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Cation disorder and size effects on the magnetic transition in Ba-containing ferromagnetic manganites

M.M. Savosta[1], A.N. Ulyanov[1], N.Yu. Starostyuk[1], M. Maryško[2], and P. Novák[2,a]

[1] Donetsk Institute of Physics & Technics, Academy of Sciences of Ukraine, Rozy Luxembourg 72, 340114 Donetsk, Ukraine
[2] Institute of Physics, Academy of Sciences of the Czech Republic, Cukrovarnická 10, 162 53 Praha 6, Czech Republic

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Abstract. The results of ^{55}Mn NMR, dc magnetization, and ac susceptibility studies are presented for $La_{0.7}Ca_{0.15}Ba_{0.15}MnO_3$, $La_{0.7}Sr_{0.15}Ba_{0.15}MnO_3$, and $La_{0.7}Ba_{0.3}MnO_3$ ferromagnetic manganites. While T_C is a function of the mean radius of the La and alkaline-earth ions and the cation disorder, the form of the temperature dependence of the magnetic moment may be expressed as function of T_C only. The phase transition is continuous for all three compounds.

PACS. 75.30.Kz Magnetic phase boundaries (including magnetic transitions, metamagnetism, etc.) – 75.50.Dd Nonmetallic ferromagnetic materials – 76.60.-k Nuclear magnetic resonance and relaxation

1 Introduction

A close interplay between the crystal structure, magnetic and transport properties in manganese oxide perovskites have recently been the subject of intense study. In particular "colossal" magnetoresistance was found near the ferromagnetic ordering temperature in the mixed valence system $A_{1-x}A'_xMnO_3$ (A = rare-earth, A′ = Ca, Sr, Ba). For doping level $x \approx 0.3$ a ferro - paramagnetic transition can be in the vicinity of the room temperature, which makes these compounds suitable for practical applications.

For the fixed doping level the properties of the system should be fully determined by the ionic radii r_A and $r_{A'}$. Instead of r_A and $r_{A'}$ one can introduce two new parameters $\langle r_A\rangle$ and σ^2. $\langle r_A\rangle$ is the mean A site ionic radius and it controls the geometry of the perovskite lattice. $\sigma^2 = \langle r_A^2\rangle - \langle r_A\rangle^2$ quantifies the disorder connected with the random distribution of A and A′ cations having the different size. The same two parameters can be used to characterize the system even when there are more types of the alkaline-earth ions present in the A sublattice. A phenomenological relationship between T_C and $\langle r_A\rangle$ was established by Hwang *et al.* [1] for a number of manganites with x =0.3. It was found that T_C increases with increasing $\langle r_A\rangle$ more than twice, it displays a maximum for $La_{0.7}Sr_{0.3}MnO_3$ ($\langle r_A\rangle$ = 1.244 Å) and decreases continuously for $\langle r_A\rangle > 1.244$ Å. Rodriguez-Martinez and Attfield [2] have shown, however that beside the dependence of T_C on $\langle r_A\rangle$, its dependence on σ^2 plays an important role too. The question of the relative importance of $\langle r_A\rangle$ and σ^2 for the magnitude of T_C is still the matter of discussion (see *e.g.* [3,4]). An additional complication exists, when analyzing the magnetic transition in the system in question, as the phase transition can be either second or first order. Due to the inhomogeneity of the system, the ferromagnetic and paramagnetic phases may coexist below T_C, and the $M(T)$ dependence may be continuous even if the transition is first order [5]. The comparison of NMR and magnetization data then allows to determine relative volumes of these phases, as well as to demonstrate the discontinuous character of the transition. On the other hand when the transition is continuous, both methods lead to identical results for the temperature dependence of the reduced magnetic moment $m_S(T)$. Additional information is obtained from nuclear magnetic relaxation, as the relaxation rate exhibits critical behavior for $T \to T_C$ and diverges at $T = T_C$. In our recent papers using above procedure we showed that the transition is continuous in $La_{0.85}Na_{0.15}MnO_3$ (T_C = 315 K) [6] while it is of the first order in $Pr_{0.7}Ba_{0.3}MnO_3$ (T_C = 175 K) and $Pr_{0.7}Ca_{0.15}Sr_{0.15}MnO_3$ (T_C = 180 K) [5]. Experimental data indicate that for manganites with high T_C the transition is likely to be continuous, while in those with lower T_C the transition is discontinuous. To clear up the problem we performed an extensive study of the character of the magnetic transition in a series of $La_{0.7}A'_{0.3}MnO_3$ manganites. The results of this study are published elsewhere [7]. In this paper we describe the results of ^{55}Mn NMR, dc magnetization and ac susceptibility studies for $La_{0.7}Ca_{0.15}Ba_{0.15}MnO_3$, $La_{0.7}Sr_{0.15}Ba_{0.15}MnO_3$ and $La_{0.7}Ba_{0.3}MnO_3$ manganites which correspond to the "right part" of the Hwang's [1] phase diagram ($\langle r_A\rangle > 1.244$ Å). To make the results more complete we also make use of the data for $La_{0.7}Sr_{0.3}MnO_3$ obtained by us earlier [7]. The main goal of this paper is

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[a] e-mail: `novakp@fzu.cz`

to investigate the cation disorder and size effects on T_C and character of the magnetic transition. Since the Ba ion is much larger than the La ion, the substitution of Ba for La leads to an increase of both $\langle r_A \rangle$ and σ^2. By replacing part of Ba by Ca or Sr the effects of $\langle r_A \rangle$ and σ^2 may be to a large extent separated.

2 Results and discussion

Polycrystalline samples used in the present study were prepared by the nitrate method from the oxides La_2O_3 and MnO_2, and carbonates $CaCO_3$, $SrCO_3$ and $BaCO_3$. The solutions of the initial compounds were evaporated and the powders obtained were pressed into pellets. These pellets were annealed at 950 °C for 60 h with intermediate grinding and pressing. Finally, the samples were sintered at 1150 °C for 16 h.

The measurements of the dc magnetization and ac susceptibility were carried out using the Quantum Design SQUID magnetometer. The magnetization was measured in fields up to 5 T and the spontaneous moment was then determined by extrapolating the data to zero magnetic field. The NMR spectra were registered by a two pulse spin-echo method using a noncoherent spectrometer with frequency sweep and boxcar detector signal averaging. Optimal experimental conditions for exciting the nuclei in the domains only were chosen [8]. The nuclear spin-lattice relaxation time T_1 of ^{55}Mn was determined from the recovery of the spin-echo intensity after the inversion of nuclear spins by a 180° rf pulse.

The observed ^{55}Mn NMR spectra consist of a single relatively broad line, the nuclear spin-spin relaxation time T_2 at low temperatures varies across the NMR spectrum however. The amplitude of an echo is expected to be proportional to $\exp(-2t/T_2)$, where t is a time interval between the two exciting pulses. In view of the possible effect of T_2 on the form of NMR spectrum we performed the measurements for different t and then extrapolated the data to $t \to 0$. Corrected NMR spectra of ^{55}Mn obtained at 77 K for $La_{0.7}Ca_{0.15}Ba_{0.15}MnO_3$ (a), $La_{0.7}Sr_{0.15}Ba_{0.15}MnO_3$ (b), and $La_{0.7}Ba_{0.3}MnO_3$ (c) are displayed in Figure 1; in addition the variation of T_2 across the spectra is shown. The form of the spectra in $La_{0.7}Ba_{0.3}MnO_3$ differs slightly from the single Gaussian line. This is probably due to the approximate character of our correction. In what follows, the center of gravity of the corrected spectrum was identified with the resonance frequency.

The variation of the spin-spin relaxation time across the ^{55}Mn NMR spectrum in ferromagnetic manganites was observed earlier [8–10]. In reference [9] this behavior was ascribed to the Suhl-Nakamura interaction in which the nuclear spins interact via virtual electronic spin waves. The minimum in T_2 occurs in the center of the line because the majority of the nuclear spins precess at or near this frequency. The relaxation time, corresponding to the wings of the resonance line, which is only weakly influenced by the 'extra' relaxation and the width of lines are given in Table 1. The data for $La_{0.7}Sr_{0.3}MnO_3$ [7] are added for

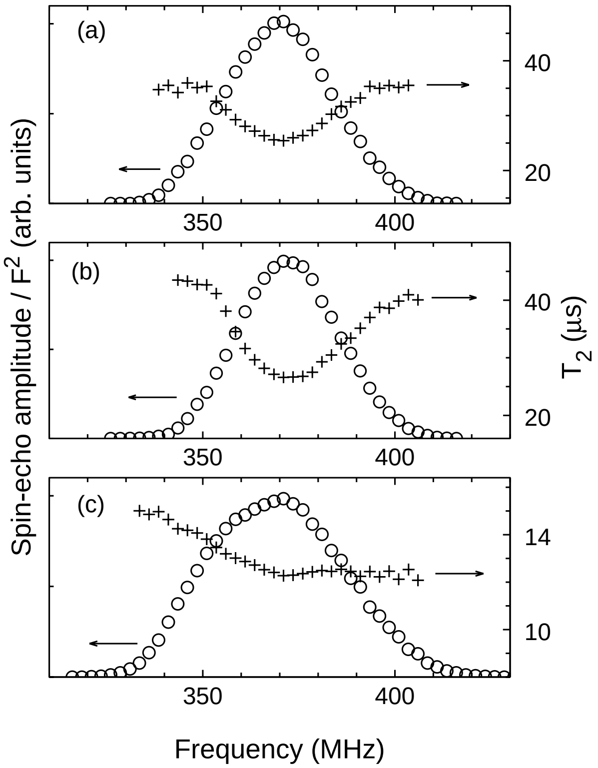

Fig. 1. NMR spectra of ^{55}Mn (○) obtained at 77 K for $La_{0.7}Ca_{0.15}Ba_{0.15}MnO_3$ (a), $La_{0.7}Sr_{0.15}Ba_{0.15}MnO_3$ (b), and $La_{0.7}Ba_{0.3}MnO_3$ (c). The crosses correspond to the spin-spin relaxation time T_2 as a function of the frequency.

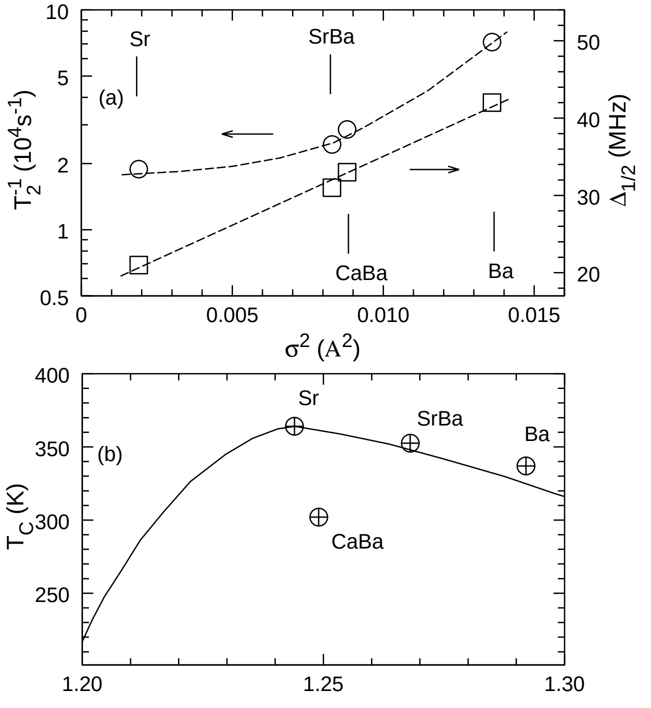

Fig. 2. (a) Dependence of the halfwidth $\Delta_{1/2}$ of the NMR line and the nuclear spin-spin relaxation rate T_2^{-1} on σ^2. (b) T_C as function of $\langle r_A \rangle$. The full curve represents the results of Hwang *et al.* (Ref. [1]).

Table 1. Mean A-site ionic radius $\langle r_{\mathrm{A}}\rangle$, cation-size variance σ^2, width $\Delta_{1/2}$ at half the amplitude of ^{55}Mn NMR line, nuclear spin-spin relaxation time T_2 at $T = 77$ K, ferromagnetic - paramagnetic transition temperature determined from the inflexion point of the susceptibility curve (T_{C}) and from the linear fit of the $T_1(T)$ data (T'_{C}) in a series of $\mathrm{La_{0.7}A'_{0.3}MnO_3}$ manganites. For each composition, $\langle r_{\mathrm{A}}\rangle$ and σ^2 were calculated using tabulated values of reference [11] for atoms in ninefold coordination.

composition	$\langle r_{\mathrm{A}}\rangle$ (Å)	σ^2 (Å^2)	$\Delta_{1/2}$ (MHz)	T_2 (μs)	T_{C} (K)	T'_{C} (K)
$\mathrm{La_{0.7}Sr_{0.3}MnO_3}$	1.244	0.0019	21	53	363.5	364.5(3.0)
$\mathrm{La_{0.7}Ca_{0.15}Ba_{0.15}MnO_3}$	1.249	0.0088	33	35	302	296(6)
$\mathrm{La_{0.7}Sr_{0.15}Ba_{0.15}MnO_3}$	1.268	0.0083	31	41	352.5	347(8)
$\mathrm{La_{0.7}\ Ba_{0.3}MnO_3}$	1.292	0.0136	42	13.5	337	-

comparison. The results show that the broadening of the NMR line as well as the decrease of T_2 is correlated with the cation disorder (Fig. 2a), but not with $\langle r_{\mathrm{A}}\rangle$. In our recent paper [8] we suggested that the spin-spin relaxation in these systems can be explained by the fluctuations of hyperfine fields caused by the hopping of the e_g electron holes of Mn ions. In this model T_2 is proportional to $1/\tau$, τ being the mean correlation time of the hopping. The present results confirm the validity of this model as cation disorder is expected to promote the localization of the e_g electron holes and thus it increases τ.

The increase of the temperature leads to a rapid decrease of T_2 in a similar way as was found for (La, Na) system [8]. We were able to observe the NMR signal until $T_2 \simeq 0.5$-1 μs, which limits the maximal temperature of our measurements. For (La, Ba) system, where spin-spin relaxation is shortest (see Fig. 1), we were able to observe NMR up to $T = 0.83\ T_{\mathrm{C}}$ only. Accordingly, the critical behavior of the relaxation near T_{C} was not examined in this case.

The temperature dependence of the reduced magnetic moment determined from the magnetization measurements for the (La, CaBa), (La, SrBa) and (La, Ba) samples is compared with the reduced NMR frequency in Figures 3, 4, and 5, respectively. In the insets the ac susceptibility and T_1 *vs.* temperature are shown. To compare the form of $M(T), f(T)$ dependence for these samples with the one for (La, Sr) compound (see below) the data are displayed as function of the reduced temperature T/T_{C}. The inflection point of the susceptibility curve was accepted as the Curie temperature (see Tab. 1).

Inspecting the data for (La, CaBa) sample in Figure 3, a slight difference between the temperature dependence of the reduced magnetization and reduced NMR frequency above $\simeq 0.87\ T_{\mathrm{C}}$ may be found, pointing to the possible development of the paramagnetic phase. The difference $\simeq 3\%$ is in the limit of the experimental error of the two methods, however. On the other hand, the critical behavior of T_1 when approaching T_{C} (inset in Fig. 3) is clearly seen. The transition temperature determined from linear fit of the relaxation data is in good agreement with T_{C} deduced from the ac susceptibility (see Tab. 1). For (La, SrBa) and (La, Ba) samples (Figs. 4 and 5) the reduced NMR frequency coincides with the reduced magnetization in the whole temperature range where both measurements were performed. For (La, SrBa) sample the transition temperature determined from the fit of the relaxation data is again in agreement with T_{C} deduced from the ac susceptibility (see Tab. 1). We concluded therefore that the magnetic phase transition is continuous for all three samples studied.

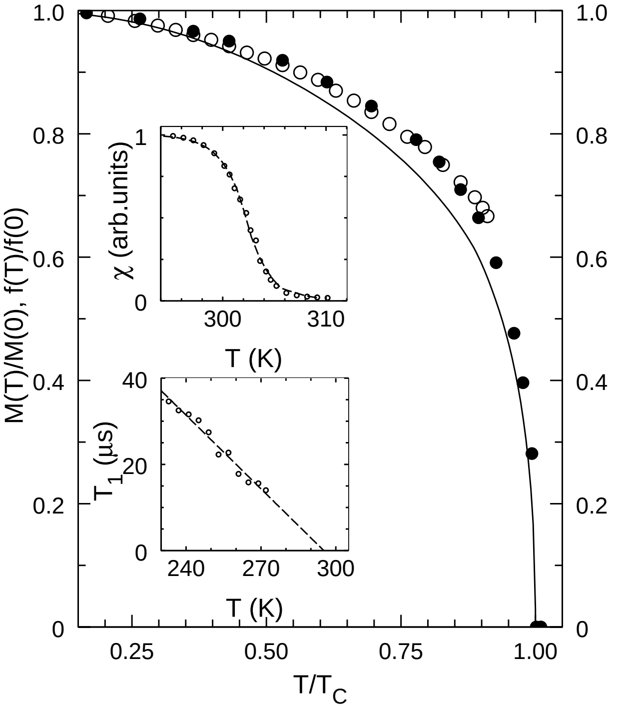

Fig. 3. The temperature dependence of the reduced magnetization (•) and the reduced NMR frequency (○) in $\mathrm{La_{0.7}Ca_{0.15}Ba_{0.15}MnO_3}$. The full curve represents the data for $\mathrm{La_{0.7}Sr_{0.3}MnO_3}$ of reference [7]. In the lower inset the spin-lattice relaxation time T_1 *vs.* T is displayed together with a linear fit (dashed line). In the upper inset the ac susceptibility *vs.* T is shown.

We now turn to the question of how the form of $m_S(T)$ depends on $\langle r_{\mathrm{A}}\rangle$ and σ^2. To this end the data for Ba-containing samples are compared with the results for (La, Sr) compound. The NMR and magnetization data for $\mathrm{La_{0.7}Sr_{0.3}MnO_3}$ [7] lead to $m_S(T)$, which is displayed in Figures 3, 4, 5 as a solid curve. The increase of the cation disorder in (La, CaBa) comparing to (La, Sr) results in the suppression of T_{C} from 364 to 302 K (Fig. 2b). At the same time, as seen from Figure 3, the character of $m_S(T)$ changes and it becomes steeper when $T \to T_{\mathrm{C}}$. σ^2 of (La, SrBa) is very close to σ^2 of (La, CaBa), while the mean

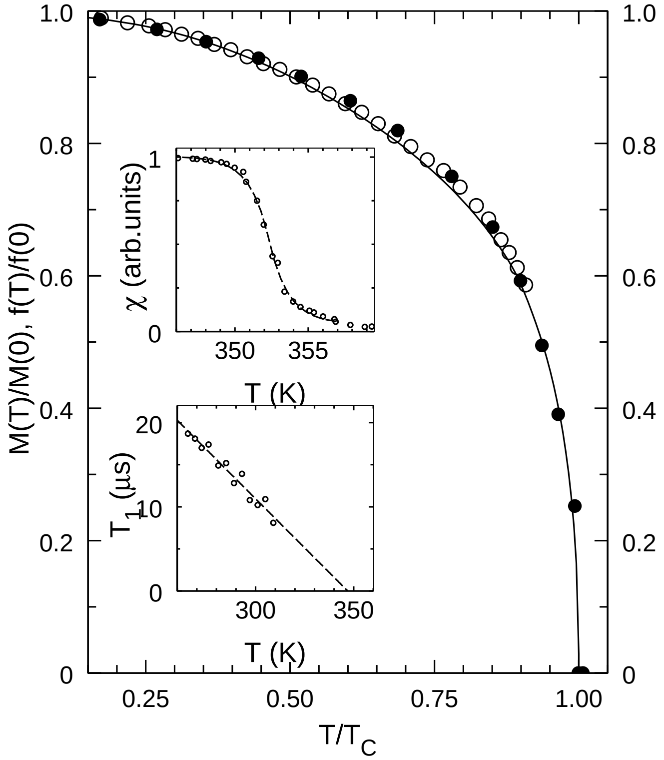

Fig. 4. The same as in Figure 3, but for $La_{0.7}Sr_{0.15}Ba_{0.15}MnO_3$.

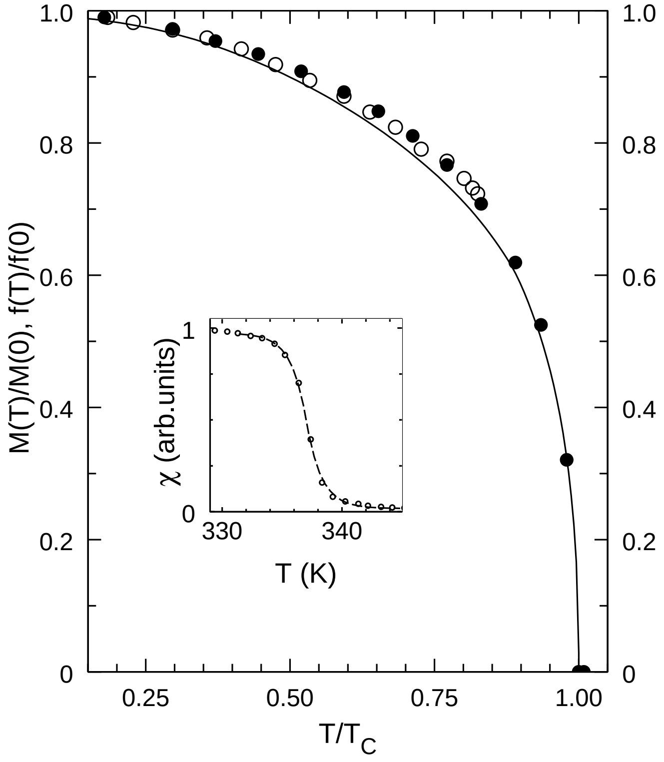

Fig. 5. The temperature dependence of reduced magnetization (•) and reduced NMR frequency (○) in $La_{0.7}Ba_{0.3}MnO_3$. The full curve represents the data for $La_{0.7}Sr_{0.3}MnO_3$ of reference [7]. In the inset the ac susceptibility *vs.* T is shown.

A-site ionic radius is larger. The increase of $\langle r_A \rangle$ restores T_C to 352.5 K (Fig. 2b), which is close to $T_C = 364$ K of (La, Sr). The important fact is that also the temperature dependence of the reduced magnetic moment returns close to the data for (La, Sr) compound (Fig. 4). Finally, further increase of both $\langle r_A \rangle$ and σ^2 in (La, Ba) results in $T_C = 337$ K which lies between the Curie temperature of (La, CaBa) and (La, SrBa). Accordingly, the form of the temperature dependence of the reduced magnetic moment for (La, Ba) represents the intermediate case (Fig. 5).

From the above analysis we can conclude that both $\langle r_A \rangle$ and σ^2 are important for the value of the Curie temperature. The form of $m_S(T)$ becomes steeper for $T \rightarrow T_C$ when the Curie temperature decreases. The results presented in this paper concern only the "right part" of the Hwang's phase diagram [1]. We note, however, that an analogous behavior occurs also in the other part of the Hwang's diagram, when T_C changes from 364 K ($La_{0.7}Sr_{0.3}MnO_3$) to 265 K ($La_{0.7}Ca_{0.3}MnO_3$) [7]. As showed in [7] this fact may be explained by an increase of the strength of the spin-lattice interaction when T_C decreases. The form of the temperature dependence of reduced magnetic moment depends rather on the resulting value of T_C than on the cation disorder or mean A-size ionic radius individually.

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