COMMENTS

Comment I on "Grain-boundary effects on the electrical resistivity and the ferromagnetic transition temperature of La$_{0.8}$Ca$_{0.2}$MnO$_3$" [Appl. Phys. Lett. 77, 118 (2000)]

T. Zhu,[a] J. R. Sun, and B. G. Shen

State Key Laboratory for Magnetism, Institute of Physics and Center for Condensed Matter Physics, Chinese Academy of Sciences, Beijing 100080, People's Republic of China

Fu has reported on the grain-boundary effects on the electrical resistivity and the ferromagnetic transition temperature of La$_{0.8}$Ca$_{0.2}$MnO$_3$.[1] He has reported the large disparities of ferromagnetic transition temperature (T_C) and metal–semiconductor transition temperature (T_p) for La$_{0.8}$Ca$_{0.2}$MnO$_3$ as shown in his Figs. 2 and 3. This result has been attributed to the grain-boundary effect on grain and which, according to the author, is the cause of the large disparities of T_C and T_p. He explains this in terms of the enhancement of the ferromagnetic double exchange interaction due to strain of grain at grain boundaries. In our view, his result could be simply explained as follows and need not invoke the grain-boundary effect.

First of all, the manganite sample by sol–gel processing always has an excess of oxygen; thus the Mn^{4+} content is much higher than the stoichiometric value. Usually, the lower annealed temperature, the higher Mn^{4+} content.[2] Hence the Mn^{4+} content of sample (a) in Fu's work may be larger than 0.2 (0.2 Ca substitution), although the molar ratio of La:Ca:Mn is close to the stoichiometric value according to the measurement of the inductively coupled plasma (ICP). Then the Mn^{4+} content decreases to the theoretical value of 0.2 as the annealed temperature increases or the annealed time is prolonged. This is to say, samples (a)–(f) are best to interpret as La$_{0.8}$Ca$_{0.2}$MnO$_{3+\delta}$ due to the strong dependence of the oxygen or Mn^{4+} content on the preparation or annealing routine. The author pointed out that little change of the T_C and the T_p was observed in any of his samples when they were annealed in O$_2$ at a temperature of 650 °C for 10 h. However, this also supports the fact that his sample already has an excess of oxygen thus the oxygen or Mn^{4+} contents are changed little. In addition, the method of redox titration is a *direct* way by which to determine the Mn^{4+} content in manganites.

It is well known that the ferromagnetism and the resulting metallic behavior in manganites arise from the mixed valency of Mn ions (Mn^{3+}/Mn^{4+}). From the phase diagram of La$_{1-x}$Ca$_x$MnO$_3$ as a function of T and x,[3] the T_C decreases with a decrease of x in the range of $0 < x < 1/3$. Different from the subtle change of T_C when x is around 1/3, the T_C changes *dramatically* when x is around 0.2. For example, T_C's for $x = 0.21$, 0.25, and 0.3 are 208±5, 240±5, and 260±5 K, respectively,[4] thus the T_C can change greatly, from 240 to 190 K when x only decreases from 0.25 to 0.2. Therefore, a small change of the Mn^{4+} content of around 0.2 should also induce a large change of the T_C. This is the main reason why the T_C of sample (a), with larger Mn^{4+} content, is higher than that of samples (b)–(d). In addition, sample (e) is first annealed at 1100 °C for 24 h, then gently milled into powder, and finally annealed under the same conditions as sample (a). So the Mn^{4+} content of sample (e) is closer to the stoichiometric value than that of sample (a). Thus the T_C of sample (e), about 200 K, is lower than that of sample (a). Furthermore, the tendency of a change in the T_p is also similar to that of the T_C if the connectivity effect on the T_p is neglected.[5]

Incidentally, there is another important feature that can be concluded from his Fig. 2 which is neglected by the author. The low temperature resistivity of the sample increases with increasing grain size. If the resistivity properties are independent of the oxygen stoichiometric effect, as supposed by the author, this experiment feature is quite contrary to the results reported previously. For example, Gupta *et al.* reported that the low temperature resistivity of polycrystalline LCMO films with identical O^{2-} or Mn^{4+} content decrease with increasing grain size.[6] In fact, the feature mentioned above is simple to explain by the phase diagram of La$_{1-x}$Ca$_x$MnO$_3$. For the μm-sized samples by sol–gel processing, the Mn^{4+} content decreases with an increase of annealing temperature or time. However, the change of resistivity is mainly determined by the change of Mn^{4+} content when the Mn^{4+} content is around 0.2, thus the resistivity increases with a decrease of the Mn^{4+} content. Before any quantitative conclusion can be drawn, the author has to address two questions, one related to the actual Mn^{4+} content and the other to the doping density of Ca^{2+}. Because, with the decrease of Ca^{2+} doping, the T_C will change dramatically, leading to a sensitive change in the T_C on the actual Mn^{4+} content.

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[a]Author to whom correspondence should be addressed; electronic mail: tzhu@g203.iphy.ac.cn

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Therefore, with the present measurement it is premature to conclude that it is the grain-boundary effect that leads to a large disparity of the T_C and the T_p.

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