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LETTER TO THE EDITOR

Observation of three different ferromagnetic phases with predictable T_cs in $La_2MnCo_{0.5}Ni_{0.5}O_6$

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Abstract

The perovskite-type oxide $La_2MnCo_{0.5}Ni_{0.5}O_6$ has been found to form in three different ferromagnetic phases with different transition temperatures, when a low-temperature synthesized sample is annealed at different temperatures. The interesting magnetic behaviour of the compound is due to the combination of different spin states of Mn, Co and Ni in the different phases of the compound. The magnetic transition temperatures of the three phases of the compound can be predicted from the T_cs of La_2MnCoO_6 and La_2MnNiO_6.

Ferromagnetism is induced in the antiferromagnetic compound $LaMnO_3$ when Mn is partially replaced by other transition metal ions of similar sizes. Though this class of Mn-site substituted compounds was first reported in the 1960s [1–4], only limited studies have been performed on these materials, when compared to the large volume of experimental and theoretical reports on the corresponding ferromagnetic compounds obtained on substitution of La by divalent ions. The Mn-site substituted system is not yet understood properly, mainly due to the complexity of the possible spin states of Mn and the substituted ions [5–8]. This becomes more complicated when the concentrations of Mn and the substituted ion, M, become identical, i.e. for the composition $LaMn_{0.5}M_{0.5}O_3$ or the double perovskite formula La_2MnMO_6, due to possible charge disproportionation. Different types of ferromagnetic exchange mechanisms have been proposed to explain the origin of ferromagnetism in these compounds, which are mainly the superexchange mechanisms Mn^{3+}–O–Mn^{3+}, Mn^{3+}–O–M^{3+}, Mn^{4+}–O–M^{2+} and/or the Mn^{3+}–O–Mn^{4+} double exchange mechanism. These explanations are based on the observation of different spin states of the constituent ions in the compounds studied.

Recent studies on La_2MnCoO_6 (LMC) [9, 10] and La_2MnNiO_6 (LMN) [11] indicated that two different spin states each of the constituent ions are possible in two different ferromagnetic phases of the compounds. Single-phase forms of these compositions could be obtained when they are synthesized by low-temperature methods. A combination of spin states of Mn and

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M (Co, Ni) are possible when the two phases are present together in samples synthesized by the usual ceramic route. For both the above compositions, two different ferromagnetic phases were identified, one of which is stable only at relatively lower temperatures and is converted to another phase when heated at higher temperatures. This was found to be due to a charge disproportionation involving different spin states of Mn, and Co or Ni. In the case of LMN, the charge disproportionation is $Mn^{4+} + Ni^{2+} \rightarrow Mn^{3+} + Ni^{3+}$, where a low-$T_c$ phase is converted to a high-T_c phase. On the other hand, an unusual double charge disproportionation, $Mn^{4+} + Co^{2+} \rightarrow Mn^{3+} + Co^{3+} \rightarrow Mn^{4+} + Co^{2+}$, was found in the case of the Co compound. The low-T_c phase was converted back after heating the high-T_c phase of the compound at a higher temperature [12].

Between LMC and LMN, the high-T_c phase of the Ni compound was found to have a higher magnetic transition temperature by 50 K, probably due to contributions from additional ferromagnetic exchange interactions involving Mn^{3+} and low-spin Ni^{3+} (low-spin Co^{3+} is a diamagnetic ion). To study the role of this additional interaction, a composition containing Co and Ni in equal amounts was prepared, i.e. the composition $La_2MnCo_{0.5}Ni_{0.5}O_6$ (LMCN). Surprisingly, it was found that this system exhibits three different ferromagnetic phases, obtained after annealing at different temperatures.

LMCN was synthesized by a low-temperature method [9, 11], as followed for the synthesis of the end members LMC and LMN. The compound obtained at a low synthesis temperature was annealed in air at different temperatures in the range 200–1300 °C for 12 h each and furnace cooled to room temperature. Magnetic measurements were performed on the samples annealed at different temperatures, using a vibrating sample magnetometer. Curie temperatures were determined as the temperature at which a maximum is observed in the dM/dT versus T curves. Powder x-ray diffraction measurements of the samples annealed at different temperatures showed the formation of orthorhombic perovskite phases with slightly differing lattice parameters.

The zero-field-cooled (ZFC) magnetization (M_{ZFC}, measured using a field of 50 Oe) curves of LMCN annealed at different temperatures in the range 200–1300 °C are shown in figure 1. The magnetization curves of the two different phases of LMC and LMN are shown in figure 2 for comparison. For both LMC and LMN, broad ferromagnetic transitions are observed below 150 K for samples annealed at 200 °C. For LMCN also, the sample annealed at 200 °C shows a ferromagnetic transition at the same temperature, as shown in figure 3. The broadness of this magnetic transition is due to the fine particle natures of the compounds synthesized at very low temperatures because, for bulk samples of LMC, a sharp magnetic transition is observed at this temperature (see figure 2).

Earlier detailed studies showed that Co and Ni are present as Co^{2+} and Ni^{2+} in LMC and LMN, respectively, and Mn is present as Mn^{4+} in the phases undergoing the magnetic transition below 150 K [9–12]. As there is no variation in the magnetic transition temperature when Co^{2+} is replaced fully by Ni^{2+}, it can be assumed that the major contributions to ferromagnetism comes from Mn^{4+} ions only, i.e. from Mn^{4+}–O–Mn^{4+} exchange interactions. It is also possible that the contribution from Mn^{4+}–O–Co^{2+} and Mn^{4+}–O–Ni^{2+} superexchange interactions are identical since both Co^{2+} ($t_{2g}^5 e_g^2$) and Ni^{2+} ($t_{2g}^6 e_g^2$) have the same number of e_g electrons and there is no contribution from the t_{2g} electrons of these ions. The latter mechanism seems to be more plausible, as Mn^{4+}–O–Mn^{4+} exchange interactions are known to be antiferromagnetic. In both cases, no change in the magnetic transition temperature is expected when Co is partially substituted by Ni and this is what is observed for LMCN.

For LMC, a high-T_c phase, in single-phase form, was obtained when the low-T_c phase was further annealed at 700 °C and it was converted back to the low-T_c phase after further annealing at 1300 °C. On the other hand, for LMN, the high-T_c phase, in single-phase form,

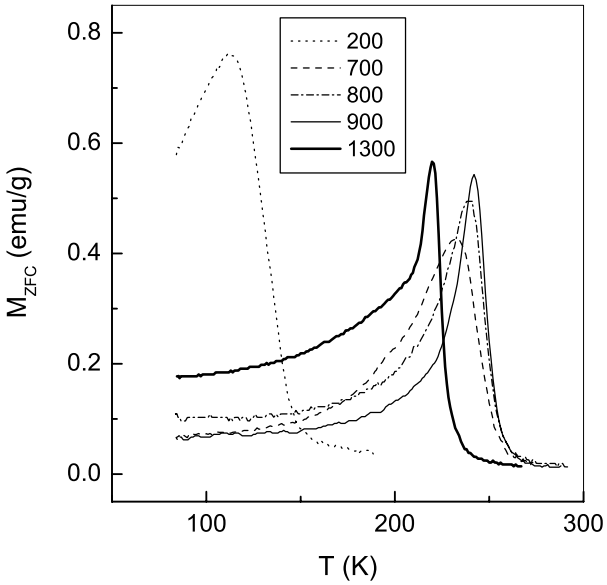

Figure 1. The ZFC magnetization curves ($H = 50$ Oe) of LMCN, annealed at different temperatures. The numbers indicate the annealing temperatures.

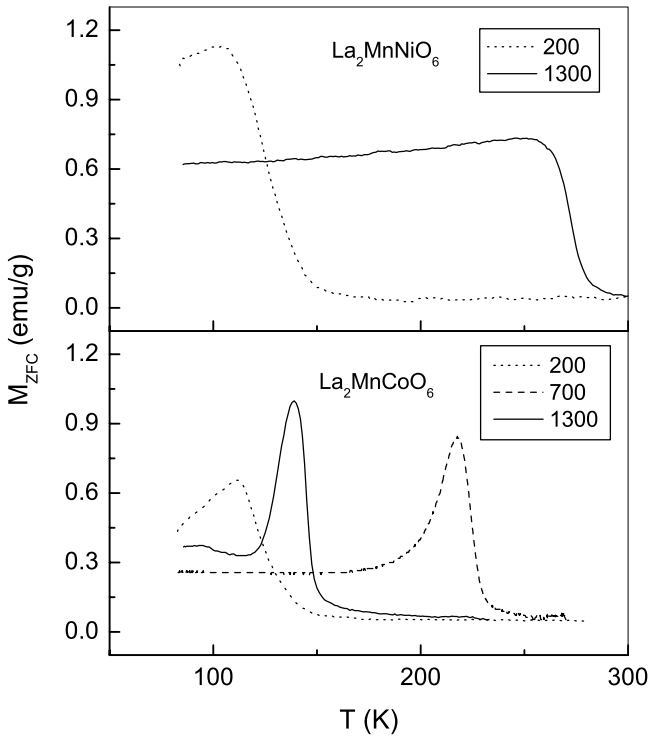

Figure 2. The ZFC magnetization curves ($H = 50$ Oe) of the two different phases of LMC and LMN. The numbers indicate the annealing temperatures.

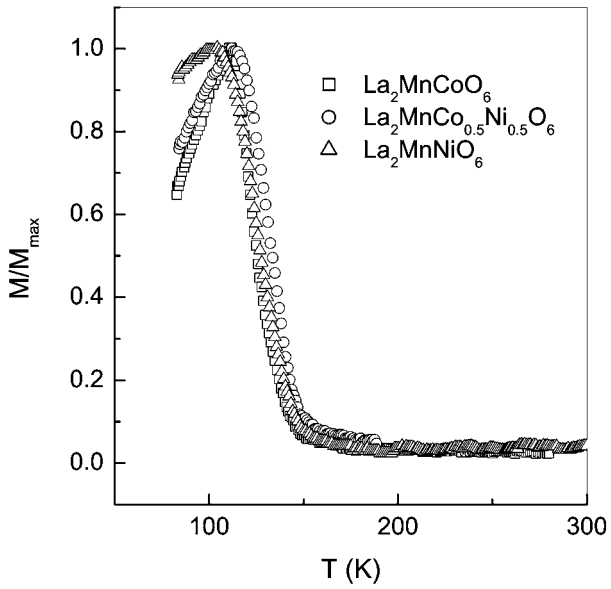

Figure 3. Comparison of the ZFC magnetization curves ($H = 50$ Oe) of LMC, LMN and LMCN, annealed at 200 °C.

was obtained only after prolonged annealing at 1300 °C. Hence LMCN was annealed at 700 °C, initially, to look for the presence of another phase. It was found that indeed another phase, with a magnetic transition below 260 K (when compared to the T_cs of 225 and 273 K for LMC and LMN, respectively), is formed. However, the magnetic transition of this sample is a little broader and the transition becomes sharp after annealing at 900 °C. It may be noted that, for LMC and LMN, the high-T_c phases were obtained after annealing at 700 and 1300 °C, respectively. For LMCN, this phase is obtained when annealed at temperatures in between 700 and 1300 °C. That is, the charge disproportionation $Mn^{4+} + Co^{2+} \rightarrow Mn^{3+} + Co^{3+}$ is completed at a higher temperature when compared to that in LMC and the charge disproportionation $Mn^{4+} + Ni^{2+} \rightarrow Mn^{3+} + Ni^{3+}$ is completed at a lower temperature when compared to that of LMN, probably due to the coexistence of both Co and Ni in equal amounts in LMCN.

For LMC, T_c of the high-T_c phase is obtained as 225 K and for LMN it is 273 K. The difference in the T_cs of LMN and LMC is 48 K. Since the T_cs of the low-T_c phases of LMC and LMN are almost identical and the magnetic transitions are broad, the T_cs of these phases are taken as the T_c of the sharp transition of LMC obtained after annealing at 1300 °C, which is found as 145 K from the dM/dT curve. Previous studies showed that, in the high-T_c phases of the two compounds, Mn is present as Mn^{3+}, and Co and Ni are present as Co^{3+} and Ni^{3+}, respectively, in their low-spin states. Since there are no unpaired electrons in low-spin Co^{3+} ($S = 0$), which is a diamagnetic ion, and low-spin Ni^{3+} ($S = 1/2$) contains one unpaired electron in its e_g orbitals, it may be assumed that the additional T_c of 48 K for LMN comes from the contribution from magnetic exchange interactions involving Ni^{3+} (Mn^{3+}–O–Ni^{3+} exchange), apart from the contributions from Mn^{3+} (Mn^{3+}–O–Mn^{3+} exchange). So the strength of different ferromagnetic exchange interactions can be taken as Mn^{3+}–O–Mn^{3+} = 225 K, Mn^{3+}–O–Ni^{3+} = 48 K and Mn^{4+}–O–M^{2+} = 145 K.

For LMCN, the magnetic transition temperature of the sample annealed at 900 °C is 248 K. By comparing with the high-T_c phases of LMC and LMN, it is possible that Co and Ni are present as low-spin Co^{3+} and Ni^{3+} ions in LMCN also, as the transition temperature

is in between those of LMC and LMN. The strength of the magnetic exchange interaction in LMCN can be taken as the sum of the strength of the Mn^{3+}–O–Mn^{3+} interaction (225 K) and 50% of the Mn^{3+}–O–Ni^{3+} interaction (48 K), as half of Co is replaced by Ni. It is interesting to note that the T_c of LMCN, which is 248 K, is comparable to the sum of the T_c of LMC and half of the difference between the T_cs of LMN and LMC, $225 + 24 = 249$ K. This indicates that the above assumption—the strength of Mn^{3+}–O–Mn^{3+} exchange interactions is 225 K and that of Mn^{3+}–O–Ni^{3+} is 48 K—is valid.

As LMC was found to be converted back to its low-T_c phase ($T_c = 145$ K) and the high-T_c phase of LMN ($T_c = 273$ K) was obtained in single-phase form after annealing at 1300 °C, LMCN was also annealed above 900 °C and up to 1300 °C. Surprisingly, it was found that LMCN follows neither LMC nor LMN. Instead, it was found that the sample annealed at 1300 °C undergoes a ferromagnetic transition below 230 K, i.e. the Curie temperature is reduced from 248 K. The T_c of this sample is obtained as 226 K from the dM/dT curve.

It may be noted that the magnetic transition temperature of LMCN annealed at 1300 °C (226 K) is comparable to the T_c of the high-T_c phase of LMC (225 K) which is obtained after annealing at 700 °C. This scenario is possible only if the magnetic environment in LMCN annealed at 1300 °C is identical to that in LMC annealed at 700 °C. i.e. there is no contribution from Co or Ni to the magnetic exchange interactions. This is very unlikely as Ni will always have some unpaired electrons in the 2+ or 3+ states and may contribute to either ferromagnetic or antiferromagnetic exchange interactions. On the other hand, since Mn and Ni are present as Mn^{3+} and Ni^{3+} in LMN and as Mn^{4+} and Co^{2+} in LMC after heating at 1300 °C, it may be assumed that in LMCN also 50% of Mn is present as in LMN and the other 50% as in LMC, with Ni and Co in the respective spin states for charge neutrality. On the basis of this assumption, the T_c can be calculated as $(225+48)/2+145/2 = 209$ K, which is less, by 17 K, from the experimental value. Another possibility is that Ni and an equivalent amount of Mn are present in LMCN as in the high-T_c phase of LMN (Mn^{3+} and Ni^{3+}) and out of the total Co and the rest of Mn, half of the Mn and Co are present in an environment as in the high-T_c phase of LMC (Mn^{3+} and Co^{3+}) and the other half as in the low-T_c phase of LMC (Mn^{4+} and Co^{2+}). This will give a calculated T_c of $(225 + 48)/2 + 225/4 + 145/4 = 229$ K, which is very close to the observed T_c of 226 K. If the latter condition is valid, it has to be speculated that the Mn, Co and Ni ions are present in the LMCN lattice in some ordered form and those Co ions close to Ni remain as Co^{3+} and the remaining Co ions are converted back to Co^{2+} ions because of a charge disproportionation involving the Mn ions. This assumption needs to be studied further by detailed neutron diffraction experiments.

Thus, the present study shows that three ferromagnetic phases are possible for LMCN, which is a solid solution of the ferromagnetic compounds LMC and LMN exhibiting two different ferromagnetic phases each. The three ferromagnetic phases are obtained when the compound is synthesized by a low-temperature method and annealed at different temperatures. Different ferromagnetic phases are possible due to a combination of the different spin states of Mn, Co and Ni. The ferromagnetic transition temperatures of the three phases can be calculated from the T_cs of the different phases of the end members.

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