Tricritical points in La-based ferromagnetic manganites

V. S. Amaral[a] and J. P. Araújo
Departamento de Física and CICECO, Universidade de Aveiro, 3810-193 Aveiro, Portugal

Yu. G. Pogorelov and J. B. Sousa
IFIMUP, Departamento de Física, Universidade do Porto, 4150 Porto, Portugal

P. B. Tavares
Departamento de Química, Universidade de Trás-os-Montes e Alto Douro, 5001-911 Vila Real, Portugal

J. M. Vieira
Departamento de Engenharia Cerâmica e do Vidro and CICECO, Universidade de Aveiro, 3810 Aveiro, Portugal

P. A. Algarabel and M. R. Ibarra
Departamento Fisica Materia Condensada and ICMA, CSIC-Universidade de Zaragoza, 50009 Zaragoza, Spain

(Presented on 14 November 2002)

A detailed study of the magnetization $M(H,T)$ of manganites near T_C is presented. Analysis, in the framework of Landau theory of phase transitions ($G=G_0+1/2AM^2+1/4BM^4+1/6CM^6-MH$) reveals that for $La_{0.67}Ca_{0.33}MnO_3$ ($T_C=267$ K), $La_{0.8}MnO_3$ ($T_C=250$ K), and $La_{0.60}Y_{0.07}Ca_{0.33}MnO_3$ ($T_C=150$ K) the phase transition is first-order and the B coefficient is temperature dependent, negative near T_C. In field ($H<H_C^*$) and temperature ($T_C<T<T_C^*$) ranges, below the critical point of the first-order phase transition, clear features are found, with hysteresis. For $La_{0.60}Y_{0.07}Ca_{0.33}MnO_3$, $H_C^*\sim 20$ kOe, $\Delta T=T_C^*-T_C\sim 20$ K. For $La_{0.67}Ca_{0.33}MnO_3$, on the other hand, H_C^* is only 250 Oe and $\Delta T<1$ K. These effects are related with electronic and elastic energy contributions coupled to the magnetic order parameter. The analysis of the vanishing of B above T_C suggests that a tricritical point should occur at $T\sim 310$ K, in agreement with the temperature at which the magnetic and structural transitions in $La_{0.7}(Ca_{1-y}Sr_y)_{0.3}MnO_3$ coincide. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1558271]

One of the most appealing features of colossal magnetoresistance (CMR) manganites are the conspicuous first-order magnetic phase transitions, accompanied by metal–insulator and structural transitions with large discontinuities in the magnetic, electric, or lattice properties.[1] These are typically found when the low temperature phase is a charge/orbital ordered state (divalent doping ~ 0.5) or when magnetic and structural phase transitions are close, leading to magnetic field-driven structural transitions as in $La_{0.83}Sr_{0.17}MnO_3$ (Ref. 1) or in the recently studied $La_{0.7}(Ca_{1-y}Sr_y)_{0.3}MnO_3$ for $y\sim 0.5$.[2]

The behavior of ferromagnetic manganites in the vicinity of the magnetic transition, particularly in systems with $\sim 33\%$ doping, for which Curie temperatures T_C are usually highest and no clear discontinuities in properties are observed, has been the subject of several studies. These point to a most likely first-order transition (in zero magnetic field) when T_C is sufficiently low. A change from first to second order has been reported to occur from $La_{2/3}Ca_{1/3}MnO_3$ ($T_C\approx 265$ K) to $La_{2/3}Sr_{1/3}MnO_3$ ($T_C\approx 360$ K) using magnetization[3] and nuclear magnetic resonance studies.[4] In the latter system, the determination of critical exponents was possible and scaling relations were verified,[5] but in the former such analysis was unsuccessful.[6,7] Evidence for the first-order character of the transition in $La_{2/3}Ca_{1/3}MnO_3$ was also given by low field magnetization measurements and a Landau theory analysis.[8,9] However, the nature and microscopic details of the phase transition in ferromagnetic manganites are still a controversial issue even for the most studied $La_{1-x}Ca_xMnO_3$ system. Recently, Salamon *et al.*[10] brought this subject back to the center of discussion arguing that CMR in the optimally doped $x=0.33$ can be viewed as a Griffiths singularity, driven by intrinsic randomness. We present a study of the magnetic properties of La-based CMR manganites in the vicinity of the ferromagnetic–paramagnetic phase transition, that suggests that it occurs in the vicinity of a tricritical point, associated with the coupling between the magnetic and electronic-structural order parameters. We use the macroscopic Landau theory of phase transitions. To describe in a consistent way first- and second-order transitions an expansion of the energy $G(T,M)$ up to sixth power of the magnetization,[11] $G(T,M)=G_0+\frac{1}{2}AM^2+\frac{1}{4}BM^4+\frac{1}{6}CM^6-MH$, with A and $C>0$. The parameter A is usually assumed to take the form $A=a(T-T_0)$, where T_0 is a characteristic temperature, close to the transition point (Curie law). From minimization of $G(T,M)$ one obtains the magnetic equation of state $H/M=A+BM^2+CM^4$ and the condition for a first-order transition is $B<0$.

In this case, in the presence of the magnetic field, M presents a discontinuity at the phase transition up to a critical magnetic field H_C^* and temperature T_C^*. This critical point is determined by the condition $A(T_C^*)=9B^2(T_C^*)/20C(T_C^*)$. Further analysis of the model for $B<0$ shows that at

[a]Electronic mail: vamaral@fis.ua.pt

higher temperatures and magnetic fields, $M(H)$ still presents anomalous features with a maximum in dM/dH at a characteristic magnetic field $H_C(T)=(A(T)-21B^2(T)/100C(T))\sqrt{-3B(T)/10C(T)}$. Particularly, for constant a, B, and C, $H_C(T)$ increases linearly with temperature, $H_C(T)\sim(T-T_0^*)$, where $T_0^*>T_0$, and corresponds at each temperature to the critical value of the magnetization $M_C^2=-3B/10C$. In contrast, in the case of a second-order phase transition, $B>0$ and dM/dH does not show any maximum.

Ferromagnetic ceramic manganites were prepared by standard solid-state methods:[9] $La_{0.67}Ca_{0.33}MnO_3$ (LaCaMn) with $T_C\sim 267$ K, vacancy doped $La_{0.8}MnO_3$ (La_Mn) with $T_C\sim 250$ K, and $La_{0.60}Y_{0.07}Ca_{0.33}MnO_3$ (LaYCaMn), with $T_C\sim 150$ K. The magnetization $M(H,T)$ was measured in the paramagnetic phase in the vicinity of T_C using a Quantum Design superconducting quantum interference device magnetometer (55 kOe) and an Oxford Instruments vibrating sample magnetometer (120 kOe). The field dependence of the magnetization for the LaYCaMn sample in the paramagnetic phase ($T>150$ K) is presented in Fig. 1(top). $M(H)$ presents an anomalous upward inflection with maxima in dM/dH at an almost constant magnetization value ($\sim$35 emu/g) and, below about 170 K, large field cycling irreversibility is observed, with, however, $M(H=0)=0$ and M for decreasing field is higher than for increasing field. Only at very high temperatures that the magnetization recovers a regular behavior. To analyze the magnetic behavior we use Arrott plots of isotherms (H/M versus M^2) shown in Fig. 1(bottom). One can immediately associate this anomalous behavior with a negative B coefficient in the equation of state, as it is given by the initial slope of the Arrott plot isotherms. Analogous behaviors are found in LaCaMn (Ref. 9) and La_Mn samples, but without any prominent observation of field cycling irreversibility. The characteristic field $H_C(T)$ for the maxima in dM/dH is shown in Fig. 2. It presents an almost linear temperature dependence. Above $\sim$220 K, dM/dH becomes very shallow and the maximum is not clearly observed. The irreversibility region at lower temperatures is clearly delimited and one can tentatively identify the branching point (at $T_C^*\sim 170$ K) as the critical point for first-order phase transition. To confirm this qualitative picture, the data were analyzed using the equation of state and the coefficients A, B, and C were determined. As expected, the M^2 coefficient presents a linear temperature dependence (Curie–Weiss) of $A\sim a(T-T_0)$, shown in Fig. 3(bottom). Shown in Fig. 3(top) is the temperature dependence of B, which is indeed negative in most of the experimental range, from 150 up to $\sim$260 K, about twice T_C. C is always positive. In the LaCaMn (Ref. 9) and La_Mn samples the behavior is analogous, but the temperature range where $B<0$ is much shorter, from T_C up to 298 and 290 K, respectively. It should be remarked that at lower temperatures the fit may not be so reliable due to the irreversibility effects, and the fit range was restricted to the higher magnetization region, from maximum M^2 down to the minima of the Arrott plot isotherms. In Fig. 3(bottom) both sides of the equality $A=0.45B^2/C$ that determines the critical point are plotted as a function of temperature. Apparently, both curves do not cross, but the extrapolation of the high temperature data (T

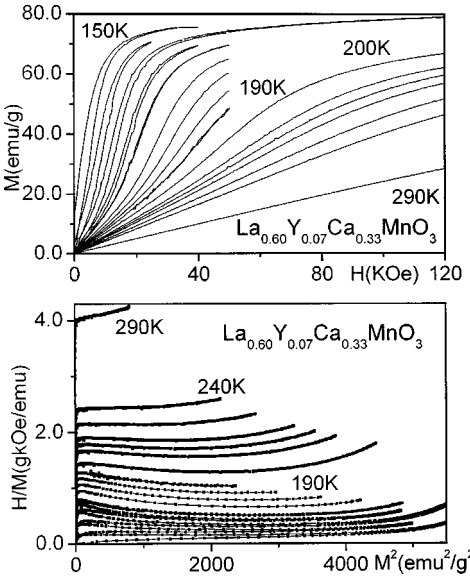

FIG. 1. (Top) $M(H)$ for the LaYCaMn sample ($T>150$ K). (Bottom) Arrott plots of isotherms (H/M vs M^2). $M(H)$ presents an upward inflection and, below about 170 K, large field cycling irreversibility.

$\geqslant 175$ K) clearly leads to $T_C^*=166$ K, and therefore, from Fig. 2, $H_C^*=20$ kOe, at the limit of the irreversibility region. Figure 4 shows the analogous plot for the LaCaMn sample. In this case, the extrapolation gives $T_C^*=266$ K. To determine H_C^* an alternative procedure is shown in the inset, where the linear temperature dependence of $A=a(T-T_0)$, with constant a and $T_0=265.4$ K is used to calculate both $T_C^*-T_0$ and $H_C^*=H_C(T_C^*)$. For slowly varying $B(T)$ and $C(T)$ parameters, as in this sample,[9] both quantities are nearly proportional. From the plateau region between 270 and 285 K, one reliably obtains $T_C^*-T_0\approx 0.6$ K and $H_C^*\approx 250$ Oe. This value agrees with the field below which $M(T)$ in the LaCaMn sample showed thermal cycling hysteresis effects.[9] The fact that first-order transition effects are absent in the ferromagnetic insulator $La_{0.67}Cd_{0.25}MnO_3$ ($T_C=148$ K)[9] suggests that the key point in determining such behavior is not a low T_C value but instead is the presence of another contribution or competing order parameter in the metallic ferromagnetic samples. Jaime *et al.*[12] considered the metallic electron concentration as a magnetically coupled secondary order parameter in an M^4 expansion leading to a

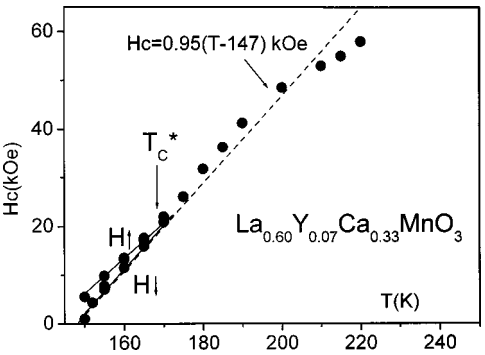

FIG. 2. $H_C(T)$ for the maxima in dM/dH, presenting an almost linear temperature dependence. The irreversibility region at lower temperatures is clearly delimited. T_C^* is the critical point for the first-order phase transition.

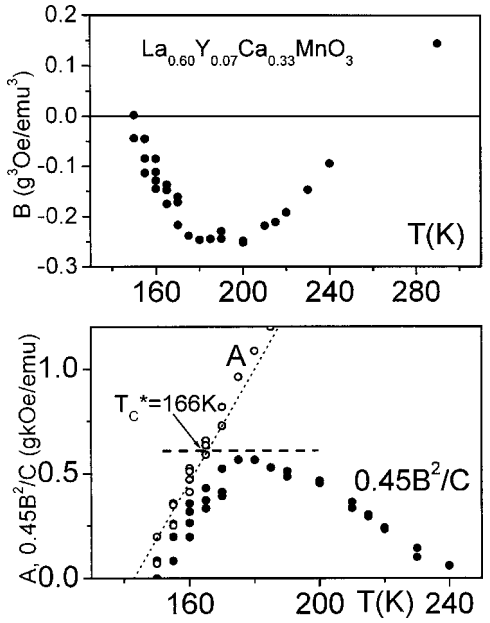

FIG. 3. (Top) Temperature dependence of B, negative from 150 K up to ~260 K. (Bottom) Temperature dependence of both sides of the equality $A=0.45B^2/C$ that determines the critical point plotted as a function of temperature. Extrapolation of the high temperature data gives $T_C^*=166$ K, at the limit of the irreversibility region.

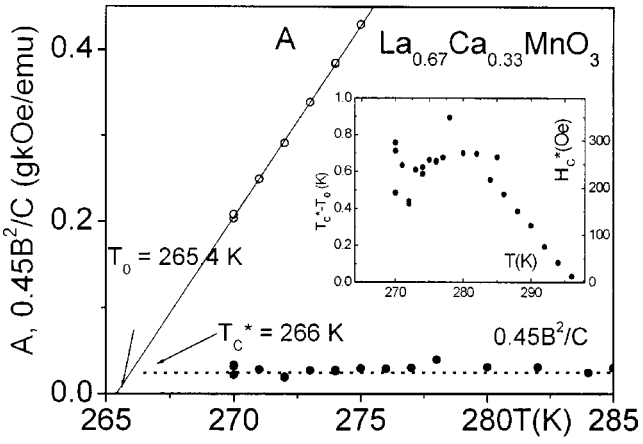

FIG. 4. Similar plot as in Fig. 3 for the LaCaMn sample, giving $T_C^*=266$ K. Inset: $T_C^*-T_0$ and $H_C^*=H_C(T_C^*)$ determined from $B(T)$ and $C(T)$. Data below 285 K give $T_C^*-T_0\approx 0.6$ K and $H_C^*\approx 250$ Oe.

reduction of the Landau coefficient B. Novák *et al.*[4] considered the dependence of the double exchange energy on the interatomic distances and therefore the relevance of magnetoelastic couplings in a M^4 expansion of the free energy. The competition of magnetic and charge density wave order parameters in layered manganites leading to first order transition effects was also considered by Berger *et al.*[13] A microscopic analysis of the double exchange model using a variational mean-field approach by Alonso *et al.*[14] led to a Landau-type free energy expansion up to sixth power in M. This study strongly supports the overall picture that the electronic condensation energy and electron–lattice interaction couple to the magnetic degree of freedom to produce anomalous (first-order-like) behavior in the presence of a magnetic field. In fact, thermal expansion effects near T_C are much stronger in LaCaMn and LaYCaMn than in LaSr manganites.[1,4] On the other hand, ferromagnetic insulator manganites like the LaCdMn sample usually do not present anomalies of thermal expansion near T_C and the magnetostriction is very small.[1] The Landau theory with coupled order parameters[11,15] leads to a rich variety of behaviors, and a most interesting situation occurs when $B=0$ at the transition, when the system crosses from first- to second-order phase transitions, leading to a tricritical point. The fact that in the samples studied the temperatures T_B at which $B(T)$ vanishes are of the same order (260–290 K), although T_C varies by almost a factor of 2 (150–267 K), suggests that the same mechanism should drive the tendency of B to zero. If, as a function of some parameter Y, $B(T,Y)$ would be zero at the tricritical point ($T_B=T_C$), we find that this should occur at a temperature $T_C\sim 310$ K, from the extrapolation to zero of T_C-T_B as a function of T_C in our samples. This value curiously matches the point in the $La_{0.7}(Ca_{1-y}Sr_y)_{0.3}MnO_3$ system for which the magnetic and structural transitions are equal ($y=0.47$, $T_S=T_C=310$ K). Recent work by Kim *et al.*[16] showed that another tricritical point exists in the system $La_{1-x}Ca_xMnO_3$ at doping level $x=0.40$ and $T_C=265.5$ K.

J. P. Araújo acknowledges a scholarship from FCT. Work was partially supported by FCT, Contract No. POCTI/CTM/35462/99, Project No. MAT2000-1756, and the High Field Infrastructure Cooperative Network HPRI-1999-CT-0013.

[1] *Colossal Magnetoresistive Oxides*, edited by Y. Tokura (Gordon and Breach, Singapore, 2000); *Colossal Magnetoresistance, Charge Ordering and Related Properties of Manganese Oxides*, edited by C. N. R. Rao and B. Raveau (World Scientific, Singapore, 1998).
[2] Y. Tomioka, A. Asamitsu, and Y. Yokura, Phys. Rev. B **63**, 02421 (2000).
[3] J. Mira, J. Rivas, F. Rivadulla, C. Vázquez-Vázquez, and M. A. López-Quintela, Phys. Rev. B **60**, 2998 (1999).
[4] P. Novák, M. Marysko, M. M. Savosta, and A. N. Ulyanov, Phys. Rev. B **60**, 6655 (1999).
[5] K. Ghosh, C. J. Lobb, R. L. Greene, S. G. Karabashev, D. A. Shulyatev, A. A. Arsenov, and Y. Mukovskii, Phys. Rev. Lett. **81**, 4740 (1998).
[6] M. Ziese, J. Phys.: Condens. Matter **13**, 2919 (2001).
[7] H. S. Shin, J. E. Lee, Y. S. Nam, H. L. Ju, and C. W. Park, Solid State Commun. **118**, 377 (2001).
[8] V. S. Amaral, J. P. Araújo, Yu. G. Pogorelov, J. M. B. Lopes dos Santos, P. B. Tavares, A. A. C. S. Lourenço, J. B. Sousa, and J. M. Vieira, J. Magn. Magn. Mater. **226–230**, 837 (2001).
[9] V. S. Amaral, J. P. Araújo, Yu. G. Pogorelov, P. B. Tavares, J. B. Sousa, and J. M. Vieira, J. Magn. Magn. Mater. **242–245**, 655 (2002).
[10] M. B. Salamon, P. Lin, and S. H. Chun, Phys. Rev. Lett. **88**, 197203 (2002).
[11] N. Boccara, *Symétries Brisées* (Hermann, Paris, 1976); D. I. Uzunov, *Introduction to the Theory of Critical Phenomena* (World Scientific, Singapore, 1993).
[12] M. Jaime, P. Lin, S. H. Chun, M. B. Salamon, P. Dorsey, and M. Rubinstein, Phys. Rev. B **60**, 1028 (1999).
[13] A. Berger, J. F. Mitchell, D. J. Miller, and S. D. Bader, J. Appl. Phys. **89**, 6851 (2001).
[14] J. L. Alonso, L. A. Fernández, F. Guinea, V. Laliena, and V. Martín-Mayor, Phys. Rev. B **63**, 054411 (2001).
[15] Y. Imry, J. Phys. C **8**, 567 (1975).
[16] D. Kim, B. Revaz, B. L. Zink, F. Hellman, J. J. Rhyne, and J. F. Mitchell, Phys. Rev. Lett. **89**, 227202 (2002).