3.5-\delta}$ charge disproportionation. The extreme case of the latter is separated and spatially ordered Mn^{3+} and Mn^{4+} ionic species. In accordance with this approach the dominant electron–phonon coupling mechanisms involve breathing-type distortions of the MnO_6 octahedron that stabilize a Mn^{4+} small polaron, or a Jahn–Teller (JT) type of distortion around the Mn^{3+} sites. The structural transition that takes place below T_{CO} is then considered as a static ordering of the Mn–O bond lengths concomitant the electronic localization.

A phenomenological approach to phase transitions (PT) in the framework of Landau theory allows viewing the low symmetry phase as the outcome of a PT for both models [9]. Recent refinements of the CO superstructure of some half-doped manganites [11, 13–15] have shown that the phases feature a high level of symmetry owing to the small magnitude of the monoclinic distortion. This renders discrimination between models rather difficult. On these grounds it was suggested [13] that single-crystal data refinement seems preferable and previous analyses based on powder diffraction data may seem biased and dubious to some extent. However, the most recent powder diffraction work [16] points to some deficiency intrinsic to single crystals of perovskites. Due to the small lattice distortions which accompany CO there is a need to consider a twinning effect and in [13] six twin domains were supposed. By combining x-ray and neutron diffraction patterns on $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$, which is considered as a paradigmatic case of a CO/OO compound, refinements based on the two ordering schemes were compared. It was found definitely that to some extent a better description of certain details of the profile

gave refinements within the conventional CE picture. This is in agreement with the latest theoretical conclusions [9] that the conventional CE model works better at exactly half-doping, $x = 0.5$.

Another point of concern in explaining the transport properties is the band tuning mechanism, which is accepted in general to hold in rare-earth manganites $\text{RE}_{1-x}\text{A}_x\text{MnO}_3$ and relates the width of the electronic e_g band to the average radius of the A-site cations, $\langle r_A \rangle$. Change in $\langle r_A \rangle$ alters the mobility of the itinerant e_g electrons, producing a reverse change in the temperature of charge ordering, T_{CO} . This mechanism was found insufficient to explain the complex charge transport properties and unusually high T_{CO} of Bi(Ca, Sr) against La(Ca, Sr) manganites. In reasoning regarding the findings for Ca-doped Bi–Mn oxides, effects associated with the Bi $6s^2$ lone pair electrons were highlighted by suggesting that the lone pair character is strongly screened and the effective ion size of Bi^{3+} ($r_i \approx 1.16 \text{ \AA}$) is smaller than La^{3+} ($r_i \approx 1.22 \text{ \AA}$).

There is enhanced interest in Mn-site doping since it is an efficient way to directly modify double exchange. Various magnetic and non-magnetic ions were employed as dopants mainly in the CMR rare-earth manganites in an effort to extend the CMR effect to RT and above it. The influence of doping on CO/OO phenomena is itself much less often addressed and we undertook a study intended to help elucidate this problem for the case of Fe substitution for Mn. The substitution of Fe for Mn in the manganites is an intricate problem for the following reason. Ionic radii of Mn^{3+} and Fe^{3+} are practically equivalent, $\langle r_i \rangle = 0.645 \text{ \AA}$ [17], so one could expect no structural changes with Fe substitution. On the other hand, the numbers of d electrons and the effective magnetic moments are different for Mn^{3+} and Fe^{3+} . There are four 3d electrons ($t_{2g}^3 e_g^1$) and an effective magnetic moment of $\mu_{\text{eff}} = 4.9 \mu_B$ for Mn^{3+} and five 3d electrons ($t_{2g}^3 e_g^2$) and effective magnetic moment of $\mu_{\text{eff}} = 5.9 \mu_B$ for Fe^{3+} . Thus even though Mn^{3+} and Fe^{3+} have equivalent ionic radii the magnetic interactions and some other electronic properties, like charge and orbital ordering, could be affected under substitution of Fe^{3+} for Mn^{3+} . There are several papers on Fe-substituted manganites [18–32], as a rule with low Fe concentrations. The main conclusion of most of these papers is that Fe substitution for Mn introduces additional antiferromagnetic interactions. Here we note that in [32] there was found an abrupt disappearance of the charge ordered state for rather low levels of dopant (approximately 1–2%). There are also a few papers on another 3d ion (Co and Cr) substituting for Mn [33, 34]. Chromium substitution gradually reduces the charge ordering transition temperature and increases the low temperature magnetoresistance [34]. The problem of Fe and Ga substitution for Mn was also treated theoretically in [35].

The purposes of the present paper are: (i) to investigate the possibility of the existence of Bi–Ca manganites with extended substitution of Fe for Mn with the objective of exploring the unknown phase diagram; and (ii) to study the changes of magnetic and transport properties influenced by Fe substitution. We undertook a systematic study of the main magnetic properties and electrical resistivity of the powder compounds $\text{Bi}_{0.5}\text{Ca}_{0.5}\text{Fe}_x\text{Mn}_{1-x}\text{O}_3$ ($0 < x \leq 0.6$). Some preliminary neutron diffraction findings are reported as well.

2. Experimental details

Samples with composition $\text{Bi}_{0.5}\text{Ca}_{0.5}\text{Fe}_x\text{Mn}_{1-x}\text{O}_3$ ($x = 0, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5$, and 0.6) were synthesized by a common solid state reaction. The initial compounds of Bi_2O_3 , CaCO_3 , MnCO_3 , and Fe_2O_3 with analytical grade of purity were used. Samples were obtained by mixing and grinding the stoichiometric amounts of starting materials in an agate mortar. The homogenized powders were pressed into cylindrical (12 mm in diameter and 2 mm in height)

pellets at 430 MPa, and were subjected to heat treatment for 6 h at 800 °C and 6 h at 900 °C. After calcinations, the samples were reground, pelletized again, and the final heat treatment was performed for 30 h at 1000 °C in air.

The initial materials and the synthesis procedure were controlled by means of x-ray powder diffraction (XRD), performed on a DRON-3 diffractometer using Cu K α radiation. CELLREF and POWDERCELL programs were used to extract the lattice parameters. Neutron diffraction measurements were carried out on samples with $x = 0.05, 0.1, 0.2, 0.3, 0.4,$ and 0.5 at room temperature. The patterns were collected in the range 5°–119° for 2θ with a constant step of 0.1° at the Budapest Neutron Centre by using the diffractometer PSD with a neutron wavelength of $\lambda = 1.0691 \text{ \AA}$.

DC magnetic susceptibility was measured by means of a Faraday-type magnetic balance in the temperature range 400–1300 K in a field of 7 kOe and with high temperature vibrating sample magnetometer in the temperature range between 300 and 400 K. The error in magnetic susceptibility readings is less than 5%, and those in the temperature measurements are less than 3%. The powders were fixed by moderate pressure in unsealed quartz containers. Since the materials have been synthesized at high temperatures in air, the measurements were performed in air too. AC magnetic susceptibility was measured for the same samples between room temperature (RT) and 650 K in a magnetic field of 50 Oe amplitude and a frequency of 80 Hz.

Magnetization between 5 and 250 K was measured by a vibrating sample magnetometer PAR 4500 in fields up to 16 kOe and between RT and 600 K by a home-made vibrating sample magnetometer in fields up to 7 kOe.

DC resistivity was measured between 77 and 600 K by a standard four-probe technique by using a SOLARTRON-7081 scanning multimeter. The samples were $\approx 1.5 \times 1.5 \times 8 \text{ mm}^3$ parallelepipeds, cut from the pressed and sintered pellet of the corresponding powder. The magnetic field applied was up to ± 7 kOe.

3. Sample characteristics

Iodometric titration has shown a stoichiometric content of all the samples within a 1.5% limit of accuracy. There is no additional direct information about the oxygen content. Traces of MnFe₂O₄-type impurities were detected in the compositions with $x \geq 0.3$ by XRD and neutron diffraction analysis.

Both XRD and neutron diffraction patterns of all the Bi_{0.50}Ca_{0.5}Mn_{1-x}Fe_xO₃ ($0 < x \leq 0.6$) compounds at room temperature were indexed in the orthorhombic *Pnma* space group. For Bi_{0.5}Ca_{0.5}MnO₃ a nearly monoclinic symmetry (actually triclinic) was deduced at RT ($T < T_{CO}$) without true space group specification [1]. As already reported, for our sample with $x = 0$ the deviation from orthorhombicity seemed to be small and we could obtain [36] a realistic description of the structure when it was refined within the *Pnma* supergroup of the average cell, although it does not allow for 1:1 or partial charge ordering.

Figure 1 presents the variation of lattice parameters with Fe substitution and demonstrates that the unit cell volume expands with increasing x , contrary to anticipation, for a small structural impact if any. The details of the structural analyses are beyond the scope of the present investigation and will be published elsewhere. Here we shall briefly outline the principal findings.

Indeed, all the Fe-substituted compounds remain orthorhombic but in the cell metric there are two distinct ranges manifesting the structural influence of Fe doping. For $0.05 \leq x \leq 0.2$ the cell parameters obey the relation $b/\sqrt{2} \leq c < a$. The combination of octahedral tilting and a cooperative Jahn–Teller distortion (orbital ordering) is known to produce such *O'*-type distorted perovskite structures. More importantly, the strong static Jahn–Teller distortion

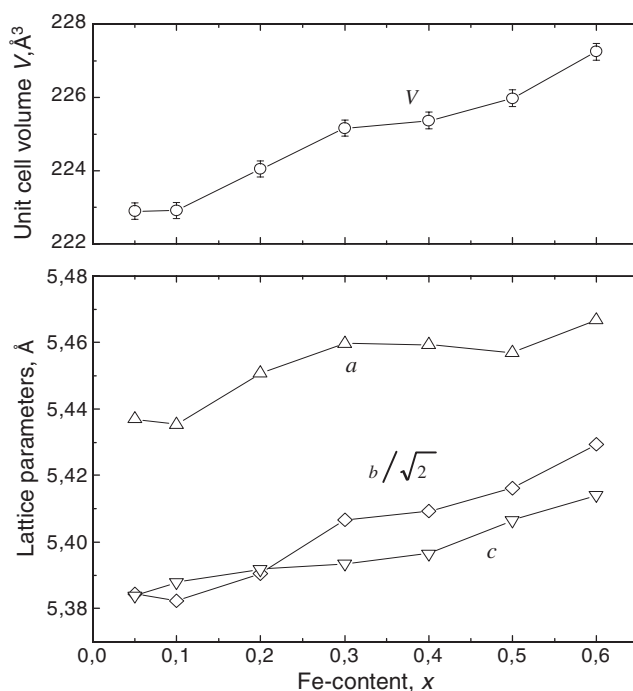


Figure 1. Fe substitution dependence of the lattice parameters, a , $b/\sqrt{2}$, c and unit cell volume V .

observed in $\text{Bi}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ ($x = 0$) becomes much reduced. 5% Fe doping already causes approximately equal $b/\sqrt{2}$ and c . For $0.3 \leq x \leq 0.6$ the relation changes to $b/\sqrt{2} \leq c < a$. A closer inspection of structural features (bond lengths, lattice distortions) shows that the distortions of BO_6 units ($B = \text{Mn}, \text{Fe}$) depend on the Fe content. The analysis confirms that doping with iron destabilizes static Jahn–Teller distortion and the result is a more symmetric orthorhombic matrix.

Some typical plots of inverse susceptibility versus temperature for $T > 400$ K are shown in figure 2. All the curves consist of linear Curie–Weiss-type regions at high temperatures. The samples with $x < 0.3$ remain purely paramagnetic down to 300 K, as seen from the magnetization measurements shown below. Some deviations from the pure Curie–Weiss law indicating a tendency to ferromagnetic or ferrimagnetic ordering were observed at lower temperatures for the samples with Fe substitution $x \geq 0.3$. Having in mind the results of XRD and neutron phase analysis, these deviations can be attributed to the existence of some extra magnetic phases of $\text{Mn}_y\text{Fe}_{3-y}\text{O}_4$, apart from the main ones.

The thermomagnetic (σ versus T) curves, plotted in a field of 2 kOe, indicate some spontaneous magnetization above RT for the samples with $x \geq 0.3$. The ZFC and FC branches of the thermomagnetic curves coincide, indicating thus that the used field of 2 kOe is enough for saturation of a spontaneously magnetized phase. The existence of transitions to a magnetic ordered state for these samples is also confirmed by the AC susceptibility measurements. As seen in figure 3, magnetization (σ versus H) curves plotted at RT show that the samples with $x \leq 0.2$ are purely paramagnetic at RT, but for these with $x \geq 0.3$ some magnetically ordered states coexist with the paramagnetic ones. These magnetically ordered states belong to the magnetic impurities already commented on. The coercivities for the samples exhibiting some magnetic order at RT do not exceed 250 Oe and fields of a few kOe are enough to saturate the magnetically ordered phases in all cases. These transitions could be attributed to the

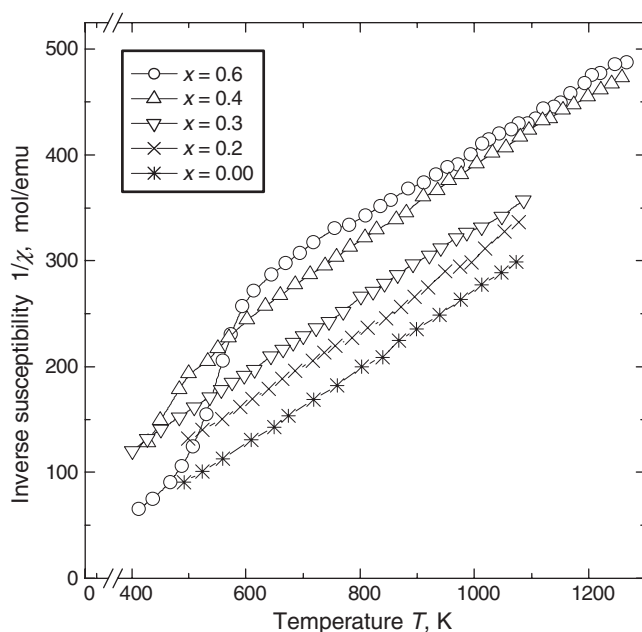


Figure 2. Temperature dependence of the inverse magnetic susceptibility for some $\text{Bi}_{0.5}\text{Ca}_{0.5}\text{Fe}_x\text{Mn}_{1-x}\text{O}_3$ compounds.

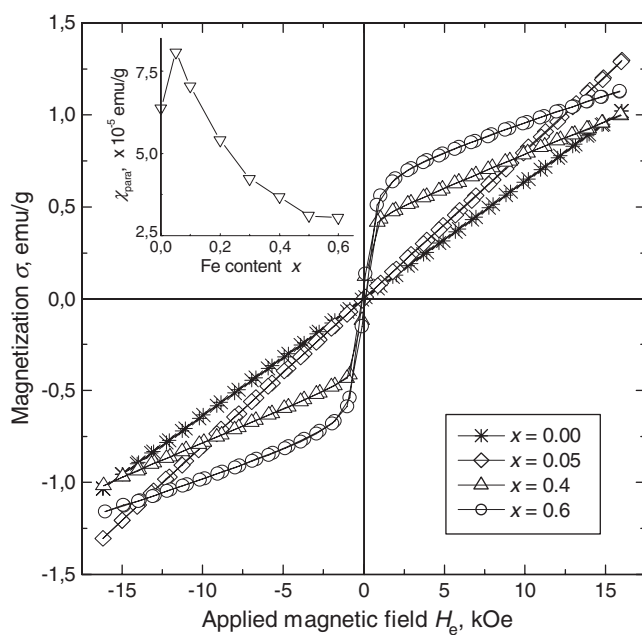


Figure 3. Room temperature magnetization curves for some $\text{Bi}_{0.5}\text{Ca}_{0.5}\text{Fe}_x\text{Mn}_{1-x}\text{O}_3$ compounds. The inset shows the Fe content dependence of the paramagnetic susceptibility, extracted from the linear extrapolation of magnetization curves.

above-mentioned small amounts of extra magnetic phases of $\text{Mn}_y\text{Fe}_{3-y}\text{O}_4$, whose magnetic properties are well known [37]. From their transition temperatures, Θ_C , and the saturation magnetization at RT it was estimated that in all cases the concentrations of such magnetic impurities are less than 2 wt%, in agreement with the results of neutron diffraction analysis. Such small amounts of magnetic impurities could not substantially affect the results of high temperature susceptibility measurements, which are discussed below.

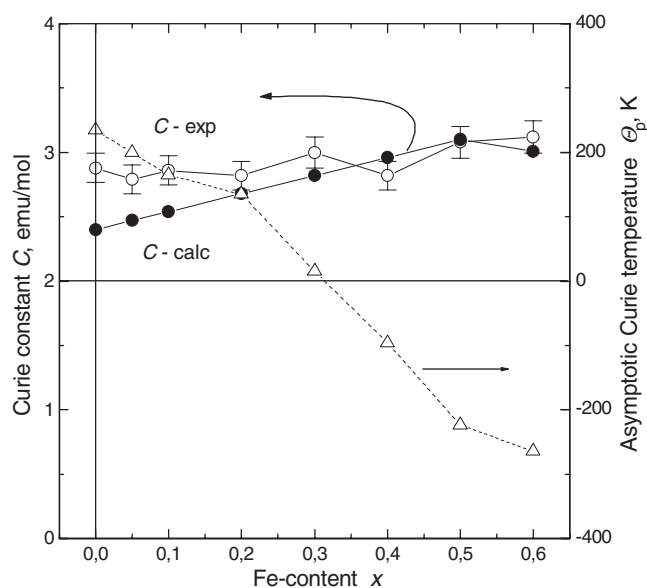


Figure 4. Fe content dependence of the Curie constants, C , and asymptotic Curie temperatures, Θ_p , for $\text{Bi}_{0.5}\text{Ca}_{0.5}\text{Fe}_x\text{Mn}_{1-x}\text{O}_3$.

4. Results and discussion

The values of the Curie constant, C , and asymptotic Curie temperature, Θ_p , extracted from the linear regions of the $1/\chi$ versus T curves for the set of compounds under study are summarized in figure 4. The values of the asymptotic Curie temperature, Θ_p , decrease monotonically with increasing x . Their sign is positive for the lower Fe substitution up to $x \leq 0.3$, indicating a predominance of ferromagnetic interactions between magnetic ions, but it becomes negative for $x > 0.3$, indicating the predominance of antiferromagnetic interactions. This result is in accordance with previous findings for Fe-doped perovskite-type manganites: that the substitution of Fe for Mn leads, as a rule, to the involvement of predominantly antiferromagnetic interactions [18–34]. For the non-doped $\text{Bi}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ ($x = 0$) the measured $\Theta_p = 235 \pm 5$ K is close to the value $\Theta_p \approx 210$ K found in [1].

The Curie constants calculated assuming ideal stoichiometries of the compounds with the commonly used effective magnetic moments of ions: $\mu_{\text{eff}}(\text{Mn}^{3+}) = 4.9 \mu_B$, $\mu_{\text{eff}}(\text{Mn}^{4+}) = 3.8 \mu_B$, $\mu_{\text{eff}}(\text{Fe}^{3+}) = 5.9 \mu_B$ [38], and $\mu_{\text{eff}}(\text{Fe}^{4+}) = 2.7 \mu_B$ [39], are also shown in figure 4. The existence of Fe^{4+} is considered only for the sample with $x = 0.6$ with the ionic ratio corresponding to $\text{Bi}_{0.5}\text{Ca}_{0.5}\text{Fe}_{0.5}^{3+}\text{Fe}_{0.1}^{4+}\text{Mn}_{0.4}^{4+}\text{O}_3$. The experimentally obtained Curie constant values increase linearly with increasing Fe substitution, x . The values coincide within the limit of experimental errors with the calculated ones for the samples with $x > 0.3$, but for $x \leq 0.3$ the measured Curie constant values are higher than the calculated ones. For the non-doped $\text{Bi}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ the measured value of $C = (2.9 \pm 0.1) \text{ emu mol}^{-1}$ practically coincides with the value of $C \approx 3 \text{ emu mol}^{-1}$ estimated graphically from figure 10 of [1], and both of them are higher than the calculated one. It is worth noticing that the enhanced Curie constants are obtained only for the samples with $x \leq 0.3$, for which the ferromagnetic interactions are predominant, as seen in the figure 4. When the Curie temperature changes its sign to a negative one for $x > 0.3$, which means that the antiferromagnetic interactions become predominant, the calculated and measured Curie constant values are equal. There exist also some other experimental data concerning the effective magnetic moments of $\mu_{\text{eff}}(\text{Mn}^{3+}) = 5.25 \mu_B$ and $\mu_{\text{eff}}(\text{Fe}^{3+}) = 3\text{--}4.4 \mu_B$, obtained for LaMnO_3 and LaFeO_3 respectively [40]. The closeness

of the measured Curie constant values and the ones calculated with the common values for Mn^{3+} , Fe^{3+} , and Fe^{4+} , as well as a tendency of increasing Curie constant with substitution for Mn^{3+} with Fe^{3+} , indicate that the magnetic moments of Mn^{3+} and Fe^{3+} in our case obviously differ from their values for LaMnO_3 and LaFeO_3 .

One possible explanation for the observed enhancement of the measured Curie constant values for the samples with $x \leq 0.3$ is as follows. The predominant ferromagnetic interactions, typical for these samples, favour a formation of small clusters, consisting of a few magnetic ions, which contribute to the paramagnetic response of the system and thus to the Curie constant, and exist up to the highest temperatures used. For the samples with $x > 0.3$ the predominant antiferromagnetic interactions destroy these clusters and each of the magnetic ions contributes to the Curie constant individually. The problem of the existence of some magnetic clusters in such manganites is commented on in a number of works. On the other hand, in recent papers [11, 14] the presence of a mixture of Zener pairs ($\text{Mn}^{3+}\text{--Mn}^{4+}$) with $S = 7/2$ and non-paired Mn^{3+} ions with $S = 2$ in the paramagnetic state was discussed. As a consequence of this, the magnetic moment μ_{eff} and Curie constant of the mixture will be enhanced.

The magnetic susceptibility, χ_{para} , calculated from the linear regions of σ versus H curves changes non-monotonically with increasing iron content, as shown in the inset of figure 3. The maximum of χ_{para} is at $x = 0.05$ and for all $x > 0.05$ χ_{para} it decreases monotonically with increasing x .

The sample with $x = 0$ needs some more attention because this compound is basic to the present investigation and it is relatively well studied. The sample is purely paramagnetic at RT, but the magnetic susceptibility is lower than for the sample with $x = 0.05$. There are maxima at 320 K in the thermomagnetic curves, plotted in both DC and AC magnetic fields. This effect has already been reported in several papers [1, 2, 41, 42] for the same compound. It has been attributed to lowering of the symmetry of the crystal lattice from orthorhombic above 320 K to monoclinic below this temperature. Charge ordering was suggested to be a physical reason for this phase transition. Charge ordering is observed in a number of rare-earth manganites as well as in some other magnetic oxides (see e.g. [43–46] and references therein). For some compounds, such as $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$, $0.3 \leq x \leq 0.6$ [47, 48], $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$ [49], the temperature of the transition to a charge/orbital ordered state, $T_{\text{CO/OO}}$, is well above the temperature of transition, T_{N} , to a magnetically ordered state (antiferromagnetic for all these manganites). This is the situation in our case too—according to Bokov *et al* [1] and Frontera *et al* [41] for $\text{Bi}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ the charge ordering temperature is $T_{\text{CO}} = 320$ K and the Néel temperature is $T_{\text{N}} = 125$ K. The observed reduction of RT magnetic susceptibility as well as the existing maxima of magnetization curves, both in the paramagnetic region, are obviously results of this complicated, structural and charge/orbital ordering, phase transition. When the e_g orbitals of Mn^{3+} ions are fixed along a certain crystallographic axis their paramagnetic spins are also bonded due to the spin–orbital coupling, and cannot follow magnetic field as easily as when the orbital order does not exist. The monotonic decrease of the RT magnetic susceptibility with increasing Fe substitution for $x \geq 0.05$ can be considered as an indication that Fe substitution suppresses such a phase transition, at least above RT.

Magnetization curves at 7 K plotted in fields up to 16 kOe indicate a lack of saturation. In order to study the low temperature magnetic behaviour of the compounds in more detail, sets of thermomagnetic curves have been plotted between 7 and 250 K in different magnetic fields up to 16 kOe in both zero-field-cooled (ZFC) and field-cooled (FC) regimes.

Figure 5 presents thermomagnetic curves for $\text{Bi}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$. A typical Hopkinson-type maximum exists at $T_{\text{max}1} = 38$ K in the ZFC curve and the low field ZFC and FC curves deviate substantially (such a behaviour is often called a spin-glass-like effect). Such a hysteresis exists practically for almost all the samples and it will be commented on later. There is a clear broad

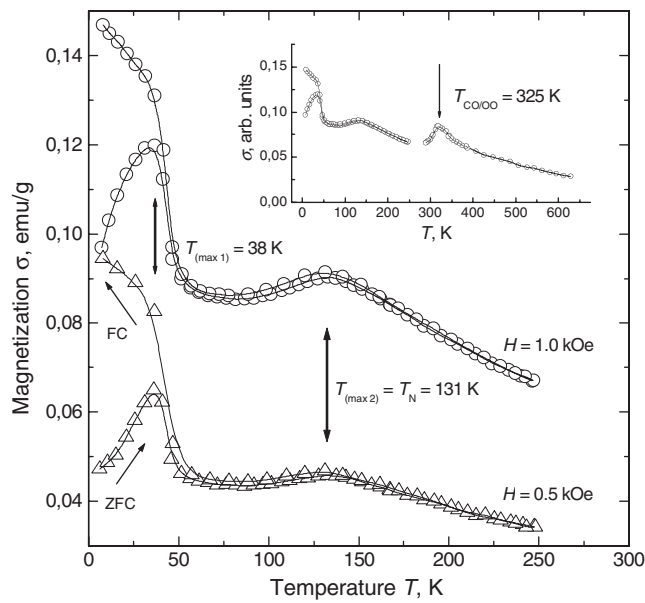


Figure 5. ZFC and FC thermomagnetic curves of $\text{Bi}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$. A thermomagnetic curve measured above RT is shown together with the low temperature one in the inset.

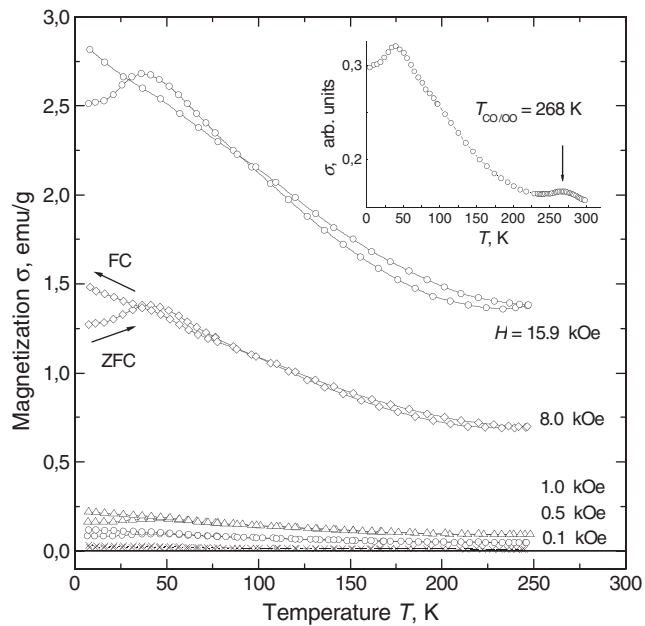


Figure 6. ZFC and FC thermomagnetic curves of $\text{Bi}_{0.5}\text{Ca}_{0.5}\text{Fe}_{0.05}\text{Mn}_{0.95}\text{O}_3$. The entire thermomagnetic curve plotted below RT in a field of 2 kOe is shown in the inset.

maximum of antiferromagnetic type at $T_N = (131 \pm 3)$ K for all the fields used. This transition temperature is in the range of $T_N = 120\text{--}133$ K, reported elsewhere [1, 2, 41, 42]. FC and ZFC thermomagnetic curves coincide down to about 50 K, which is an indication that the magnetic order below T_N is a pure antiferromagnetic one.

Figure 6 displays the thermomagnetic curves of the sample with $x = 0.05$. No visible antiferromagnetic-type maxima exist between 50 and 250 K for all the fields used. However a clear maximum exists at (268 ± 3) K, as shown in the inset, and FC thermomagnetic curves practically do not deviate from the ZFC ones in the region of this maximum. Thus

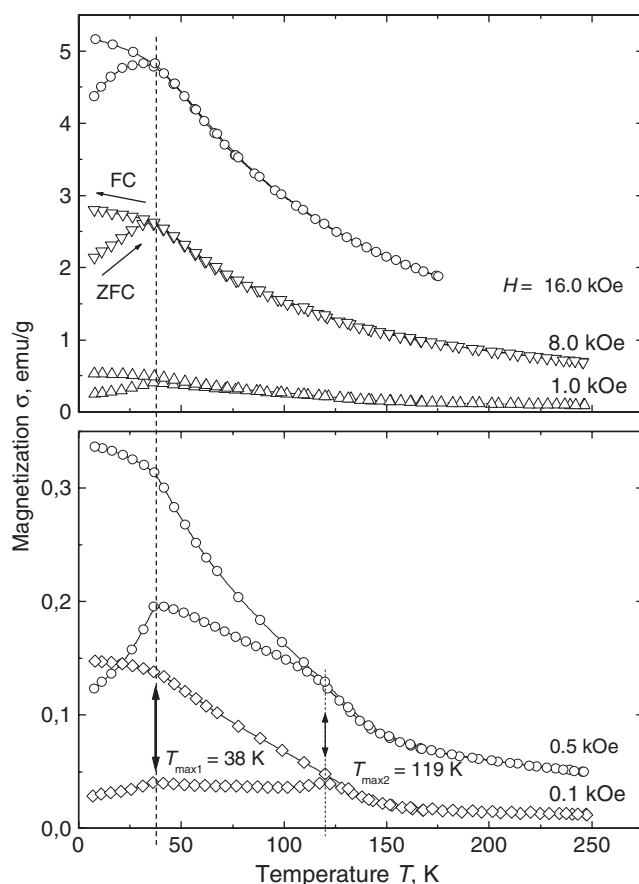


Figure 7. ZFC and FC thermomagnetic curves of $\text{Bi}_{0.5}\text{Ca}_{0.5}\text{Fe}_{0.1}\text{Mn}_{0.9}\text{O}_3$.

the temperature of $T = (268 \pm 3)$ K could be considered as a temperature of CO/OO transition. Thermomagnetic curves plotted in fields above 1 kOe behave rather strangely. FC curves are placed below ZFC ones for temperatures below about 100 K in the regions of their maxima. The cause of this feature remains unclear at present and more investigations, including investigations of non-magnetic properties, are necessary for further speculations. The low temperature Hopkinson-type maximum is at $T_{\text{max}1} = 48$ K, which is the highest temperature for these maxima among all the samples. One could expect the substitution of $x = 0.05$ of Fe for Mn to shift both the antiferromagnetic transition and CO/OO transitions towards the lower temperature. Thus the broad antiferromagnetic maximum overlaps with the sharper Hopkinson-type maximum, increasing its temperature effectively and changing its usual character.

Thermomagnetic curves of the sample with $x = 0.1$ are shown in figure 7. There are clear maxima of low field ZFC curves at $T_{\text{max}1} = 38$ and $T_{\text{max}2} = 119$ K, and FC curves deviate significantly from ZFC ones below $T_{\text{max}2}$, but this effect is smeared in high fields. The deviation of FC curves from the ZFC ones can be considered as an indication that the transition at $T_{\text{max}2}$ is of magnetic nature. It is not of pure antiferromagnetic type. Either some ferromagnetic/ferrimagnetic phase coexists with the main antiferromagnetic one, or the antiferromagnetism is accompanied by a so-called weak ferromagnetism of Dzyaloshinskii–Moriya type, or the antiferromagnetic state is frustrated. The latter possibility seems to be the

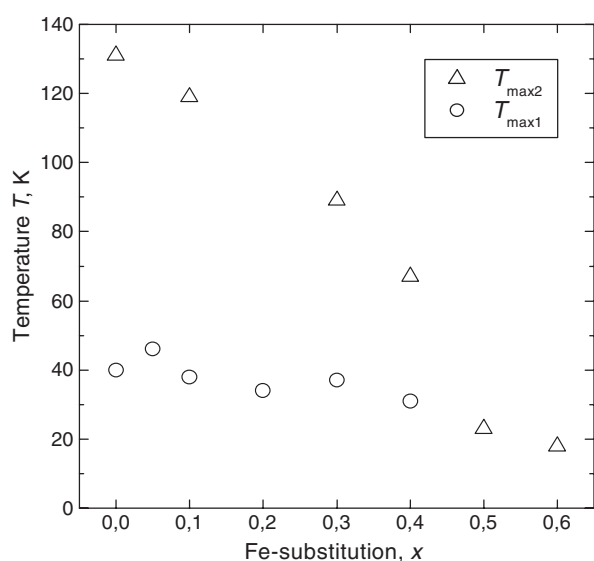


Figure 8. Fe content dependence of $T_{\max 1}$ and $T_{\max 2}$ (see the text).

most reasonable, because it explains the fact that, as a rule, the Hopkinson-type thermomagnetic hysteresis disappears in fields higher than a few kOe.

The magnetic behaviour is almost the same for all other samples with higher x . The Fe substitution dependences of both transition temperatures, $T_{\max 1}$ and $T_{\max 2}$, are presented in figure 8. With increasing x the maximum at $T_{\max 1}$ decreases, shifts to lower temperature, and practically disappears for $x > 0.4$.

A typical Hopkinson-like effect exists below 50 K for the manganite with $x = 0$. It consists of a maximum in the ZFC thermomagnetic curve and a substantial discrepancy between the ZFC and FC curves. Such behaviour has been observed for a number of manganites in the same temperature range. This effect could be a result of different factors—a kind of magnetic disorder, magnetic frustration, the existence of small magnetic particles or clusters, etc. In all cases the main physical reason for it is that the system is energetically degenerate, and the main physical parameter responsible for the effect is magnetic anisotropy. In our case Mn^{3+} is the ion with a larger one-ion anisotropy whose first anisotropy constant $|K_1|$ decreases drastically when temperature changes between 0 and 100 K [50]. The amount of Mn^{3+} ions decreases with increasing Fe substitution and is considered to be zero for $x \geq 0.5$. The intensities of the Hopkinson-like maxima of ZFC thermomagnetic curves at $T_{\max 1}$ decrease in the same way as the amount of Mn^{3+} ions decreases, indicating the importance of Mn^{3+} ions. This can be considered as an indication that the effect is an intrinsic one for the manganites studied, but not of the existence of some extra magnetic phases, for example hausmanite (Mn_3O_4). However, more extended and detailed investigations are necessary for a better understanding this effect.

Another feature takes place for the samples with Fe substitution $x \geq 0.3$. Field cooling curves start to deviate from the ZFC ones at a temperature above $T_{\max 2}$, but without any typical maxima in the ZFC curves, as shown in figure 9. This deviation becomes stronger and the temperature at which this deviation occurs increases with increasing field. The above-described effect could not be attributed to some well defined magnetic state, for which the discrepancy between low field FC and ZFC thermomagnetic curves is accompanied by a maximum in the latter, as well as the effect being smeared with increasing field. Our suggestion is that this effect is a result of the formation of some magnetic clusters, which cannot exist without a magnetic field.

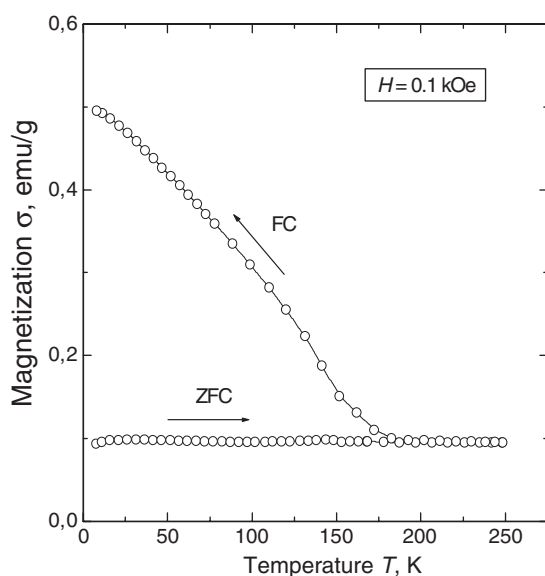


Figure 9. Low field ZFC and FC thermomagnetic curves of $\text{Bi}_{0.5}\text{Ca}_{0.5}\text{Fe}_{0.5}\text{Mn}_{0.5}\text{O}_3$.

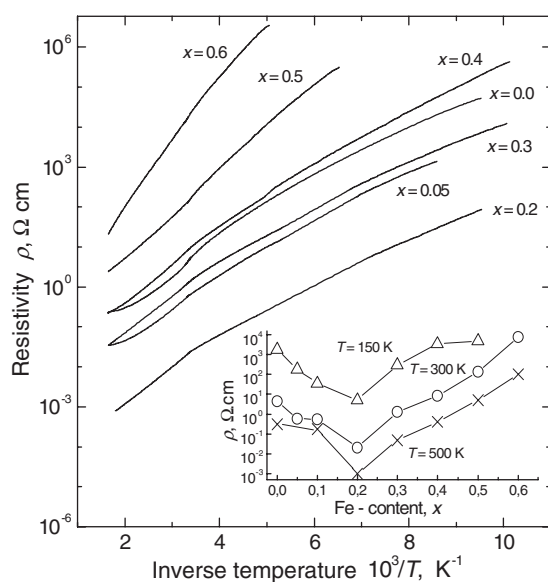


Figure 10. Temperature dependence of the resistivity for some $\text{Bi}_{0.5}\text{Ca}_{0.5}\text{Fe}_x\text{Mn}_{1-x}\text{O}_3$ compounds. The Fe content dependences of the resistivity at certain temperatures are shown in the inset.

All the samples studied exhibit a semiconductor-type electrical resistivity as shown in figure 10. The absolute values of the resistivity depend substantially on the Fe content, and the minimum of the resistivity is obtained for the sample with $x = 0.2$ throughout the whole temperature range of the resistivity measurements, as shown in the inset of figure 10. The temperature independence of this minimum indicates that it can be attributed not to the magnetic states of the specimens, but to their crystal structure or electronic configuration.

A qualitative thermoprobe test indicates that Fe substitution for Mn modifies the charge transport—the main charge carriers are negative (electrons) for the samples with $x \leq 0.5$ and they become positive ones (holes) for $x = 0.6$.

No magnetic field dependences of the electrical resistivity of the samples were observed in fields up to 7 kOe.

5. Conclusions

The results of the present investigations of Fe-substituted $\text{Bi}_{0.5}\text{Ca}_{0.5}\text{Fe}_x\text{Mn}_{1-x}\text{O}_3$ manganites can be summarized as follows.

Single-phase $\text{Bi}_{0.5}\text{Ca}_{0.5}\text{Fe}_x\text{Mn}_{1-x}\text{O}_3$ manganites can be synthesized with extended Fe substitution up to $x = 0.6$.

All the compounds are antiferromagnetic below a certain temperature. The charge/orbital order exists in the pure form for the compounds without or with very low Fe substitutions, with $x = 0$ and 0.05. For the higher Fe substitutions such a transition is either suppressed by the existence of Fe^{3+} , or its temperature T_{CO} is equal to or lower than the corresponding Néel temperature. The temperature of the transition to the antiferromagnetic state decreases with increasing Fe substitution, and for $x \geq 0.1$ antiferromagnetism is accompanied by a weak ferromagnetism. A new magnetic cluster state exists in the paramagnetic region of the manganites with Fe substitution $x \geq 0.3$, but only in the presence of a magnetic field.

The conductivity of the compounds is of semiconducting type, and there is no magnetoresistivity effect between 100 and 600 K in fields up to 7 kOe.

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