

Comment on ` $\text{La}_{0.95}\text{Mg}_{0.05}\text{MnO}_3$: an ideal ferromagnetic system?'

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COMMENT

Comment on ‘La_{0.95}Mg_{0.05}MnO₃: an ideal ferromagnetic system?’

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Abstract

In a recent paper (Zhao J H, Song T, Kunkel H P, Zhou X Z, Roshko R M and Williams G 2000 *J. Phys.: Condens. Matter* **12** 6903), Zhao *et al* reported detailed measurements on the magnetic properties of LaMnO₃ with 5 at.% of the divalent cation Mg substituted in, which shows semiconducting ferromagnetic behaviour at low temperatures. This system has been shown to be an ideal ferromagnet with isotropic, three-dimensional Heisenberg behaviour and to have some unusual characteristics at low temperatures, in contrast with LaMnO₃ with comparable levels of Ca doping. It is shown here that the authors have actually studied the magnetic properties of the self-doped compound La_{0.95}MnO₃ for which the reported properties are not unusual.

The interesting electrical and magnetic properties of the substituted perovskite manganates La_{1-x}A_xMnO₃ (A = Ca, Sr and Ba), where the trivalent La ions in LaMnO₃ are replaced partly by divalent alkali metal ions, were first reported by Jonker and Van Santen in 1950 [1]. These interesting electrical and magnetic properties were found to be due to the conversion of a proportion of the Mn³⁺ in LaMnO₃ to Mn⁴⁺ for charge compensation. Later studies have shown that the self-doped compositions La_{1-x}MnO₃ exhibit very similar electrical and magnetic properties due to the presence of Mn³⁺ and Mn⁴⁺ in their lattice [2]. The recent discovery of very large negative magnetoresistance, known as colossal magnetoresistance (CMR), in thin films of substituted and self-doped manganates [3, 4] has initiated intensive research work on this class of materials aimed at achieving an understanding of the basic mechanisms associated with their peculiar electrical, magnetic and magnetoresistive properties. This has led to further studies on the substituted manganates with substitution at the La site or Mn site (or both) by other ions, carried out to search for materials with improved properties and also to achieve a very detailed understanding of the phenomenon of CMR. Zhao *et al* [5] recently reported magnetic properties of LaMnO₃ with a small amount of Mg²⁺ substituted at

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the La site. It has been shown that the composition $\text{La}_{0.95}\text{Mg}_{0.05}\text{MnO}_3$ behaves like an ideal ferromagnetic system and exhibits unusual characteristics. The magnetic behaviour of this compound contrasts with that of LaMnO_3 with comparable levels of Ca doping. A detailed study of the electrical properties of this compound was also reported later by Zhao *et al* [6]. In this comment we show, on the basis of magnetic and powder x-ray diffraction measurements, that the $\text{La}_{0.95}\text{Mg}_{0.05}\text{MnO}_3$ composition which was shown to be an ideal ferromagnetic system is in fact the self-doped composition $\text{La}_{0.95}\text{MnO}_3$.

Two compounds, $\text{La}_{0.95}\text{MnO}_3$ (LMO1) and the reported composition $\text{La}_{0.95}\text{Mg}_{0.05}\text{MnO}_3$ (LMMO1), were synthesized under identical conditions from the respective oxides by following the procedure reported by Zhao *et al* [5]. The samples were furnace cooled to room temperature. The powder x-ray diffraction patterns of the two compounds are shown in figure 1. The two XRD patterns are exactly identical, indicating the formation of a rhombohedral perovskite phase. The patterns could be indexed on a rhombohedral unit cell with lattice parameters $a = 5.495 \text{ \AA}$, $\alpha = 60.66^\circ$ for $\text{La}_{0.95}\text{MnO}_3$ and $a = 5.497 \text{ \AA}$, $\alpha = 60.62^\circ$ for $\text{La}_{0.95}\text{Mg}_{0.05}\text{MnO}_3$. That the XRD patterns of $\text{La}_{0.95}\text{MnO}_3$ and $\text{La}_{0.95}\text{Mg}_{0.05}\text{MnO}_3$ are identical indicates that it is not possible to confirm the formation of the Mg-substituted composition from the powder XRD pattern of the sample. Formation of the perovskite phase and absence of reflections due to the starting materials and any other impurity phases do not constitute a guarantee of the formation of the expected composition. If MgO has not reacted and remains as a separate phase, its presence may not be observed in the XRD pattern because of the very low amount of the MgO phase (in this case $\sim 0.8 \text{ wt\%}$ if MgO remains unreacted).

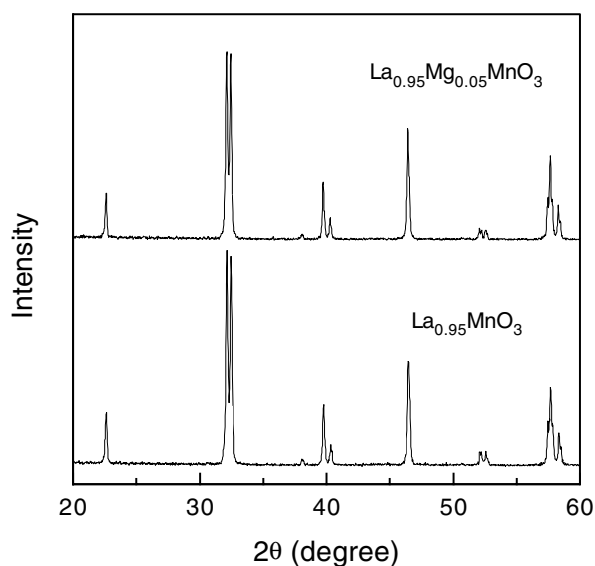


Figure 1. Powder x-ray diffraction patterns of $\text{La}_{0.95}\text{MnO}_3$ (LMO1) and $\text{La}_{0.95}\text{Mg}_{0.05}\text{MnO}_3$ (LMMO1).

If Mg^{2+} cannot be substituted for La^{3+} in LaMnO_3 , it is expected that the presence of MgO could be detected in the XRD patterns for larger values of x in the expected compositions in $\text{La}_{1-x}\text{Mg}_x\text{MnO}_3$. Therefore, we have attempted to synthesize the composition $\text{La}_{0.67}\text{Mg}_{0.33}\text{MnO}_3$ and the self-doped compound $\text{La}_{0.67}\text{MnO}_3$ under identical conditions. Moreover, the synthesis and properties of the composition $\text{La}_{0.67}\text{Mg}_{0.33}\text{MnO}_3$ were reported earlier by the same group [7] as had studied the properties of $\text{La}_{0.95}\text{Mg}_{0.05}\text{MnO}_3$. Zhou

et al [7] have shown that single-phase composition is obtained, and unusual insulating behaviour is observed for $\text{La}_{0.67}\text{Mg}_{0.33}\text{MnO}_3$ as compared to the behaviours of Ca- or Sr-substituted compositions. We have prepared the composition $\text{La}_{0.67}\text{Mg}_{0.33}\text{MnO}_3$ under synthesis conditions identical to those reported by Zhou *et al* [7]. Powder x-ray diffraction patterns of $\text{La}_{0.67}\text{Mg}_{0.33}\text{MnO}_3$ and $\text{La}_{0.67}\text{MnO}_3$ are compared in figure 2. The two compositions show almost identical patterns from a rhombohedral perovskite lattice and weak reflections due to manganese oxide are observed in both patterns. It was found that the powder XRD pattern of $\text{La}_{0.67}\text{Mg}_{0.33}\text{MnO}_3$ exhibits weak reflections corresponding to MgO as an impurity phase. The powder XRD pattern of the Ca-substituted compound $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$, heated only up to 1000 °C (compared to 1200 °C used for the preparation of the Mg-substituted composition) is also shown in figure 2, to show the absence of reflections due to oxides of manganese or calcium in the Ca-substituted compound prepared at so much lower a temperature. All the reflections in the pattern of the Ca-substituted compound can be indexed to an orthorhombic unit cell. The reflections of the Ca-substituted compound are extremely broad, as if the particle sizes are very small, and this is due to the compositional inhomogeneity problem as discussed previously [8].

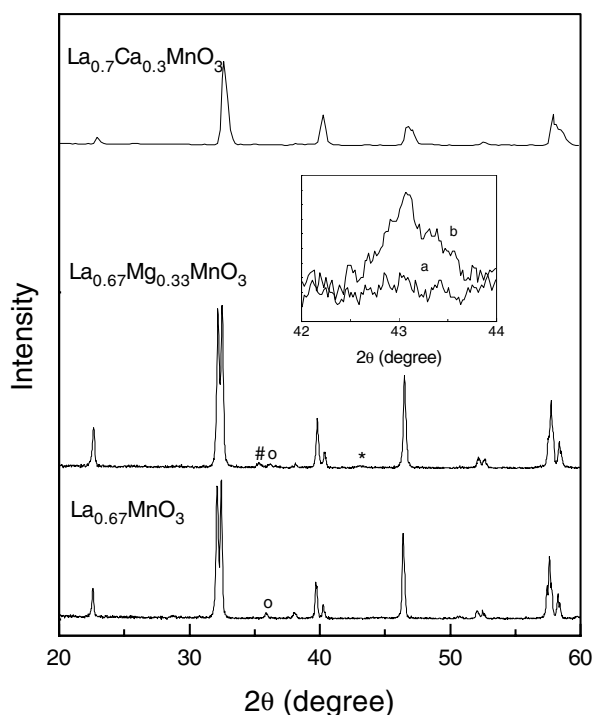


Figure 2. Powder x-ray diffraction patterns of the compositions $\text{La}_{0.67}\text{MnO}_3$, $\text{La}_{0.67}\text{Mg}_{0.33}\text{MnO}_3$ and $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$. The reflections marked by *, o and # are due to MgO, Mn_3O_4 and MnO_2 , respectively. Inset: enlarged XRD patterns of (a) $\text{La}_{0.67}\text{MnO}_3$ and (b) $\text{La}_{0.67}\text{Mg}_{0.33}\text{MnO}_3$ clearly showing the (200) reflection from MgO.

The actual composition of the self-doped manganates, $\text{La}_{1-x}\text{MnO}_{3+\delta}$, contains some vacancies at the manganese sites and the true composition is represented as $\text{La}_{1-x}\text{Mn}_{1-y}\text{O}_{3-z}$ [9]. The presence of a small amount of Mn_3O_4 is generally observed in the powder XRD patterns of these compositions [4, 9, 10] for larger values of x ; this may correspond to an equivalent amount of Mn deficiency. This is in accordance with the $\text{La}_2\text{O}_3\text{--Mn}_2\text{O}_3$ phase

diagram for $\text{Mn}/(\text{La} + \text{Mn}) > 0.5$ [11]. The fact that the presence of Mn_3O_4 and MgO is observed in the XRD pattern of the proposed composition $\text{La}_{0.67}\text{Mg}_{0.33}\text{MnO}_3$ implies that Mg^{2+} is not substituted for La^{3+} as expected and the perovskite phase obtained is a self-doped composition.

The temperature variations of the magnetization (field-cooled, FC, and zero-field-cooled, ZFC) for $\text{La}_{0.95}\text{MnO}_3$ (LMO1) and $\text{La}_{0.95}\text{Mg}_{0.05}\text{MnO}_3$ (LMMO1) are compared in figure 3. $\text{La}_{0.95}\text{MnO}_3$ and $\text{La}_{0.95}\text{Mg}_{0.05}\text{MnO}_3$ each show a ferromagnetic transition, at $T_c \approx 162$ and 184 K, respectively. The higher value of the Curie temperature for the Mg-added composition, compared to that reported ($T_c = 147$ K) by Zhao *et al* [5], is due to the relatively large Mn^{4+} content in the sample prepared in the present study. This is also evidenced from the rhombohedral structure of the compound compared to the orthorhombic structure reported by Zhao *et al* [5]. It is known that, for the self-doped compositions $\text{La}_{1-x}\text{MnO}_3$, it is difficult to control the $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio which is determined by various factors like method of synthesis, temperature, oxygen pressure and cooling speed [10]. For the same composition, the Curie temperature increases with increasing Mn^{4+} content and the structure changes from orthorhombic to rhombohedral for higher Mn^{4+} concentrations [11]. A Curie temperature as high as 240 K is reported for rhombohedral $\text{La}_{0.95}\text{MnO}_3$ by Ferris *et al* [12]. Similarly, slightly different Curie temperatures are reported by Ganguly *et al* [13] for $\text{La}_{0.7}\text{MnO}_3$ and a two-phase mixture containing $\text{La}_{0.7}\text{MnO}_3$ and CeO_2 obtained while attempting to synthesize a proposed Ce-substituted LaMnO_3 compound. In the hope of confirming that the higher T_c , compared to that reported by Zhao *et al* [5], obtained in the present study is due to the processing conditions and may not be reproducible, we synthesized another batch of the two compositions $\text{La}_{0.95}\text{MnO}_3$ and $\text{La}_{0.95}\text{Mg}_{0.05}\text{MnO}_3$. The second batch of $\text{La}_{0.95}\text{MnO}_3$ (LMO2) and $\text{La}_{0.95}\text{Mg}_{0.05}\text{MnO}_3$ (LMMO2) showed ferromagnetic transitions at 171 and 178 K (compared to 162 and 184 K for LMO1 and LMMO1), respectively. ZFC magnetization curves for two compositions belonging to the two different batches are compared in figure 4. Though the two different synthesis procedures were carried out under apparently identical preparation conditions, it appears that the difference in T_c may be due to slight differences in the atmosphere or cooling speed.

There are few reports of detailed studies on the substitution for La^{3+} in LaMnO_3 with the tetravalent ions Ce^{4+} [14, 15] and Sn^{4+} [16, 17]. The properties of these tetravalent-ion-substituted manganates were shown to be similar to those of the divalent-alkali-metal-ion-substituted compositions, owing to the presence of manganese as Mn^{3+} and Mn^{4+} in the lattice. However, Ganguly *et al* [13] and Caneiro *et al* [18] have very recently shown that the results on Ce- and Sn-substituted LaMnO_3 are questionable. Detailed studies by these authors have indicated that La is not replaced by the tetravalent ions Sn^{4+} and Ce^{4+} in LaMnO_3 and that the substituted compositions as earlier reported are multiphase systems containing $\text{La}_{1-x}\text{MnO}_3$, Mn_3O_4 and SnO_2 or CeO_2 . The magnetic properties which were thought to be characteristic of the tetravalent-ion-substituted manganates are shown to be the properties of self-doped compositions $\text{La}_{1-x}\text{MnO}_3$.

It can be argued that Mg^{2+} cannot be substituted for La^{3+} in LaMnO_3 due to the smaller ionic radius of Mg^{2+} when compared to the radius of Mn^{2+} , as shown in table 1. A comparison of the ionic radii of different ions in eightfold coordination indicates that the ionic radii of the divalent ions which can be substituted for La are comparable to or larger than that of La^{3+} . The ionic radii of the tetravalent ions Ce^{4+} and Sn^{4+} which cannot be substituted for La^{3+} are much smaller than that of La^{3+} . The ionic radius of Mn^{2+} is larger than that of Mg^{2+} and therefore Mn^{2+} should be the preferred ion for replacing La^{3+} , rather than Mg^{2+} , when they are present together.

While discussing the small jump in the low-field, zero-field-cooled magnetization at ~ 85 K

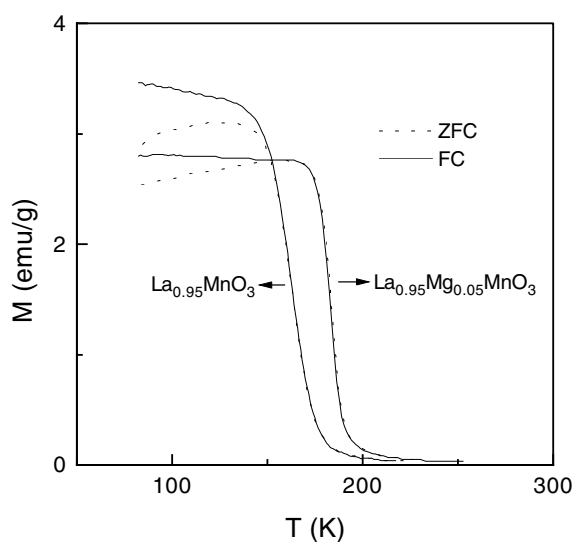


Figure 3. Field-cooled (FC) and zero-field-cooled (ZFC) magnetization curves of $\text{La}_{0.95}\text{MnO}_3$ (LMO1) and $\text{La}_{0.95}\text{Mg}_{0.05}\text{MnO}_3$ (LMMO1); $H = 50$ Oe.

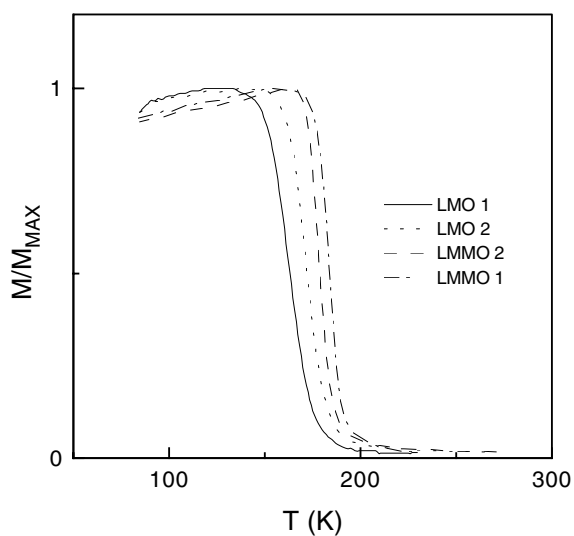


Figure 4. Comparison of the temperature variation of the ZFC magnetizations ($H = 50$ Oe) of $\text{La}_{0.95}\text{MnO}_3$ (LMO1 and LMO2) and $\text{La}_{0.95}\text{Mg}_{0.05}\text{MnO}_3$ (LMMO1 and LMMO2).

Table 1. Effective ionic radii (R) of La^{3+} and some other ions for eightfold coordination [19].

Ion	Pb^{2+}	Sr^{2+}	La^{3+}	Ca^{2+}	Ce^{4+}	Mn^{2+}	Mg^{2+}	Sn^{4+}
R (Å)	1.29	1.26	1.16	1.12	0.97	0.96	0.89	0.81

followed by a maximum just below the T_c of the proposed composition $\text{La}_{0.95}\text{Mg}_{0.05}\text{MnO}_3$, Zhao *et al* [5] argued that this is an unusual property for the Mg-substituted compound. In fact,

such a low-temperature anomaly in the zero-field-cooled magnetization or ac susceptibility is a common feature of lightly doped LaMnO_3 , observed for small values of x in the self-doped composition $\text{La}_{1-x}\text{MnO}_3$ [9, 20] as well as in the alkaline-earth-metal-doped compositions $\text{La}_{1-x}\text{A}_x\text{MnO}_3$ ($A = \text{Ca}, \text{Sr}, \text{Ba}$) [21–23]. These compositions remain ferromagnetic even below the temperature at which a jump in the ZFC magnetization is observed, as evidenced from neutron diffraction studies. This small jump in the low-field ac and dc susceptibilities, associated with a jump in the temperature variation of the coercivity, has been shown to be associated with domain wall pinning effects [24]. So, if the actual composition of the sample is envisaged as $\text{La}_{0.95}\text{MnO}_3$, the magnetic behaviour is not in contrast with that for a compound with comparable levels of Ca doping as commented by Zhao *et al* [5]. The properties reported for $\text{La}_{0.95}\text{Mg}_{0.05}\text{MnO}_3$ as an ideal ferromagnetic system are, therefore, the properties of the self-doped compound $\text{La}_{0.95}\text{MnO}_3$.

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