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Magnetotransport properties of the $\text{Sm}_{0.56}(\text{Sr}_{0.44-x}\text{Me}_x)\text{MnO}_3$ (Me = Ba, Ca, Cd) perovskites

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Abstract. The magnetization, magnetoresistance and elastic properties of $\text{Sm}_{0.56}(\text{Sr}_{0.44-x}\text{Me}_x)\text{MnO}_3$ (Me = Ba, Cd, Ca) have been investigated. It is established that $\text{Sm}_{0.56}\text{Sr}_{0.44}\text{MnO}_3$ exhibits a metamagnetic behaviour as well as anomalous elastic properties in a wide range of temperatures above the Curie point $T_C = 134$ K. Small additions of Ba, Cd and Ca ions lead to (i) an inhomogeneous magnetic state appearance and (ii) an irreversible metamagnetic behaviour below the Curie point. Further increase of Ba, Cd or Ca destroys the long-range ferromagnetic order giving rise to a spin-glass-like behaviour. Strongly reduced $\text{Sm}_{0.56}\text{Ba}_{0.44}\text{MnO}_{2.68}$ is a weak ferromagnet with $T_N = 137$ K. It is supposed that short-range charge ordering occurs in these compounds. The metamagnetic behaviour is associated with a concurrence of positive and negative superexchange interactions in the Ising antiferromagnet.

1. Introduction

The magnetotransport phenomena in perovskite type manganites attract current interest due to the colossal magnetoresistance effect whose nature is still a matter of discussion. In the doped manganites exchange interactions are strongly dependent on an Mn–O–Mn bond angle and, hence, expected to be reduced as the average size of the lanthanide reduces. Usually the critical temperature of transitions in the manganites for various doping levels is described as a function of the tolerance factor (f) which is defined as $f = (r_A + r_O)/\sqrt{2}(r_B + r_O)$ (r_A , r_B and r_O being the ionic radii of the elements A, B and oxygen respectively, for ABO_3) [1]. However, magnetic states for different doping ions (Ba, Ca or Sr) do not coincide despite the very close tolerance factors. Especially this is seen for Ba- and Bi-containing manganites [2, 3]. The ferromagnetic Curie temperature T_C around which an insulator–metal transition occurs in these manganates has been shown to be sensitive to the mismatch in the sizes of the A-site cations [4, 5].

At present $\text{Ln}_{1-x}\text{Sr}_x\text{MnO}_3$ (Ln = La, Pr, Nd) systems seem to be rather well studied [1, 6–8]. The $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ series is ferromagnetic and metallic in the interval $0.17 < x < 0.5$ whereas for $x = 0.5$ an antiferromagnetic A-type metallic state occurs [9]. $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ shows an antiferromagnet–ferromagnet transition at $T = 150$ K [10]. In the case of $\text{Ln}_{1-x}\text{Sr}_x\text{MnO}_3$ (Ln = Pr, Nd) the metallic ferromagnetic state is realized in the $0.25 < x < 0.5$ range. Above strontium content $x = 0.5$ both systems exhibit an antiferromagnetic quasimetallic state [9]. For the $x = 0.5$ composition the metallic ferromagnetic state develops slightly below room temperature and becomes insulating antiferromagnetic approximately

below 150 K. For the Nd-based series antiferromagnetic and charge ordering coexist [11] whereas for $\text{Ln}_{1-x}\text{Sr}_x\text{MnO}_3$ ($\text{Ln} = \text{La}, \text{Pr}$) antiferromagnetism appears in the charge-disordered phase. The magnetic and transport properties of Sm-based manganites are less understood at present. It is shown [1, 6] that these compounds in the range $x \sim 0.44$ exhibit a metamagnetic behaviour above the Curie point $T_C = 131$ K. The concentrational insulator-metal transition occurs near $x \approx 0.3$. In contrast to the $\text{Ln}_{1-x}\text{Sr}_x\text{MnO}_3$ ($\text{Ln} = \text{La}, \text{Pr}, \text{Nd}$) compounds the ferromagnetic ordering in $\text{Sm}_{0.56}\text{Sr}_{0.44}\text{MnO}_3$ seems to be a first order transition. According to [12] $\text{Eu}_{0.58}\text{Sr}_{0.42}\text{MnO}_3$ is a spin glass below 40 K; however in the temperature range below 120 K the metamagnetic behaviour is observed. The irreversibility and anomalies in the magnetostriction, magnetization and magnetoresistance isotherms have been observed at low temperatures (<90 K) for $\text{Gd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ [13]. These anomalies have been attributed to the establishment of a charge-ordered state. However, there are no structural findings in favour of such an assumption. According to [13], for temperature lower than ~ 42 K, the charge-ordered state coexists with the cluster-glass state. It is necessary to note that the metamagnetic behaviour is more pronounced for compositions with larger $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio than the optimal one 1:1 for the charge-ordered state. For better understanding of the magnetic properties of the manganites with small lanthanide ions we have undertaken the study of the $\text{Sm}_{0.56}(\text{Sr}_{0.44}\text{Me}_x)\text{MnO}_3$ systems where Sr^{2+} is replaced by divalent ions with strongly different ionic size. The effect of oxygen content on magnetic properties of $\text{Sm}_{0.56}\text{Sr}_{0.44}\text{MnO}_{3-\gamma}$ was studied also.

2. Experiment

The $\text{Sm}_{0.56}\text{Sr}_{0.44-x}\text{Me}_x\text{MnO}_3$ ($\text{Me} = \text{Ca}, \text{Cd}, \text{Ba}$) perovskites have been obtained by mixing Sm_2O_3 , SrCO_3 , Mn_2O_3 and MeO in adequate proportions. A 5% weight excess of CdO was chosen to compensate for an evaporation of Cd ions during the synthesis. The mixtures were first heated in air at 900°C for 2 h. The samples of the $\text{Sm}_{0.56}\text{Sr}_{0.44-x}\text{Cd}_x\text{MnO}_3$ series were prepared at 1260°C for 2 h in air in a closed crucible and finally cooled down to room temperature with a rate of 100 K h^{-1} . $\text{Sm}_{0.56}\text{Sr}_{0.44-x}(\text{Ca}, \text{Ba})_x\text{MnO}_3$ ($0 \leq x \leq 0.44$) samples were obtained at 1450°C with a cooling rate of 100 K h^{-1} . $\text{Sm}_{0.56}\text{Ba}_{0.44}\text{MnO}_3$ was reduced in an evacuated silica tube using metallic tantalum as a getter. X-ray patterns of the samples have shown them to be nominally single phase.

The average manganese oxidative state of some samples was determined by thermogravimetric analysis (the samples were reduced in hydrogen at high temperature). The magnetization was measured with a vibrating sample magnetometer. Magnetotransport measurements were carried out using a standard four-terminal method. The magnetic field was provided by a 120 kOe superconducting coil. Young's modulus was measured with a resonance method using cylindrical samples with a length about 6 cm and diameter 0.3 cm.

3. Results and discussion

The x-ray study for all the samples shows a perovskite pseudocubic structure with small orthorhombic distortions. The pseudocubic unit cell parameters are listed in table 1. Substitution of Sr ions with large Ba ions leads to a monotonically increasing unit cell volume whereas doping with relatively small Ca or Cd ions brought about decrease of unit cell parameters.

Figure 1 shows the temperature dependence of the magnetization for the $\text{Sm}_{0.56}(\text{Sr}_{0.44-x}\text{Me}_x)\text{MnO}_3$ ($\text{Me} = \text{Cd}, \text{Ba}, \text{Ca}$) compounds. The field cooled magnetization

Table 1. Unit cell parameters of $\text{Sm}_{0.56}(\text{Sr}_{0.44-x}\text{Me}_x)\text{MnO}_3$ series.

Composition	Sym	a (Å)	b (Å)	V (Å ³)
$\text{Sm}_{0.56}\text{Sr}_{0.44}\text{MnO}_3$	C	3.843		56.74
$\text{Sm}_{0.56}\text{Sr}_{0.28}\text{Ca}_{0.16}\text{MnO}_3$	C	3.829		56.14
$\text{Sm}_{0.56}\text{Sr}_{0.16}\text{Ca}_{0.28}\text{MnO}_3$	C	3.820		55.74
$\text{Sm}_{0.56}\text{Sr}_{0.38}\text{Cd}_{0.06}\text{MnO}_3$	C	3.840		56.63
$\text{Sm}_{0.56}\text{Sr}_{0.32}\text{Cd}_{0.12}\text{MnO}_3$	C	3.837		56.48
$\text{Sm}_{0.56}\text{Sr}_{0.2}\text{Cd}_{0.24}\text{MnO}_3$	C	3.834		56.36
$\text{Sm}_{0.56}\text{Sr}_{0.28}\text{Ba}_{0.16}\text{MnO}_3$	C	3.851		57.12
$\text{Sm}_{0.56}\text{Sr}_{0.16}\text{Ba}_{0.28}\text{MnO}_3$	C	3.863		57.67
$\text{Sm}_{0.56}\text{Ba}_{0.44}\text{MnO}_3$	C	3.881		58.44
$\text{Sm}_{0.56}\text{Ba}_{0.44}\text{MnO}_{2.68}$	T	3.933	7.696	59.54

(FC) for the $\text{Sm}_{0.56}(\text{Sr}_{0.44-x}\text{Cd}_x)\text{MnO}_3$ ($0.08 \leq x \leq 0.24$) series is registered in a field of 14 kOe whereas for the Ba- and Ca-containing samples the measurements have been performed in a field of 11 kOe. The parent $\text{Sm}_{0.56}\text{Sr}_{0.44}\text{MnO}_3$ compound exhibits the ferromagnetic ordering at $T_C = 134$ K. The magnetic moment is $3.5 \mu_B$ per formula unit in agreement with the expected one for the pure ferromagnetic state. The substitution of Sr with Cd leads to decreasing T_C down to 80 K ($x = 0.12$). For the samples with a Cd content above $x = 0.12$ the magnetic moment decreases markedly and the transition into the paramagnetic state becomes very broad. We think that the long-range ferromagnetic order is destroyed in the $x = 0.24$ sample. Similar magnetic behaviour was observed for Ba-substituted samples despite a large difference between Cd^{2+} and Ba^{2+} ionic radii. The Ba-containing samples in the range $0.16 \leq x \leq 0.44$ show magnetization–temperature behaviour incompatible with the ferromagnetic state. There are no critical points associated with magnetic ordering. Apparently these compounds are spin glasses or antiferromagnets with inclusions of ferromagnetic clusters.

The concentrational transition from the ferromagnetic state to the spin glass for Ca-doped compounds is observed between $x = 0.16$ and $x = 0.28$ (figure 1). The samples with a relatively small content of Ca ions ($x \leq 0.16$) exhibit the metamagnetic transition occurring in a wide temperature range both above and below T_C . Figure 3 shows the field dependence of the magnetization for $\text{Sm}_{0.56}\text{Sr}_{0.44}\text{Ca}_{0.16}\text{MnO}_3$. The magnetization curves show a large magnetic hysteresis associated with the metamagnetic transition occurring in a wide magnetic field range. With decreasing temperature the critical magnetic field inducing the ferromagnetic transition decreases gradually. At liquid helium temperature there is no appreciable hysteresis because the sample becomes predominantly ferromagnetic. Similar magnetization–field behaviour is observed for Cd-substituted samples ($x \leq 0.12$).

Reduction of the oxygen content in $\text{Sm}_{0.56}\text{Sr}_{0.44}\text{MnO}_{3-\gamma}$ down to $\gamma = 0.10$ leads to collapse of long-range ferromagnetic order also. The magnetization behaviour of $\text{Sm}_{0.56}\text{Sr}_{0.44}\text{MnO}_{2.9}$ was interpreted in terms of freezing magnetic moments of clusters below $T_f = 45$ K. However, strongly reduced $\text{Sm}_{0.56}\text{Ba}_{0.44}\text{MnO}_{2.68}$ exhibits a small spontaneous magnetic moment ($0.07 \mu_B$ per manganese ion at 4.2 K) and a relatively sharp transition at $T = 137$ K into a paramagnetic state (figure 2). A reoxidized sample shows similar magnetic properties as the sample before reduction. Such a behaviour (figure 2) could be attributed to a weak ferromagnetic ground state. Apparently oxygen vacancies are ordered in this compound thus leading to a homogenous magnetic state.

The evolution of the resistivity versus temperature for the Cd-containing samples in a zero magnetic field is presented in figure 4. The samples with the Cd content $x \leq 0.12$ exhibit a peak of resistivity coinciding with the Curie point. With increase of the Cd content the peak

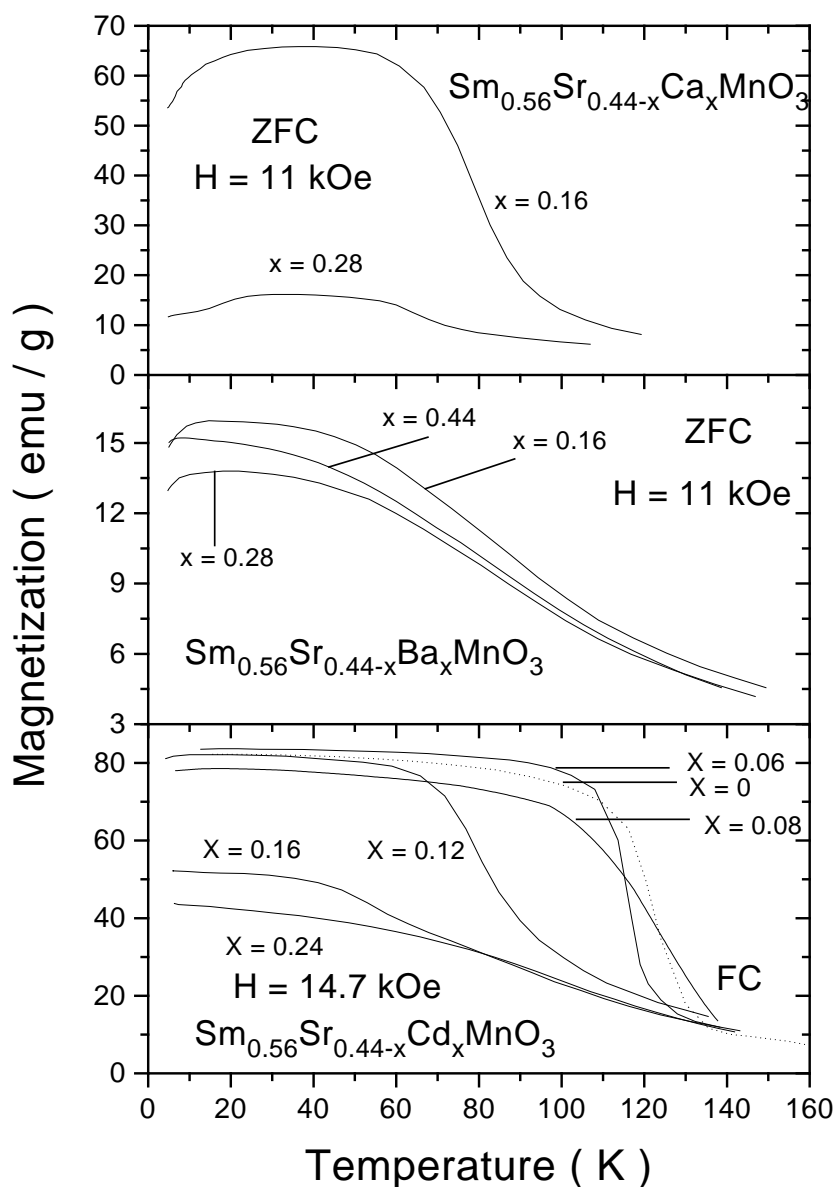


Figure 1. Magnetization against temperature for $\text{Sm}_{0.56}(\text{Sr}_{0.44-x}\text{Ca}_x)\text{MnO}_3$ (upper panel), $\text{Sm}_{0.56}(\text{Sr}_{0.44-x}\text{Ba}_x)\text{MnO}_3$ (middle panel) and $\text{Sm}_{0.56}(\text{Sr}_{0.44-x}\text{Cd}_x)\text{MnO}_3$ (lower panel).

shifts to lower temperature in agreement with magnetization data. The Ba- and Cd-containing samples with $x \geq 0.16$ are semiconducting in the whole investigated range of temperature (77–300 K). Figure 5 shows the magnetoresistivity ratio as a function of a magnetic field for $\text{Sm}_{0.56}\text{Sr}_{0.38}\text{Cd}_{0.06}\text{MnO}_3$. This composition is ferromagnetically ordered at 120 K. From figure 5 it is seen clearly that the magnetoresistance exhibits a magnetic field hysteresis above the Curie point. The magnetoresistance increases with increasing magnetic field, indicating the metamagnetic transition. Below 120 K the changes in the resistivity induced by an external

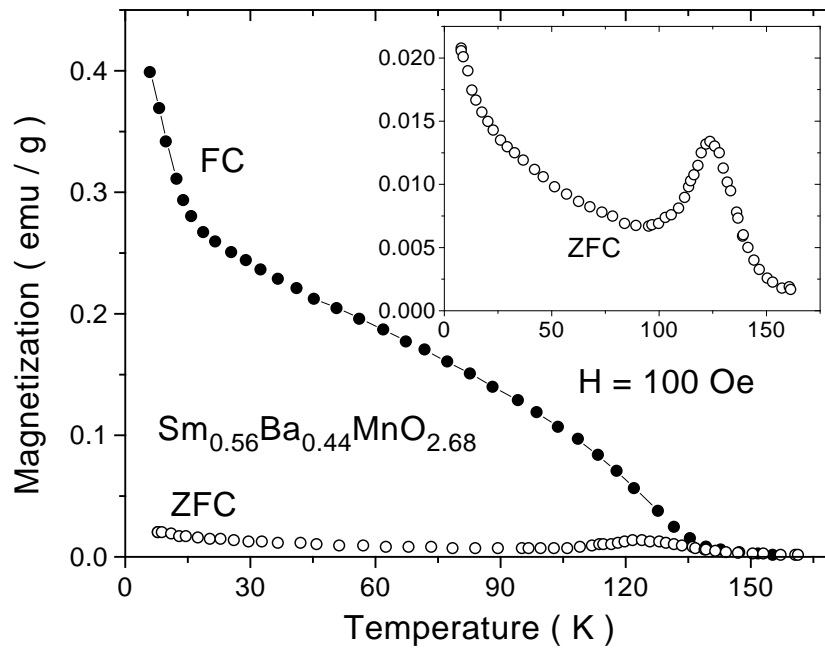


Figure 2. Magnetization against temperature for $\text{Sm}_{0.56}\text{Ba}_{0.44}\text{MnO}_{2.68}$.

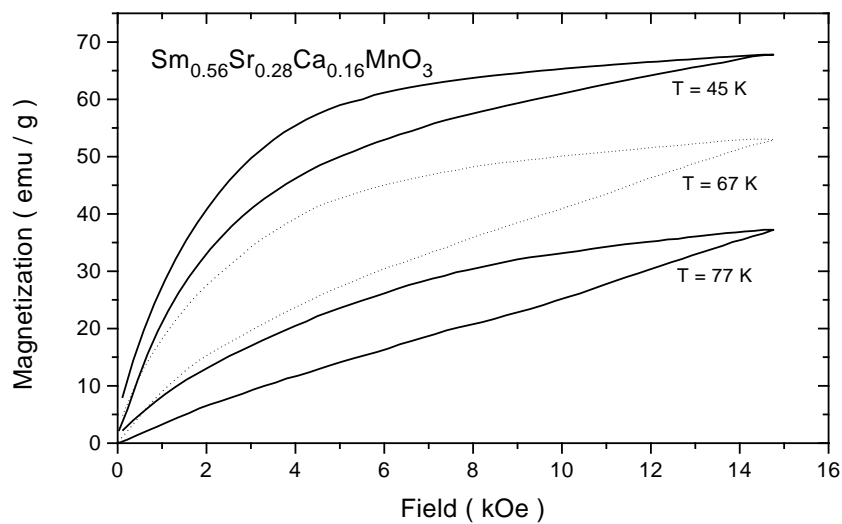


Figure 3. Magnetization against field for $\text{Sm}_{0.56}(\text{Sr}_{0.28}\text{Ca}_{0.16})\text{MnO}_3$.

field become irreversible. Both magnetoresistance and irreversibility of the resistivity increase with decreasing temperature (see also the inset to figure 4).

The results of the measurements of the Young's modulus for the $\text{Sm}_{0.56}\text{Sr}_{0.44}\text{MnO}_3$ sample are displayed in figure 6. The Young's modulus on temperature dependence shows a minimum at around 130 K. Around 200 K a modulus rise with increasing temperature is observed. The transition occurs in a wide temperature range. Above 500 K Young's modulus decreases

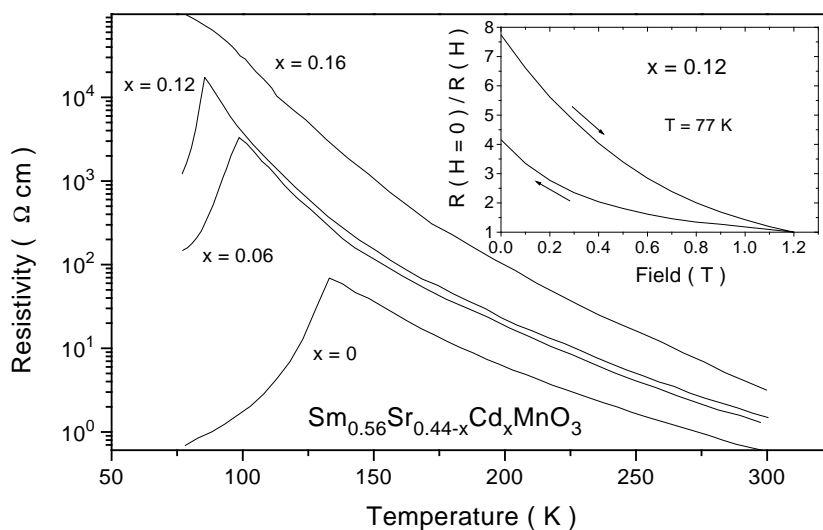


Figure 4. Resistivity against temperature for $\text{Sm}_{0.56}(\text{Sr}_{0.44-x}\text{Cd}_x)\text{MnO}_3$. The inset shows magnetoresistance ratio against field for $x = 0.12$.

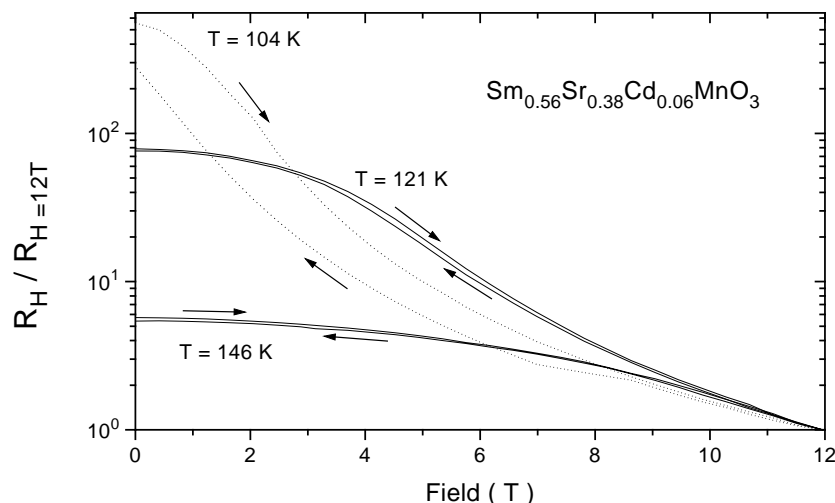


Figure 5. The magnetoresistance ratio against field for the $\text{Sm}_{0.56}\text{Sr}_{0.38}\text{Cd}_{0.06}\text{MnO}_3$ sample.

with increasing temperature indicating a stabilization of the lattice. The anomaly of Young's modulus at 130 K may be ascribed to the ferromagnetic ordering. A significant reduction of Young's modulus during transition from the ferromagnetic into the paramagnetic state was observed in the $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ system [14]. By contrast, antiferromagnetic ordering in the CaMnO_3 perovskite occurs without changes of Young's modulus [14]. A very large minimum of Young's modulus appears around the temperature of charge or orbital orderings which are first order phase transitions in the manganites [14–16]. The changes of the Young's modulus observed slightly below room temperature are rather large and could be interpreted in terms of crystal structure transition due to the charge ordering. However we have not observed magnetization or resistivity anomalies in this temperature range. Apparently below

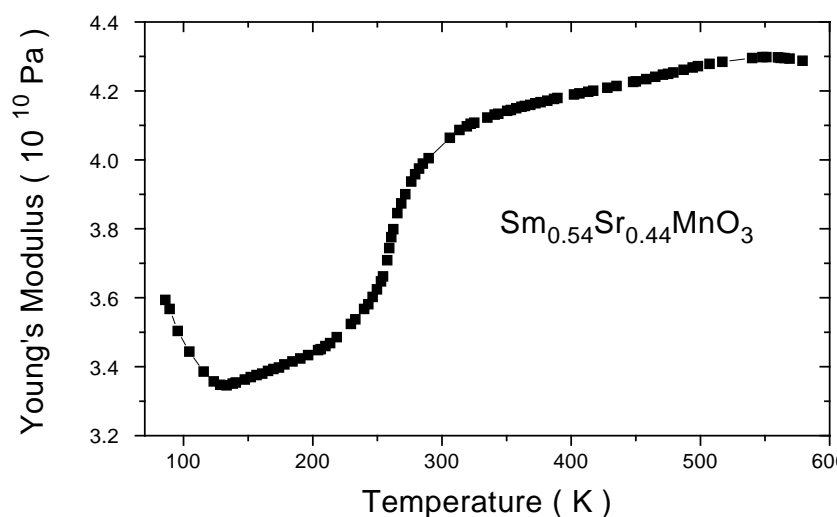


Figure 6. Young's modulus against temperature for $\text{Sm}_{0.56}\text{Sr}_{0.44}\text{MnO}_3$.

room temperature short-range charge order starts to be established and thus Young's modulus reduces as T is lowered. This process takes place down to 140 K where the reentrant transition into the ferromagnetic state destroys both antiferromagnetic and charge short-range order. In order to confirm the presence of a phase transition associated with the charge ordering we have undertaken the x-ray powder diffraction study of $\text{Sm}_{0.56}\text{Sr}_{0.44-x}\text{Me}_x\text{MnO}_3$ at 150 K. We did not observe superlattice peaks due to charge ordering; however the width of some peaks increases upon cooling. The increase of crystal structure distortion is an indication of the localization and ordering of the e_g electrons.

From literature data [9] one can conclude that the metamagnetic behaviour and the charge ordering are not strongly connected. We suppose that in $\text{Ln}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ ($\text{Ln} = \text{La}, \text{Pr}$) the charge ordering does not occur due to a strong hybridization of 3d and oxygen orbitals in these compounds. The large 3d bandwidth leads to an antiferromagnetic metallic state in the $\text{Ln}_{1-x}\text{Sr}_x\text{MnO}_3$ ($x > 0.5$; $\text{Ln} = \text{La}, \text{Pr}, \text{Nd}$) compounds. By contrast in the $\text{Ln}_{1-x}\text{Sr}_x\text{MnO}_3$ ($\text{Ln} = \text{Sm}, \text{Gd}, \text{Eu}$) an antiferromagnetic state is not metallic. In these systems the metamagnetic behaviour is observed at the rather small doping level $x = 0.4$ in comparison with systems with a large lanthanide where the critical magnitude is $x = 0.5$. We think that these features may be connected with (i) large difference between lanthanide and strontium ion size [4, 17] and (ii) oxygen nonstoichiometry increasing with decrease of lanthanide ionic radii. Our results of the thermogravimetric study indicate that the oxygen content in the $\text{Sm}_{0.56}\text{Sr}_{0.44-x}\text{Me}_x\text{MnO}_3$ series is slightly less than the stoichiometric one and really the formula is $\text{Sm}_{0.56}\text{Sr}_{0.44-x}\text{Me}_x\text{MnO}_{2.98}$. Apparently the deviation from stoichiometry increases with increasing Sr content. The oxygen nonstoichiometry favours the collapse of the long-range charge-ordered state. In agreement with experimental data the superexchange interaction Mn-O-Mn trends to become antiferromagnetic while the Mn-O-Mn angle decreases [18]. The decrease of the Mn-O-Mn bond is caused by decrease of the lanthanide size. In the case of a large difference between the size of the lanthanide and strontium ions there is a number of different Mn-O-Mn angles. Some of them correspond to the ferromagnetic exchange interaction whereas other correspond to antiferromagnetic ones. Due to an enhancement of the antiferromagnetic component of the exchange interactions the system becomes unstable

regarding the antiferromagnet–ferromagnet transitions in the doping range $0.4 \leq x < 0.5$, that is slightly less than that in the $\text{Ln}_{1-x}\text{Sr}_x\text{MnO}_3$ compounds ($\text{Ln} = \text{La}, \text{Pr}, \text{Nd}$). The anomalous elastic properties of $\text{Sm}_{0.56}\text{Sr}_{0.44}\text{MnO}_3$ in a wide range of temperature (figure 6) may be associated with a short-range charge ordering. A reentrant transition from an incipient charge-ordered state to a charge-delocalized ferromagnetic state has been earlier established in the manganate $\text{Nd}_{0.25}\text{La}_{0.25}\text{Ca}_{0.5}\text{MnO}_3$ [19]. According to [19] there is no long-range ordering in the charge-ordered state. These authors refer to this state as an incipient charge ordered state, in order to distinguish it from the normal charge-ordered state. According to our data there are some common features between charge-ordered states in $\text{Nd}_{0.25}\text{La}_{0.25}\text{Ca}_{0.5}\text{MnO}_3$ and $\text{Sm}_{0.56}\text{Sr}_{0.44}\text{MnO}_3$.

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