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LETTER TO THE EDITOR

The observation of coincident first- and second-order magnetic transitions in single crystal $La_{0.73}Ca_{0.27}MnO_3$

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Abstract

Magnetization isotherms on single crystal $La_{0.73}Ca_{0.27}MnO_3$ exhibit a metamagnetic structure generally linked with a first-order transition, a currently accepted feature of the behaviour of this system near this doping level. By contrast, field and temperature dependent ac susceptibility data display a set of pseudocritical maxima which move upwards in temperature and decrease in amplitude as the field increases, a characteristic of continuous transitions. Within experimental uncertainty these features are coincident in the (H–T) plane.

The rediscovery of colossal magnetoresistance (CMR) in mixed valent manganese perovskites (general formula $La_{1-x}A_xMnO_3$, where A is a divalent alkaline earth ion) has resulted in these systems being amongst the most intensively studied over the past decade [1]. These systems are currently viewed as important examples of strongly correlated electronic systems offering a unique combination of coupling between charge, spin, orbital and lattice/phononic degrees of freedom. Despite widespread study, many aspects of the response of these perovskites still remain unresolved, including the interrelationship between the metal–insulator and the paramagnetic to ferromagnetic (PFT) transitions in particular [2], and on the apparent inverse relationship between the value of T_c for the PFT and the magnitude of the associated CMR [1, 3] in general. A related question that has also emerged concerns the magnitude for T_c and the order of the magnetic phase transition, particularly the role played by disorder [4].

To focus on specific aspects of the behaviour of the archetypal system $La_{1-x}Ca_xMnO_3$, recent studies—particularly those involving detailed measurements and analysis of magnetization and specific heat [5, 6]—have been interpreted as indicating the occurrence of a first-order/discontinuous magnetic phase transition near optimal doping, $x \simeq 0.33$. However, the line of such first-order transitions (in the T_c versus x plane) terminates at a

tricritical point near $x = 0.4$, where similar measurements indicate the presence of a second-order/continuous transition characterized by exponent values close to those predicted for such a point [5, 7]. At still higher compositions ($x \sim 0.5$), sequential paramagnetic to ferromagnetic to antiferromagnetic phase changes (accompanied by charge ordering) are known to occur [8]; by contrast, the situation at lower concentrations ($x < 0.3$) is unclear.

Abrupt volume changes occurring at the PFT at $x = 0.25$ suggest that this transition retains first-order characteristics [8]; however, with further reductions in composition changes occur as magnetization studies on single crystals (generally regarded as the most appropriate for the investigation of critical exponents [9]) near $x = 0.2$ have been analysed to yield behaviour consistent with a second-order/continuous transition characterized by Heisenberg model exponents [10]. It is this region of the T_c versus x plane that is the subject of the present investigation. Detailed magnetization and susceptibility data on single crystal $La_{0.73}Ca_{0.27}MnO_3$ reveal a not previously predicted and hence unexpected result—a unique combination of characteristics associated with *both* first-order and second-order transitions *simultaneously*: namely, metamagnetic behaviour in magnetic isotherms occurring coincidentally with a 'crossover' line in the field and temperature dependent susceptibility.

The sample used was a 0.12 g single crystal with approximate dimensions ($10 \times 1.4 \times 1.4\ mm^3$) grown using the floating-zone technique [11], displaying a mosaicity of less than 1°. Measurements of the dc magnetization and the ac susceptibility (with static fields up to 50 kOe for the magnetization, but to a lower field of 4 kOe for the ac susceptibility (for reasons discussed below), and ac driving fields applied along the largest sample dimension in each case) were carried out simultaneously in a Quantum Design Model PPMS 6000 magnetometer/susceptometer. At each measuring temperature and field, an appropriate time delay was adopted to ensure that equilibrium conditions prevailed.

Figure 1(a) shows the zero-field ac susceptibility, $\chi(0, T)$, measured on both warming and cooling at 2.4 kHz in a 30 mOe driving field, as a function of temperature (T); there is no discernible hysteresis. These data enable a preliminary estimate of the ordering temperature $T_c \approx 232$ K to be made from the minimum slope, $d\chi/dT$. Figure 2 displays a selection of magnetic isotherms collected in the vicinity of T_c; these isotherms display a marked similarity to those reported recently for polycrystalline $x = 0.33$ specimens [6]. Complete hysteresis curves measured near and below T_c in the ordered phase yield estimates for the coercivity (summarized in figure 1(b)), the values for which do not exceed 10 Oe at any temperature, confirming the high quality of the present sample. This small coercivity is also reflected in the behaviour of magnetization isotherms reproduced in figure 2 at $T \leqslant T_c$, in which the low field (<1.5 kOe) structure originates from technical sources (domain wall motion and/or domain reorientation/rotation), a point returned to below. The striking feature evident in figure 2 is the S-shaped character of isotherms for $T > 237$ K; such a feature is generally associated with a metamagnetic transition, as reported previously for $x = 0.33$ in this system, as well as in intermetallic compounds such as Gd_2In [12] and doped $CeFe_2$ [13] (in these latter, however, the relevant transition is a field-induced one from an antiferromagnetic to a ferromagnetic phase). As at $x = 0.33$, the actual hysteresis accompanying this metamagnetic transition is confined to a narrow region of the (H–T) plane, as figure 2 confirms. From the data in this latter figure, estimates for the metamagnetic field H_M have been made in a manner analogous to that utilized for the intermetallic compounds mentioned above, namely the maximum in dM/dH. These estimates (corrected for demagnetization effects) from both field increasing and field decreasing isotherms are presented in figure 1(c), and yield a slope $dT_c/dH_M \approx 8 \times 10^{-4}$ K Oe^{-1}, smaller than that reported from magnetic measurements at $x = 0.33$ (due primarily to a slightly different criterion for identifying H_M [14]), but larger than specific heat based estimates [7]. Such field-induced shifts confirm first-order characteristics

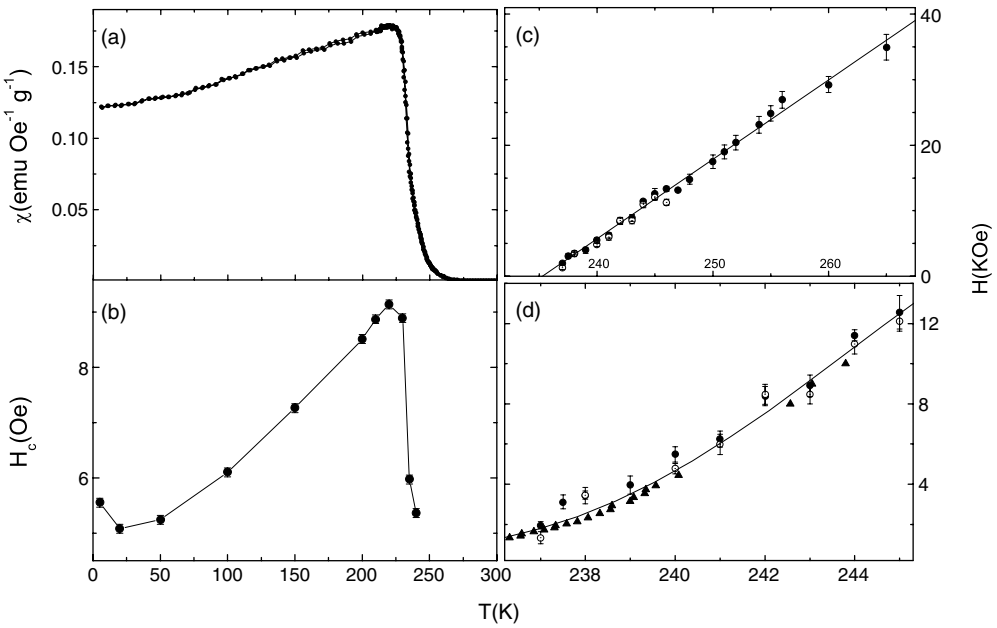

Figure 1. (a) The zero-field ac susceptibility measured on warming and on cooling. (b) The temperature dependence of the coercive field H_c. (c) The metamagnetic field plotted against temperature. The solid circles are calculated from data measured in increasing field, the open circles are calculated from data measured in decreasing field. (d) The metamagnetic boundary as described in (c) and the crossover line (▲) (the line of maxima in figure 3(a)) plotted against temperature. The solid curve is drawn through all points.

present at this transition. Analysis of the present data using a Clausius–Clapeyron like equation coupled with the volume change reported at $x = 0.25$ [8] yields comparable results to those discussed in [5] and [6]; but this is not the principal focus here.

The unique feature emerging in the present system is displayed in figure 3(a). The field and temperature dependent ac susceptibility, $\chi(H_a, T)$, measured in the vicinity of T_c exhibits a series of maxima that move upward in temperature while decreasing in amplitude as the superimposed static biasing field increases (these maxima could only be resolved for applied fields 400 Oe $\leqslant H_a \leqslant$ 4000 Oe). Maxima that behave in this way are a characteristic signature of a second-order/continuous phase transition. These maxima delineate the position of the crossover line in the (H–T) plane, above which the response is thermally dominated as opposed to being field dominated below it; this crossover line ends at $H = 0$ in an end line point—the Curie/critical temperature T_c. While the usual critical exponents governing various power-law relationships in the vicinity of T_c depend on the specific nature of the ensuing order as well as dimensionality, structure of the type evident in figure 3 displays model independent elements. The peak structure itself and its variation with field and temperature can be understood using general arguments based on the fluctuation–dissipation theorem [15], and such features are also predicted specifically by Monte Carlo/numerical calculations for both Heisenberg [16] and mean-field [17] models. The particular feature that is unexpected is presented in figure 1(d): in the region of the (H_i–T) plane (the internal field $H_i = H_a - NM$ in the usual notation) where data are accessible for both, the crossover line and the metamagnetic boundary are coincident within experimental error. That is, at $x = 0.27$, the transition simultaneously displays both first-order and second-order characteristics, and these characteristics are coincident.

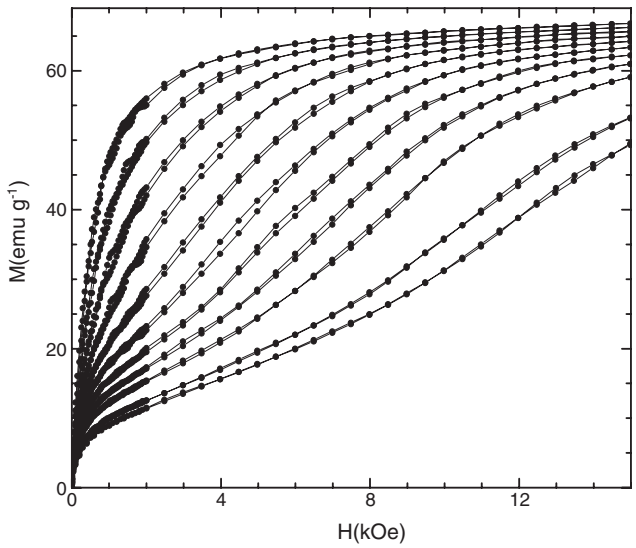

Figure 2. A selection of magnetization isotherms, showing limited hysteresis, for temperatures increasing from 234 K (top) to 245 K (bottom) in 1 K steps for applied fields up to 15 kOe. While data have been collected to higher fields, the hysteresis becomes difficult to resolve above this field, although the metamagnetic field can be estimated up to 35 kOe (see figure 1(c)).

Further examination of figure 2 reveals that while the metamagnetic transition can be followed to higher fields than the crossover line (a result attributable to the suppression in amplitude and broadening in temperature of the susceptibility maxima defining the latter with increasing field), the converse is true in the low-field limit (where technical components in the magnetization, discussed above, preclude reliable estimates for H_{M} from being made as $H \rightarrow 0, T \rightarrow T_{\mathrm{c}}$ (essentially below $\sim$1.5 kOe)). Nevertheless the influence—and hence continued presence—of the metamagnetic transition as $H \rightarrow 0$ can be inferred, albeit indirectly, from a detailed analysis of the behaviour of the crossover line/critical maxima evident in figure 3(a).

In situations where a second-order/continuous transition occurs in isolation, this critical peak structure is predicted to obey a series of asymptotic power-laws, and the analysis of experimental data on a variety of systems (including the pyrochlore $Tl_2Mn_2O_7$ [18], other doped manganese perovskites [19], as well as dilute metallic alloys [20]) not only confirms such power-law predictions, but also enables exponent values (which are model dependent) to be extracted from such data. Specifically, the relevant power-laws predicted to occur at a conventional second-order transition by the usual static scaling law relating the (reduced) magnetization to the linear scaling fields t ($=|T - T_{\mathrm{c}}|/T_{\mathrm{c}}$) and h ($\sim H_{\mathrm{i}}/T_{\mathrm{c}}$) include [16, 21]:

(i) the relationship between the peak temperature (T_{m}) and (internal) field H_{i}, the locus of the crossover line, namely

$$t_{\mathrm{m}} = \frac{T_{\mathrm{m}} - T_{\mathrm{c}}}{T_{\mathrm{c}}} \propto H_{\mathrm{i}}^{(\gamma+\beta)^{-1}} \tag{1}$$

which, for the crossover exponent $(\alpha + \beta) > 0$, predicts that t_{m} increases as H_{i} increases (as observed),

(ii) the dependence of the (critical) maximum amplitude, $\chi(h, t_{\mathrm{m}})$, on (internal) field, H_{i}

$$\chi(h, t_{\mathrm{m}}) \propto H_{\mathrm{i}}^{1/\delta-1} \tag{2}$$

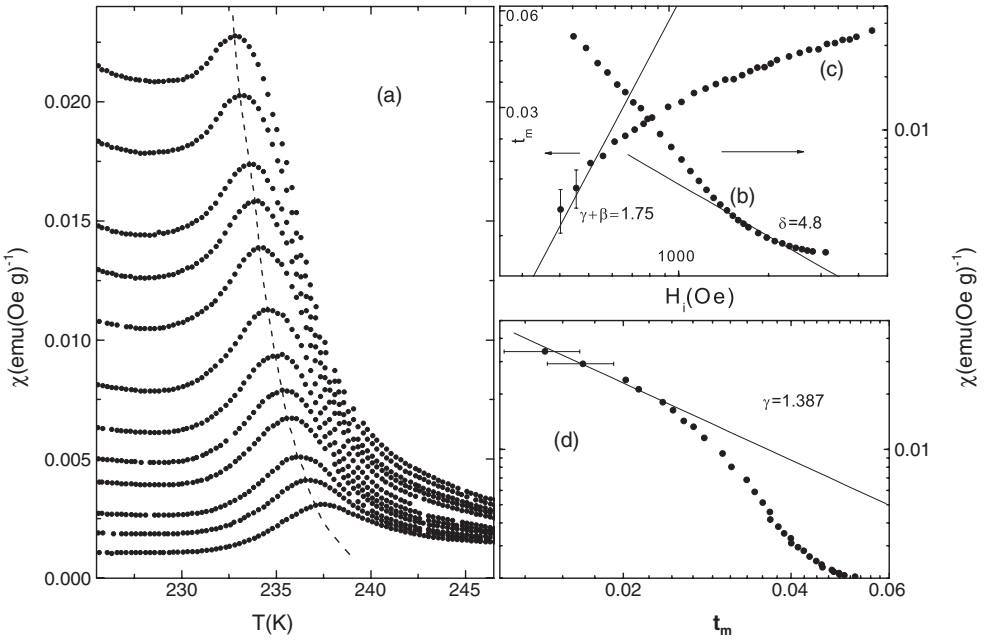

Figure 3. (a) The ac susceptibility $\chi(H_a, T)$, measured in applied fields H_a increasing from 600 Oe (top) to 800 Oe in 50 Oe steps, in 100 Oe steps to 1200 Oe, in 200 Oe steps to 1600 Oe, and finally in 2000 Oe (bottom); the locus of these maxima—the crossover line—is shown by the dashed curve; double logarithmic plots of (b) the susceptibility maxima (from (a)) against internal field H_i (a test of equation (2)), (c) the (reduced) peak temperature (from (a)) against internal field (a test of equation (1)), (d) the susceptibility maxima against reduced peak temperature (a test of equation (3)). The solid lines show Heisenberg model exponents for comparison, the latter having been predicted to represent the universality class for double exchange [23], but clearly do *not* fit the present data.

which, for $\delta > 1$, leads to this amplitude decreasing with increasing field (also observed); equation (2) also enables δ to be determined directly from the field dependence of these maxima without a prior knowledge of T_c [16–21], and

(iii) the relationship between this same amplitude and the reduced peak temperature:

$$\chi(h, t_m) \propto t_m^{-\gamma}. \tag{3}$$

However, as figures 3(b)–(d) show, these power-laws are *not* obeyed here, which, we contend, reflects the continued influence/presence of the metamagnetic transition as $H \to 0$ (the lines drawn in these figures are guides, *not* attempts to establish experiment values). In qualitative terms, expressing the magnetization M along isotherms near the critical temperature in the usual power-law form, $M \propto H_i^{1/\delta}$, would—given their S-shaped behaviour through the metamagnetic transition—lead to large (effective) values for δ (on the flattened section of the isotherm), which would subsequently decrease as the field increases. This is indeed the behaviour evident in figure 3(b) (the test of equation (2)), with related effects in figures 3(c) (a test of equation (1)) and 3(d) (testing equation (3)).

In summary, the transition at $x = 0.27$ displays features characteristic of both continuous and discontinuous transitions that are—within experimental uncertainty—coincident. This behaviour is fundamentally different from crossover effects from sequential second-order to a first-order transition as $T \to T_c$, where the first-order transition line would lie *below* that

for the continuous transition, a situation for which the power-laws discussed above would be expected to occur, as the transition is approached from higher reduced temperatures. Such a situation has been raised as a possibility (but not generally confirmed) by muon spin relaxation measurements at $x = 0.33$ [22], and a value for the exponent $\beta = 0.345$ reported. Here these transitions are essentially coincident, as the *lack* of power-laws confirm. Given the first-order-like character of the heat capacity anomaly, reported at slightly higher Ca doping [5, 6], an anomaly which would dominate any second-order features, the combination of measurements presented here offers a unique approach to revealing these dual characteristics.

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References

[1] Coey J M D, Viret M and von Molnar S 1999 *Adv. Phys.* **48** 167
Coey J M D, Viret M and von Molnar S 2000 *Colossal Magnetoresistive Oxides* ed Y Tokura (Amsterdam: Gordon and Breach)
[2] Adams C P *et al* 2000 *Phys. Rev. Lett.* **85** 3954
Lynn J W *et al* 2001 *J. Appl. Phys.* **89** 6846
Dai P *et al* 2000 *Phys. Rev. Lett.* **85** 2553
[3] Ramirez A 1997 *J. Phys.: Condens. Matter* **9** 8171
[4] Moreo A *et al* 2000 *Phys. Rev. Lett.* **84** 5568
[5] Kim D *et al* 2002 *Phys. Rev. Lett.* **89** 227202
[6] Gordon J E *et al* 2001 *Phys. Rev.* B **65** 02441
[7] Huang K 1987 *Statistical Mechanics* (New York: Wiley)
[8] Radaelli P G *et al* 1995 *Phys. Rev. Lett.* **75** 4488
[9] Kim D *et al* 2002 *Phys. Rev.* B **65** 214424
[10] Hong C S, Kim W S and Hur N H 2001 *Phys. Rev.* B **63** 092504
[11] Shulyatev D, Karabashev S, Arsenov A and Mukovskii Y 1999 *J. Cryst. Growth* **199** 511
[12] Stampe P A *et al* 1997 *J. Phys.: Condens. Matter* **9** 3763
[13] Kunkel H P *et al* 1996 *Phys. Rev.* B **53** 15099
[14] Differing criteria have also been used to estimate H_M in intermetallic compounds. See, for example, Radha S *et al* 1994 *Phys. Rev.* B **50** 6866 and [13] above
[15] Kunkel H P *et al* 1988 *Phys. Rev.* B **37** 5880
[16] Campostrini M *et al* 2002 *Phys. Rev.* B **65** 144520
[17] Roshko R M and Williams G 1984 *J. Phys. F: Met. Phys.* **14** 703
[18] Zhao J H *et al* 1999 *Phys. Rev. Lett.* **83** 219
[19] Zhao J H *et al* 2000 *J. Phys.: Condens. Matter* **12** 6903
[20] Wang Z *et al* 1992 *J. Phys.: Condens. Matter* **4** 10385
[21] Williams G 2001 *Proc. Int. Conf. on Magnetic Materials (Calcutta, 2000)*; *J. Alloys Compounds* **326** 36
[22] Heffner R H *et al* 1996 *Phys. Rev. Lett.* **77** 1869
[23] Alonso J L *et al* 2001 *Nucl. Phys.* B **596** 587