

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

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REPLY TO COMMENT

Reply to Comment on ‘ $\text{La}_{0.95}\text{Mg}_{0.05}\text{MnO}_3$: an ideal ferromagnetic system?’

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Abstract

Detailed alternating-current susceptibility and low-field magnetization measurements on samples of Mg-substituted LaMnO_3 , which x-ray data indicate are orthorhombic, not rhombohedral, show that (i) various oxides of Mn and Mg, which should be present if self-doping occurs, are present at such low levels that they cannot be detected and (ii) the extent of the self-doping of the parent compound $\text{La}_{1-y}\text{MnO}_3$, if it occurs at all in the sample in question, is at the 1% level. This confirms that Mg does substitute for La in this system.

Joly *et al* [1] have submitted a comment on previous work by Zhao *et al* [2] claiming that the samples studied in [2] were not Mg-substituted $\text{La}_{1-x}\text{Mg}_x\text{MnO}_3$, but instead, self-substituted $\text{La}_{1-y}\text{MnO}_3$. Such conclusions are based primarily on x-ray data with some ancillary low-field magnetization measurements. We submit that conclusive evidence exists that the samples that we produced were indeed formed by Mg replacing La in the LaMnO_3 system, in contrast to the materials that Joly *et al* [1] have fabricated, although we make no specific claims with regard to the latter. Not only are our samples orthorhombic, but there is also no indication in the x-ray data, and more importantly in the low-temperature ac susceptibility, of the presence of impurity phases based on the oxides of either Mn or Mg. There appears to be a general consensus that Ca, Sr and Ba can replace La substitutionally in LaMnO_3 . Despite early claims [3] that this could also be accomplished with Mg, the relatively small effective radius of the latter ion seems to have raised some doubts. We contend that these are unfounded, for the following reasons.

- (1) Samples of $\text{La}_{1-x}\text{Mg}_x\text{MnO}_3$ with x between 0.05 and 0.65 have been fabricated (although only data at $x = 0.05$ and 0.33 have been published to date). All of these samples are orthorhombic, and none of them show any indication of impurity phases, specifically MgO and Mn_3O_4 (which would be necessary to maintain charge neutrality if substitution does not take place, as reported in [4] and discussed below). In the x-ray data, Joly *et al* [1] find evidence of such phases in the *rhombohedral*-structured samples that they have produced, at least at $x = 0.33$. We contend that this is a pivotal difference, as explained below.

- (2) A previously published, comprehensive study of what Joly *et al* [1] claim we had made—namely self-doped LaMnO_3 (i.e. $\text{La}_{1-y}\text{MnO}_3$)—carried out by de Brion *et al* [4] showed:
- (a) that self-doped samples of $\text{La}_{1-y}\text{MnO}_3$ retain the orthorhombic structure only below $y = 0.03$, transforming to a rhombohedral arrangement at higher self-doping levels ($y = 0.07$);
 - (b) that self-doping, by necessity, causes the formation of impurity phases, specifically Mn_3O_4 . This is seen as a very clear signal in the ac susceptibility near 40 K—figure 3 of de Brion *et al* [4]—which, incidentally, is lower than the temperatures examined by Joly *et al* [1]. This feature is directly linked to the onset of magnetic order in this oxide [5].

For this reason we have measured the ac susceptibility of all our samples down to 4.2 K and find no such feature in any of them (see, for example, figure 1 in Zhao *et al* [2]). We would agree that x-ray data do not provide the most sensitive means of detecting the presence of the impurity phases in question at *low* substitution levels (as might occur in $\text{La}_{0.95}\text{Mg}_{0.05}\text{MnO}_3$); the ac susceptibility is a far more sensitive probe due to the strong signal originating from this magnetically ordered phase.

While the absence of any detectable Mn_3O_4 or MgO impurity phase, in both x-ray and sensitive ac susceptibility measurements, at doping levels up to $x = 0.6$ leads us to suggest that the comments offered by Joly *et al* [1] are not valid for the orthorhombic-structured samples that we have produced, low-field magnetization data acquired *above* the magnetic ordering temperature of the $\text{La}_{0.95}\text{Mg}_{0.05}\text{MnO}_3$ sample produced by us also lend support to this contention. Notwithstanding the uncertainties in the ordering temperature(s) reported by Joly *et al* [1] (discussed in more detail below), close examination of the low-field magnetization curve of the $\text{La}_{0.95}\text{Mg}_{0.05}\text{MnO}_3$ sample shown in figure 9 of [2] reveals a small anomaly near 180 K, within the range of ordering temperatures reported for low levels of self-doped $\text{La}_{1-y}\text{MnO}_3$. *If* this anomaly is associated with the presence of this self-doped parent compound, then the extent of the presence of the latter ‘impurity’ phase in the $\text{La}_{0.95}\text{Mg}_{0.05}\text{MnO}_3$ specimen produced by us is of the order of 1%.

In addition, we contend that the following points are germane.

- (i) The Curie temperatures reported in the comment by Joly *et al* [1] mentioned above were estimated using an unspecified criterion, in contrast to the approach adopted by Zhao *et al* [2].
- (ii) The variation in T_c of some 9 K for different batches shows considerably more variance than that (about 2 K) resulting from the procedures reported in Zhao *et al* [2]. This indicates a higher degree of instability—for whatever reason—in the specimens fabricated by Joly *et al* [1].
- (iii) The Curie temperature reported for the $\text{La}_{0.95}\text{Mg}_{0.05}\text{MnO}_3$ sample of Joly *et al* [1] is far closer to that reported by de Brion *et al* [4] for their self-doped $\text{La}_{0.93}\text{MnO}_3$ specimen than it is to that of our $\text{La}_{0.95}\text{Mg}_{0.05}\text{MnO}_3$ sample. Both of the former are close to 180 K, while ours is significantly lower at 147 K. While this supports the conclusion that Joly *et al* [1] have produced a self-doped rhombohedral specimen, it also indicates a significant difference from the orthorhombic sample(s) that we have fabricated. Indeed the *general* trend of an increase in T_c with increased levels of self-doping in rhombohedral specimens [1, 4, 6] is opposite to the decrease in T_c that we observe as the level of Mg substitution is increased in our orthorhombic samples.
- (iv) The behaviour reported for the $x = 0.33$ specimen [7] fits well into the phase diagram constructed by Rao *et al* [8] using a global stability index. On the basis of the assumption being questioned, namely that Mg^{2+} substitutes for La^{3+} in this system, Brown [9] has

calculated a global stability index $R1 = 0.519$ at this Mg doping level. This places this sample in the so-called TMI region where magnetic order is not accompanied by a metal–insulator transition. These are indeed the measured properties of this specimen. Similar conclusions are reached [7] through a related analysis of Rodriguez-Martinez and Attfield [10].

- (v) By extending ac susceptibility measurements down to 4.2 K, we are also ensuring sensitivity to the presence of mixed MnMgO phases, with ordering temperatures below 40 K [11]. No such oxides of this type were detected.
- (vi) By contrast, one of our group (X Z Zhou) carried out measurements of the above type on Sn-doped $\text{La}_{1-x}\text{Sn}_x\text{MnO}_3$ and did indeed find evidence of impurity phases in that system using both x-ray and ac susceptibility techniques. Although this is not the system in question here, it does confirm that our procedures have the sensitivity to detect the presence of such phases when they are present. In this context it should also be pointed out that in the case of Ce, another ion of small ionic radius, recent results [12] also conflict with the claim of Joly *et al* [1] that Ce cannot be substituted for La in LaMnO_3 .
- (vii) Finally, the magnetic properties reported for $\text{La}_{0.95}\text{Mg}_{0.05}\text{MnO}_3$ are unusual [2], not conventional (even for self-doped $\text{La}_{1-y}\text{MnO}_3$), as Joly *et al* [1] claim.

Specifically, the presence of a technical hardness irreconcilable with the measured coercivity appears to be a ubiquitous—not contrasting—feature of doped manganese perovskites. This was linked, in turn, with the presence of a large, non-critical component in the ac magnetic response at and below T_c , which persists to relatively high dc applied fields [2]. Such a component appears to complicate the analysis of critical behaviour in many such systems, probably causing the differences in critical exponent values reported for them [13]. We know of no other study that has attempted to establish this point. If it does exist, we would welcome a reference to it.

References

- [1] Joly V L J, Joy P A and Date S K 2001 *J. Phys.: Condens. Matter* **13**
- [2] Zhao J H, Song T, Kunkel H P, Zhou X Z, Roshko R M and Williams G 2000 *J. Phys.: Condens. Matter* **12** 6903
- [3] Yoo Jin S, Radlowski C A and Karch J A 1994 *Am. Chem. Soc., Div. Fuel Chem.* **39** 238
(Yoo Jin S, Radlowski C A and Karch J A 1994 *Chem. Abstracts* **121** 211800)
- [4] de Brion S, Ciorcas F, Chouteau G, Lejay P, Radaelli P and Chaillout C 1999 *Phys. Rev. B* **59** 1304
- [5] Dwight K and Menyuk N 1960 *Phys. Rev.* **119** 1470
- [6] Zheng L Q and Fang Q F 2001 *J. Phys.: Condens. Matter* **13** 3411
- [7] Zhou X Z, Kunkel H P, Zhao J H, Stampe P A and Williams G 1997 *Phys. Rev. B* **56** R12 714
- [8] Rao G H, Bärner K and Brown I D 1998 *J. Phys.: Condens. Matter* **10** L757
- [9] Brown I D 1998 private communication
- [10] Rodriguez-Martinez L M and Attfield J P 1996 *Phys. Rev. B* **54** R15 622
- [11] Jacobs I S and Kouvel J S 1961 *Phys. Rev.* **122** 412
- [12] Kang J S, Kim Y J, Lee B W, Olson C G and Min B I 2001 *J. Phys.: Condens. Matter* **13** 3779
- [13] Williams G 2001 *J. Alloys Compounds* at press