The origin of ferromagnetism in the two different phases of $LaMn_{0.5}Co_{0.5}O_3$: evidence from x-ray photoelectron spectroscopic studies

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Abstract
Core-level Mn and Co 2p x-ray photoelectron spectroscopic studies give evidence for different spin states of Mn and Co in the two different phases of the ferromagnetic compound $LaMn_{0.5}Co_{0.5}O_3$. Ferromagnetism in the high-T_c ($T_c \approx 230$ K) phase of the compound arises from Mn^{3+}–O–Mn^{3+} superexchange interactions, whereas in the low-T_c ($T_c \approx 150$ K) phase Mn^{4+}–O–Co^{2+} superexchange interactions are responsible for the ferromagnetism.

1. Introduction

Interesting magnetic properties are observed when the composition of the antiferromagnetic insulator $LaMnO_3$ is modified by substitution at the Mn site with other transition metal ions (Gilleo 1957, Goodenough *et al* 1961). Ferromagnetism is observed for $0 < x < 1$ in $LaMn_{1-x}M'_xO_3$ where M$'$ = Co, Ni, etc (Wold *et al* 1958, Goodenough *et al* 1961, Blasse 1965, Jonker 1966). Ferromagnetism in $LaMnO_3$ can also be induced by the substitution of divalent ions for trivalent La (Jonker and Van Santen 1950). In $La_{1-x}A_xMnO_3$ (A = Ca, Sr, etc), ferromagnetism originates from double-exchange interaction between Mn^{3+} and Mn^{4+} ions (Zener 1951). However, substitution of other transition metal ions at the Mn site of ferromagnetic compositions in $La_{1-x}A_xMnO_3$ destroys the ferromagnetism due to suppression of Mn^{3+}–Mn^{4+} double-exchange interactions (Ahn *et al* 1996, Li *et al* 1999). The origin of the ferromagnetism in $LaMn_{1-x}M'_xO_3$ is not yet understood properly and different models are proposed in the literature, based on the results obtained from magnetic measurements. Goodenough *et al* (1961) have argued that Mn^{3+}–O–Mn^{3+} superexchange interactions are predominant in $LaMn_{1-x}M'_xO_3$ and the M$'$ ions are in their low-spin trivalent state. Evidence favouring this scenario is provided by the observation of ferromagnetism when M$'$ = Ga which is a non-magnetic trivalent ion. Blasse (1965) and Jonker (1966) later demonstrated that ferromagnetism in $LaMn_{1-x}Co_xO_3$ arises from positive Mn^{4+}–O–Co^{2+} superexchange

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interactions. Recently, Troyanchuk *et al* (2000) have concluded that in $LaMn_{1-x}Co_xO_3$, Co^{2+}, Mn^{3+}, and Mn^{4+} ions are distributed randomly in the lattice for $0.1 \leqslant x \leqslant 0.35$ and that there are ferromagnetic exchange interactions of the type Co^{2+}–O–Mn^{4+}, Mn^{3+}–O–Mn^{3+}, and Mn^{3+}–O–Mn^{4+}, the last one (double exchange as found in $La_{1-x}A_xMnO_3$) being the most dominant. On the other hand, for $0.4 \leqslant x \leqslant 0.8$, the data are interpreted in terms of phase separation into domains where the Co^{2+} and Mn^{4+} ions are ordered.

Recently it has been shown (Joy *et al* 2000a) that two different phases of $LaMn_{0.5}Co_{0.5}O_3$ can be synthesized in single-phase forms by a low-temperature method of synthesis, and mixed phase behaviour is observed for the samples prepared by the processing procedures followed in the earlier reports (Goodenough *et al* 1961, Troyanchuk *et al* 1997). High-temperature magnetic susceptibility studies have indicated that the spin states of Mn and Co are different in the two different phases of the compound (Joy *et al* 2000b). In this paper we show evidence for the presence of different spin states of Mn and Co in the two different phases of $LaMn_{0.5}Co_{0.5}O_3$, from x-ray photoelectron spectroscopic (XPS) studies.

2. Experimental procedure

The two different phases of $LaMn_{0.5}Co_{0.5}O_3$ were synthesized by a low-temperature method at 700 °C and a high-temperature ceramic method at 1300 °C as reported (Joy *et al* 2000a). Two Al-substituted compositions, $LaMn_{0.4}Al_{0.1}Co_{0.5}O_3$ and $LaMn_{0.5}Co_{0.4}Al_{0.1}O_3$, were also prepared by the low-temperature method under identical conditions. Magnetization measurements were performed using an EG&G PAR 4500 vibrating-sample magnetometer. Photoemission spectra were recorded on a VG Microtech Multilab ESCA 3000 spectrometer equipped with a twin anode of Al and Mg. All measurements were made at room temperature using a non-monochromatized Mg Kα x-ray source ($h\nu = 1253.6$ eV). The base pressure in the analysis chamber was 4×10^{-10} Torr. Extreme care was taken to minimize the surface contamination problem by scraping thoroughly and repeatedly over the surfaces of the samples with a stainless steel blade *in situ* under high vacuum. The scraping was repeated until the higher-binding-energy shoulder in the O 1s XPS showed a minimum and no further decrease in intensity, as reported in the literature (Chainani *et al* 1992, Saitoh *et al* 1995). Sample surface cleanliness was also confirmed by the absence of any impurity signal at ∼10 eV in the valence band spectra. The energy resolution of the spectrometer was determined from the full width at half-maximum of metallic gold and the value obtained is better than 0.8 eV for Mg Kα radiation at a pass energy of 20 eV. Adventitious carbon on a gold surface shows a C 1s core-level peak at 284.9 eV and all binding energies (BE) are referenced to this peak at 284.9 eV. The errors in all the BE values are within 0.1 eV.

3. Results and discussion

Figure 1 shows the temperature variation of the zero-field-cooled (ZFC) and field-cooled (FC) magnetizations of the two different phases of $LaMn_{0.5}Co_{0.5}O_3$. One of the phases shows a ferromagnetic transition at $T_c = 228$ K (the high-T_c phase) and the second phase undergoes a ferromagnetic transition at $T_c = 148$ K (the low-T_c phase). The crystal structures of the two phases were found to be different (Goodenough *et al* 1961): rhombohedral structure for the high-T_c phase and orthorhombic structure for the low-T_c phase (Joy *et al* 2000a). ZFC magnetization curves of a sample heated to 1200 and 1300 °C for a short duration and showing magnetic transitions at temperatures in between the T_cs of the two single-phase compounds are compared with the curves for the two different single phases of the compound in figure 2.
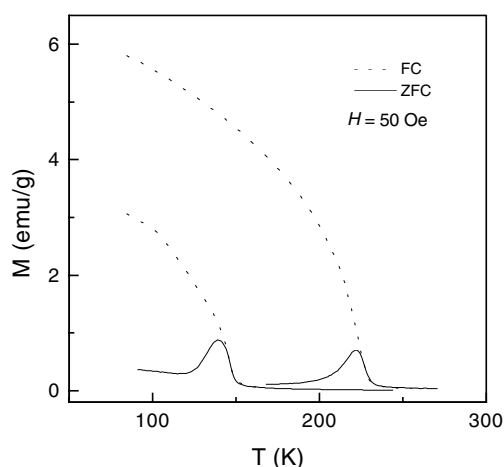
Figure 1. Field-cooled (FC) and zero-field-cooled (ZFC) magnetization curves of the two different phases of LaMn$_{0.5}$Co$_{0.5}$O$_3$; $H = 50$ Oe.
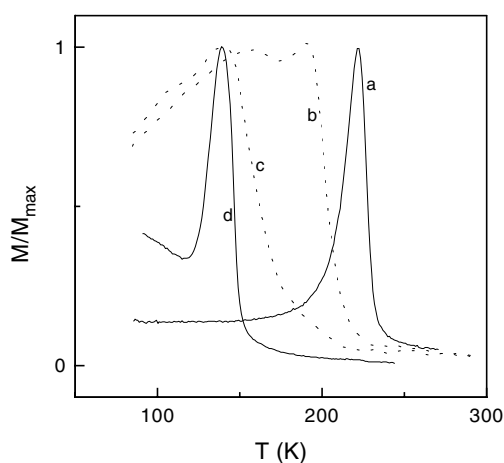
Figure 2. Normalized zero-field-cooled ($H = 50$ Oe) magnetization curves of LaMn$_{0.5}$Co$_{0.5}$O$_3$ samples heated to different temperatures: (a) 700 °C (high-T_c phase); (b) 1200 °C; (c) 1300 °C for 6 h; and (d) 1300 °C for six days (low-T_c phase).

The sample heated to 1200 °C showed a major ferromagnetic transition below the T_c for the high-T_c phase (at $\sim$200 K) and when further heated to 1300 °C for a short duration showed a broad ferromagnetic transition at $\sim$160 K. The relatively sharp magnetic transitions of these samples at different temperatures between 150 and 230 K indicate that they are not physical mixtures of the two different phases with different T_cs but compositions having different types of magnetic interaction compared to those in the low- and high-T_c phases.

The valence band XPS of the two different phases of LaMn$_{0.5}$Co$_{0.5}$O$_3$ are shown in figure 3. A broad peak around 10 eV which was observed for the unscraped samples (see the inset of figure 3) is absent in the spectra, indicating that the sample surface is free from contamination. Identical valence band features are observed for the two phases and the features are similar to those reported for LaCoO$_3$ (Chainani *et al* 1992).
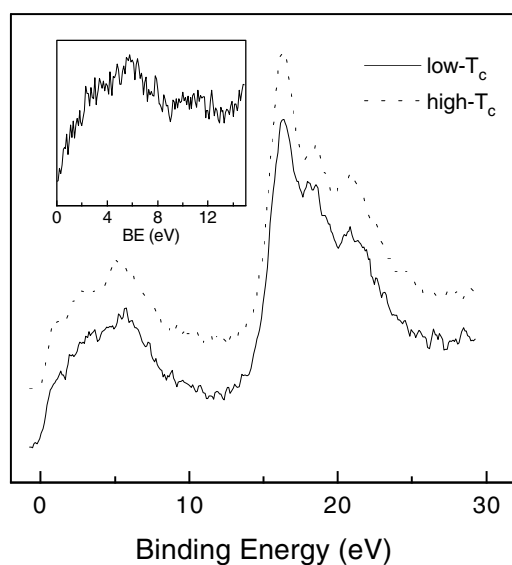
Figure 3. XPS valence bands of the two different phases of $LaMn_{0.5}Co_{0.5}O_3$. Inset: the XPS valence band of the unscraped surface of the high-T_c phase.

The 2p core-level XPS of the transition metal ions are known to be very sensitive to their 3d-electron content. However, in the same octahedral coordination environment, the Co 2p BE is lower for low-spin Co^{3+} as compared to that of high-spin Co^{2+}, contrary to what is observed for other transition metal ions (Briggs and Gibson 1974). The 2p core-level XPS of Co in the two different phases of $LaMn_{0.5}Co_{0.5}O_3$ are shown in figure 4 (curves a and d). The 2p core-level XPS of Co in the two mixed-phase samples showing magnetic transitions between 150 and 230 K are also compared in the figure (curves b and c). The spectra are almost identical; the $2p_{3/2}$ peak of the low-T_c phase (curve d) is observed at a slightly higher BE compared to that of the high-T_c phase (curve a). The mixed-phase sample undergoing a major magnetic transition (curve b in figure 2) close to the T_c of the high-T_c phase of the compound shows a Co $2p_{3/2}$ XPS peak (curve b in figure 4) at the BE of the peak of the high-T_c phase, whereas the mixed-phase sample undergoing a major magnetic transition (curve c in figure 2) close to the T_c of the low-T_c phase of the compound shows the Co $2p_{3/2}$ XPS peak (curve c in figure 4) at the BE of the peak of the low-T_c phase. This indicates that the observed difference in BE of the two single-phase compounds is not due to any experimental error and that the spin states of Co are different in the two different phases of $LaMn_{0.5}Co_{0.5}O_3$.

The Co $2p_{3/2}$ peaks are observed at 779.6 and 780.1 eV, respectively, for the high-T_c and low-T_c phases of $LaMn_{0.5}Co_{0.5}O_3$. These values are comparable to those observed for Co^{3+} in $LaCoO_3$ and $LiCoO_2$ in which the trivalent Co ions are reported to be in the low-spin configuration and for Co^{2+} in CoO with high-spin Co^{2+}, respectively (Lombardo *et al* 1983, van Elp *et al* 1991). The majority of the cobalt ions in the two mixed-phase samples have their spin states closer to that of the spin state of Co in either one of the two single phases. Recent XPS studies and electronic structure calculations (Korotin *et al* 1996, Saitoh *et al* 1997, Flavell *et al* 1999, Thomas *et al* 2000) have indicated that the intermediate spin state ($t_{2g}^5 e_g^1$) is the most probable spin state of trivalent Co ions in $LaCoO_3$ and $La_{1-x}Sr_xCoO_3$ at room temperature. On the other hand, x-ray absorption spectroscopic (XAS) studies indicate a low-spin state of Co^{3+} in $LaCoO_3$ at room temperature (Abbate *et al* 1993). Hence it is possible that the Co ions
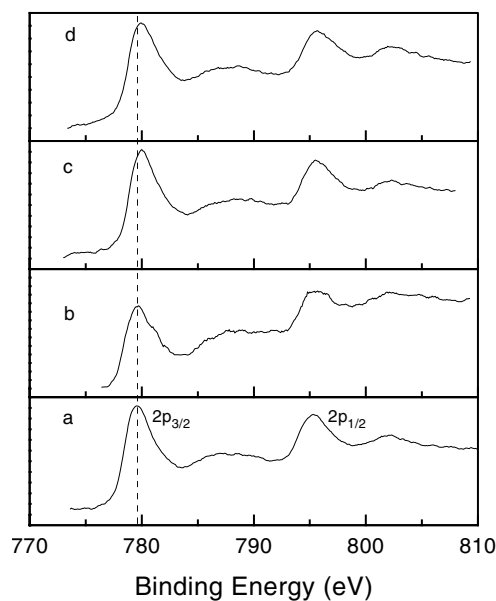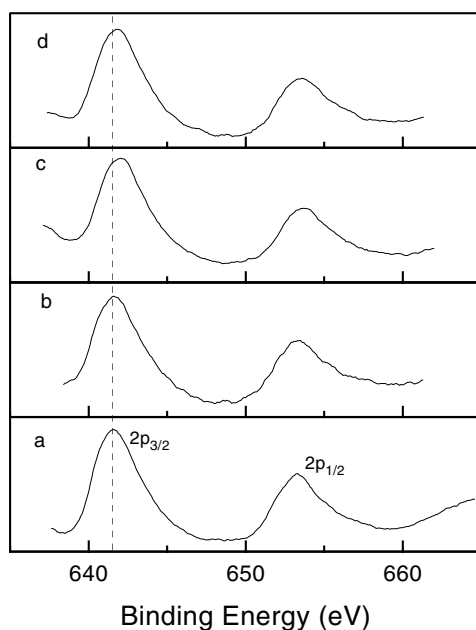
Figure 4. Co 2p photoelectron spectra of the two different phases and mixed-phase samples of LaMn$_{0.5}$Co$_{0.5}$O$_3$: (a) high-T_c phase; (b) sample heated to 1200 °C; (c) sample heated to 1300 °C for 6 h; and (d) low-T_c phase.

are present as low-spin and/or intermediate-spin Co^{3+} in the high-T_c phase of LaMn$_{0.5}$Co$_{0.5}$O$_3$. In the low-T_c phase of LaMn$_{0.5}$Co$_{0.5}$O$_3$, cobalt ions are present as high-spin Co^{2+}.

XPS of Mn 2p in the two phases of LaMn$_{0.5}$Co$_{0.5}$O$_3$ (curves a and d) and in the samples containing mixed phases (curves b and c), shown in figure 5, are also indicative of different spin states of Mn in the two different phases. The 2p$_{3/2}$ peaks of Mn in the high-T_c and low-T_c phases of the compound are observed at 641.6 eV and 641.9 eV, respectively. The BE of the Mn 2p$_{3/2}$ peak of the mixed-phase sample showing a higher magnetic transition temperature is close (curve b in figure 5) to that of the high-T_c phase and for the second mixed-phase sample the BE is close (curve c in figure 5) to that of the low-T_c phase of the compound. This is similar to what is observed in the Co 2p XPS of the mixed-phase samples, indicating a difference in oxidation state of Mn between the two different phases of LaMn$_{0.5}$Co$_{0.5}$O$_3$. The observed difference in the BE of the 2p$_{3/2}$ peak between the two phases is comparable to that reported for Mn$_2$O$_3$ and MnO$_2$ where the Mn ions are present as Mn^{3+} and Mn^{4+}, respectively (Oku *et al* 1975), or that observed in the Mn 2p XPS of La$_{1-x}$Sr$_x$MnO$_3$ (Saitoh *et al* 1995) where a maximum difference of 0.4 eV is obtained for $x = 0$ (Mn^{3+}) and $x = 0.9$ (predominantly Mn^{4+}). The present observation indicates a lower valence state of Mn (as Mn^{3+}) in the high-T_c phase and a higher valence state of Mn (as Mn^{4+}) in the low-T_c phase of LaMn$_{0.5}$Co$_{0.5}$O$_3$, and the BE values are in line with the reported values. These valence states of Mn in the two phases are in accordance with those found for Co in the same phases (trivalent Mn when Co is trivalent and tetravalent Mn when Co is divalent), which takes care of oxygen stoichiometry and preserves charge neutrality.

The XPS results give evidence for different valence states of Mn and Co in the two different phases of LaMn$_{0.5}$Co$_{0.5}$O$_3$. It is very difficult to discern the actual spin state of Co^{3+} from XPS studies. It is possible that in the case of LaMn$_{0.5}$Co$_{0.5}$O$_3$, Co^{3+} may also be in the low- or intermediate-spin state, as observed for LaCoO$_3$ from XAS and XPS studies. However,

Figure 5. Mn 2p photoelectron spectra of the two different phases and mixed-phase samples of LaMn$_{0.5}$Co$_{0.5}$O$_3$: (a) high-T_c phase; (b) sample heated to 1200 °C; (c) sample heated to 1300 °C for 6 h; and (d) low-T_c phase.

the effective paramagnetic moment (calculated from a Curie–Weiss fit to the paramagnetic susceptibility at high temperatures) of the phase with $T_c \approx 230$ K is comparable to the spin-only value calculated for Mn^{3+} and low-spin Co^{3+} ($\mu_{eff} = 3.52$ BM (BM $= \mu_B$, the Bohr magneton), $\mu_{so} = 3.46$ BM). The effective moment is less than the spin-only moment calculated for Mn^{3+} and intermediate-spin Co^{3+} ($\mu_{so} = 4.0$ BM). This implies that the trivalent cobalt ions are likely to be present in their low-spin state in the high-T_c phase of LaMn$_{0.5}$Co$_{0.5}$O$_3$ (Joy *et al* 2000b). If this is correct, then it may be assumed that ferromagnetism in this phase arises only from Mn^{3+}–O–Mn^{3+} superexchange interactions.

Magnetic properties of LaMn$_{0.5}$Co$_{0.5}$O$_3$ after substitution of Al^{3+} for Mn or Co have been studied to obtain information on the spin state of Co in the high-T_c phase. It was expected that if Co^{3+} is present in the low-spin state and ferromagnetism is due to Mn^{3+} alone, then there will not be much effect on the T_c or magnetization when Co is partially replaced by Al^{3+}. On the other hand, relatively large effects are expected on replacement of Mn^{3+} by Al^{3+}. Temperature variations of the magnetization of LaMn$_{0.5}$Co$_{0.5}$O$_3$ (LMC), LaMn$_{0.4}$Al$_{0.1}$Co$_{0.5}$O$_3$ (LMAC), and LaMn$_{0.5}$Co$_{0.4}$Al$_{0.1}$O$_3$ (LMCA), synthesized under identical conditions and heated to 700°C, are compared in figure 6. When Al is substituted for Co, it is found that the T_c or magnetization is not much affected, whereas when Al is substituted for Mn, the low-temperature magnetization is drastically decreased and T_c is shifted considerably to lower temperatures, as expected. The saturation magnetizations measured at 83 K and 15 kOe for the three compositions are compared with the expected theoretical ferromagnetic moments in table 1, assuming contributions from Mn^{3+} and different spin states of Co^{3+}. Though the measured values are much less than the theoretical values, it may be seen that the experimental values are comparable for the unsubstituted and Co-site-substituted compositions. LaMn$_{0.5}$Co$_{0.5}$O$_3$ attains full magnetic saturation at very low temperatures and under very high magnetic fields
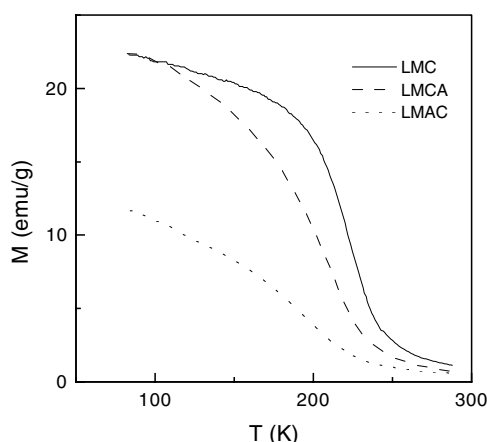
Figure 6. Temperature variations of the magnetization ($H = 5000$ Oe) of LaMn$_{0.5}$Co$_{0.5}$O$_3$ (LMC), LaMn$_{0.4}$Al$_{0.1}$Co$_{0.5}$O$_3$ (LMAC), and LaMn$_{0.5}$Co$_{0.4}$Al$_{0.1}$O$_3$ (LMCA).

Table 1. Experimental and calculated ferromagnetic moments (in Bohr magnetons) of LaMn$_{0.5}$Co$_{0.5}$O$_3$ (LMC), LaMn$_{0.4}$Al$_{0.1}$Co$_{0.5}$O$_3$ (LMAC), and LaMn$_{0.5}$Co$_{0.4}$Al$_{0.1}$O$_3$ (LMCA) heated to 700 °C.

	LMC	LMAC	LMCA
Experimental (83 K, 15 kOe)	1.39	0.91	1.36
Mn^{3+} + Co^{3+} ($S = 0$)	2.0	1.6	2.0
Mn^{3+} + Co^{3+} ($S = 1$)	3.0	2.6	2.8
Mn^{3+} + Co^{3+} ($S = 2$)	4.0	3.6	3.6

only (Goodenough *et al* 1961). The drastic drop in the observed saturation magnetization when Mn is replaced by Al is in accordance with the decrease in the expected ferromagnetic saturation moment when trivalent Co is in the low-spin state. This clearly indicates that the trivalent cobalt ions do not contribute to the magnetism in the high-T_c phase of LaMn$_{0.5}$Co$_{0.5}$O$_3$ and that the contribution to the ferromagnetism is from Mn^{3+} only.

For the second phase of LaMn$_{0.5}$Co$_{0.5}$O$_3$ with $T_c \approx 150$ K, the experimental value of μ_{eff} is close to that expected for high-spin Mn^{4+} and Co^{2+} ($\mu_{eff} = 4.01$ BM and $\mu_{so} = 3.88$ BM). The results obtained from the XPS recorded at room temperature are similar to those obtained from high-temperature (500–800 K) susceptibility studies (Joy *et al* 2000b) indicating that there is no temperature-induced spin-state transition below 800 K and that the observed spin states of Mn and Co are stable in the individual phases with different structures.

Observation of different spin states of Mn and Co (Mn^{3+}, Co^{3+} and Mn^{4+}, Co^{2+}) in the two different phases of LaMn$_{0.5}$Co$_{0.5}$O$_3$ implies that the positive ferromagnetic exchange interactions are of the type Mn^{3+}–O–Mn^{3+} in the phase with $T_c = 230$ K and Mn^{4+}–O–Co^{2+} in the phase with $T_c = 150$ K. The high-T_c phase of LaMn$_{0.5}$Co$_{0.5}$O$_3$ is obtained after processing at a lower temperature (700 °C) and the low-T_c phase is obtained after heating at 1300 °C for several days (Joy *et al* 2000a). It is possible that the samples showing ferromagnetic transitions between 150 and 230 K may contain all of the above possible oxidation states of Mn and Co due to the slow conversion Mn^{3+} + Co^{3+} → Mn^{4+} + Co^{2+} which is completed only at higher processing temperatures. The Mn and Co 2p XPS of the samples showing magnetic transitions at ∼200 K and ∼160 K were almost identical to the spectra of the high-T_c phase

and low-T_c phase of LaMn$_{0.5}$Co$_{0.5}$O$_3$, respectively. So, there is a chance that these samples processed at intermediate temperatures may have different Mn^{3+}/Mn^{4+} and Co^{3+}/Co^{2+} ratios and a non-uniform distribution of the different observed spin states of Mn and Co in the lattice. Ferromagnetism in such samples may be originating from superexchange interactions of the types Co^{2+}–O–Mn^{4+}, Mn^{3+}–O–Mn^{3+}, and Mn^{3+}–O–Mn^{4+} as proposed by Troyanchuk *et al* (2000). However, these samples are not really single-phase materials, as evidenced from the presence of more than one broad maximum or broad magnetic transition in the low-field ZFC measurements.

4. Conclusions

X-ray photoelectron spectroscopic and magnetic measurements indicate that the spin states of Mn and Co are different in the two different phases of LaMn$_{0.5}$Co$_{0.5}$O$_3$: a high-T_c phase ($T_c = 230$ K) obtained by a low-temperature synthesis method and a low-T_c phase ($T_c = 150$ K) obtained by the usual high-temperature ceramic method of synthesis. Mn and Co are present in their trivalent states with Co in the low-spin configuration in the high-T_c phase and as Mn^{4+} and high-spin Co^{2+} in the low-T_c phase of LaMn$_{0.5}$Co$_{0.5}$O$_3$. The ferromagnetism in the phase showing a higher Curie temperature originates from superexchange interactions between Mn^{3+} ions whereas the superexchange interaction between Mn^{4+} and Co^{2+} ions is responsible for ferromagnetism in the phase showing a lower Curie temperature.

Acknowledgments

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