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Evidence for an enhanced magnetoresistance accompanying a continuous phase transition in semiconducting $La_{0.67}Mg_{0.33}MnO_3$

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The field- and temperature-dependent ac susceptibility of Mg-substituted $LaMnO_3$ provides unequivocal evidence for the presence of critical fluctuations associated with a continuous paramagnetic-to-ferromagnetic transition at which all three static critical exponents are estimated independently. Furthermore, this system does not undergo a metal-insulator transition near T_c, exhibiting a monotonic increase in resistivity with decreasing temperature in available fields. Nevertheless, this system displays a near colossal magnetoresistance that peaks near T_c, indicating a probable magnetic origin for this effect but of rather different character from that found in other perovskites. [S0163-1829(97)50144-5]

The substitutional replacement of trivalent lanthanum ions by divalent alkaline earths in $LaMnO_3$ has profound effects on the Mott insulating antiferromagnetic state of the parent compound, producing ferromagnetic ordering and a metallic-like conductivity in many instances. A general explanation of such effects was provided initially by a double exchange mechanism linked to the presence of both Mn^{3+} and Mn^{4+} ions, this inhomogeneous mixed valence state being induced by the doping process.[1] Recently, however, additional mechanisms have been invoked to explain aspects of the unusual transport and magnetic properties of these systems. These additional mechanisms involve lattice distortions associated with ionic size variations resulting from doping, and arising specifically from either static (coherent) Jahn-Teller distortions or fluctuating local Jahn-Teller displacements leading to charge ordering.[2] Furthermore, the colossal magnetoresistance (cmr) found in ''optimally'' doped (i.e., 33% lanthanum replacement) manganese perovskites has been associated in recent theories[3] with a first-order paramagnetic-to-ferromagnetic transition, the origin of which is believed to play a central role in understanding the magnetoresistive process. Available experimental evidence suggests, however, that the order of this transition depends on the specific dopant used.[4–7]

Here we present unequivocal evidence for the presence of critical fluctuations accompanying a continuous magnetic phase transition, along with the first estimate for the three associated critical exponents evaluated independently. In addition, while several reports have appeared in which the effects of changes in lanthanide ion doping near the optimal level are discussed,[4–6] the system investigated here—$La_{0.67}Mg_{0.33}MnO_3$—uses little-studied Mg as a *divalent* cation. Whereas other systems[4–6] display a paramagnetic-to-ferromagnetic transition while remaining in an insulating/semiconducting state on cooling in zero field, they do exhibit field-induced metallic characteristics. The present system is unusual in that it does not show indications of an insulating-to-metallic phase change below room temperature in available fields. Neverthless, it displays a substantial magnetoresistance that peaks near the magnetic ordering temperature. These results provide further interesting correlations between the size of the substituted cation, the order of the associated paramagnetic-to-ferromagnetic phase transition, and the magnitude of the attendant magnetoresistance.

The sample of $La_{0.67}Mg_{0.33}MnO_3$ (nominal) was prepared by the standard ceramic method. Stoichiometric amounts of La_2O_3 (ultrapure), MnO_2 (type FM), and MgO (99%) were mixed for eight hours by ball milling in acetone. The dried powder was then preheated for eight hours at 800 °C, pelletized as a disk (diameter 8 mm, thickness 1.5 mm) and sintered for 24 h at 1200 °C. A bar of dimensions $(6\times1.5\times0.8)$ mm^3, suitable for transport and magnetic measurements, was cut from this disk. X-ray powder diffraction data were collected using Cu Kα radiation. Rietveld analysis confirmed the presence of a single phase with orthorhombic structure (Pbnm) and $a=5.536(1)$ Å, $b=5.512(1)$ Å, and $c=7.807(1)$ Å. The average Mn-O-Mn bond angle was estimated at 156°, so that previous conclusions[4–6] regarding the suppression of the temperature of the metal-insulator transition with decreasing bond angle (or average A site/lanthanide radius ¡r_A) is confirmed; here, however, this suppression is associated with a reduced ionic radius of the substituted divalent cation and is more marked in the sense that a metal-insulator transition is not seen in available fields above the liquid-helium range. Thus the general (and necessary) trend of an increasing magnetoresistance as the metal-insulator transition temperature falls[4] is not seen here.

Figure 1 shows the ac susceptibility $\chi(H,T)$ (measured at 2.4 kHz in a driving field of 30 mOe rms in a previously described susceptometer[8]) in various static biasing fields H_a. In zero field $\chi(0,T)$ increases rapidly as the ferromagnetic ordering temperature T_c is approached from above, peaks (at the Hopkinson maximum) just below T_c, and then declines monotonically with decreasing temperature down to 1.5 K; the latter indicates the absence of a second (antiferromagnetic) transition in this system (above 1.5 K). All the data shown in the figure were acquired on warming following zero-field cooling; no measurable difference was found between warming and cooling in zero field, as reported recently for a Sr-doped specimen[7] (see the comments below regarding the transport data). The application of static biasing fields of increasing strength results in the progressive suppression

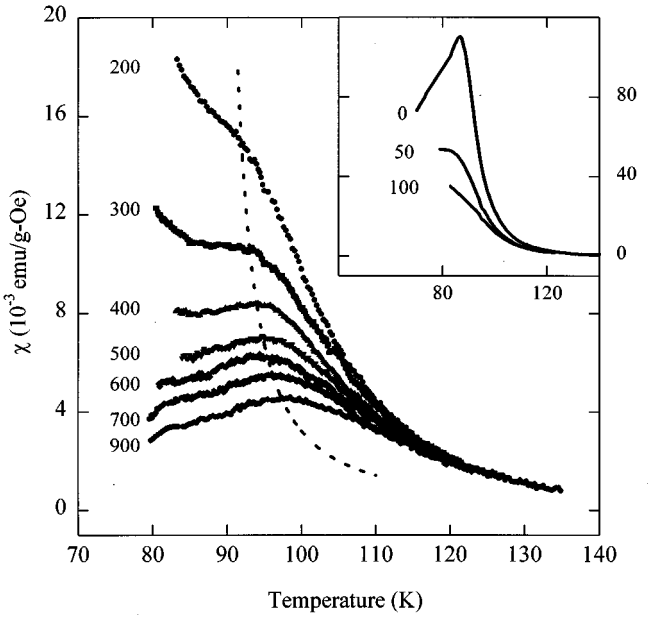

FIG. 1. The temperature dependence of the ac susceptibility $\chi(H,T)$ (in emu/g-Oe) in various fixed biasing fields (in Oe, as labeled). The dashed line represents the cross-over line defined by the locus of critical peak amplitudes and temperatures. The inset shows the zero-field susceptibility along with the response in low biasing fields, which suppress the principal maximum in both amplitude and temperature to reveal the secondary (critical) maxima.

of the principal maximum (in both amplitude and temperature), thus facilitating the observation of secondary, *critical* maxima. The latter, reproduced in the main body of Fig. 1, decrease in amplitude and shift to higher temperature T_m as H_a increases; such behavior is a unique, characteristic signature of critical fluctuations accompanying a second-order (paramagnetic-to-ferromagnetic) magnetic phase transition. The variation with H_a evident in Fig. 1 has been extensively reported previously in a variety of metallic systems,[8] and is consistent with both the predictions of the usual static scaling-law equation of state and various model calculations and can be understood on the basis of the fluctuation-dissipation theorem.[8,9] The dependence of the peak amplitude $\chi(H,T_m)$ and the reduced peak temperature t_m $[=(T_m - T_c)/T_c]$ on field have been used previously to extract estimates for the critical exponents in a variety of systems[8,11] using the scaling relations

$$\chi(H,T_m) \propto H^{1/\delta-1} \tag{1}$$

and

$$t_m \propto H^{1/(\gamma+\beta)}. \tag{2}$$

The iterative procedure by which a first estimate for T_c is chosen, and subsequently refined, has been discussed in detail previously[8] and here yields $T_c = 88.0 \pm 0.5$ K; thus only the final results are summarized in Figs. 2 and 3.

In Fig. 2(a) the critical peak amplitude $\chi(H,T_m)$ (corrected for background and demagnetizing effects[8]) is plotted against the internal field H_i (Ref. 8) on a double logarithmic scale. The solid line drawn in this figure is consistent with

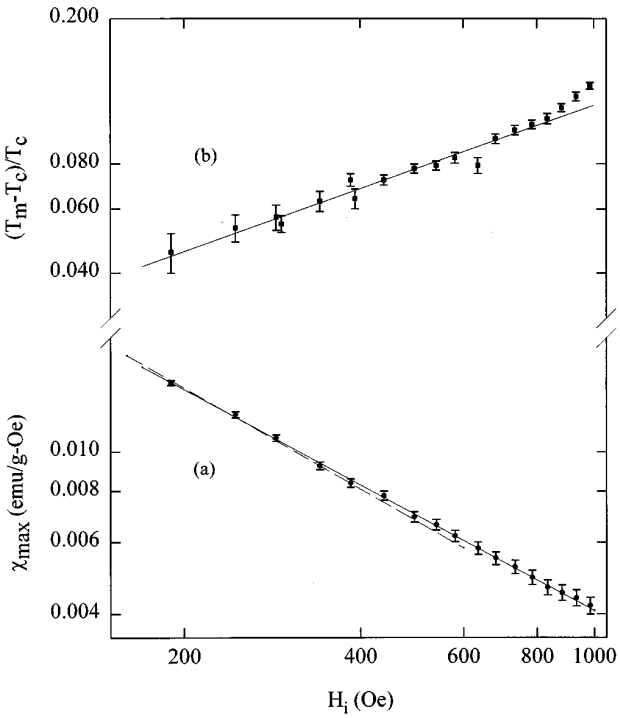

FIG. 2. (a) The critical peak amplitude $\chi(H,T_m)$ (in emu/g-Oe and corrected for background and demagnetizing effects) and (b) the (reduced) critical peak temperature $(T_m - T_c)/T_c$, plotted against the internal field H_i (in Oe), on a double logarithmic scale. The solid line in (a) represents an overall fit and yields an average value of $\delta \simeq 4.4$. The dashed line is a fit to the lower-field data $H_i < 400$ Oe; in (b) the solid line is a fit to points 1–15 and yields a slope of $0.56(7) \pm 0.07$, consistent with the 3d-Heisenberg model value for the crossover exponent of 0.571.

both the power-law dependence of Eq. (1) and an average value for the exponent $\delta \simeq 4.4$ (an estimate that is independent of the choice for T_c). Closer inspection of the latter figure reveals that the lower-field data ($180 \leqslant H_i < 400$ Oe)

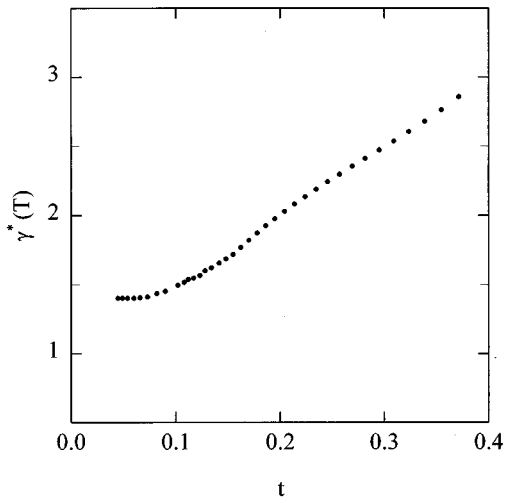

FIG. 3. The temperature dependence of the effective zero-field susceptibility exponent γ^*, plotted against the reduced temperature t $[=(T-T_c)/T_c]$. (●) represent the effective Kouvel-Fisher exponent found for $t \geqslant 0.1$, while data for $\pm < 0.1$ are obtained using Eq. (4) (see text).

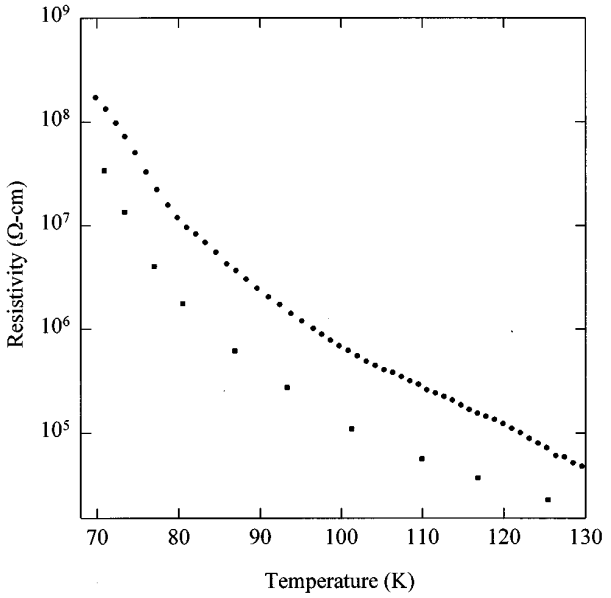

FIG. 4. The zero-field resistivity $\rho(0,T)$ (in Ω cm) as a function of temperature (in K) on a semilogarithmic scale. The resistivity rises sharply in the vicinity of T_c but displays no semiconductor-metal transition, rather continues to rise rapidly to below 70 K. The lower curve represents the temperature dependence of the resistivity in a field of 8.4 T; no field induced metallic phase is observed.

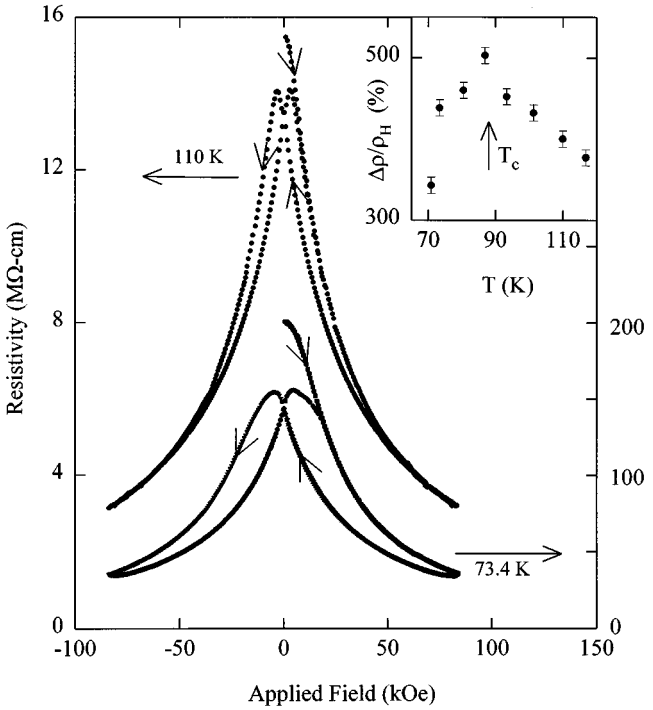

FIG. 5. The field-dependent resistivity at 73.4 and 110 K (in MΩ cm) in fields up to 8.4 T, measured on increasing followed by decreasing field and a field reversal. The magnetoresistive behavior is not only hysteretic but also fails to return to its virgin state when the field is returned to zero. The inset shows the temperature dependence of the fractional magnetoresistivity, $[\rho(0)-\rho(\mathrm{H})]/\rho(\mathrm{H})$ (in % at 8.4 T), in the vicinity of T_c.

are consistent with the 3d-Heisenberg model[10] value of δ=4.8 (the dashed line); as a corollary, effective δ^* values that decrease with increasing field which have been reported in a variety of disordered metallic systems,[8,9,11] and attributed to the presence of a distribution of exchange coupling strengths are also found in the present data, as in fields above 400 Oe a significantly reduced value of δ^* (3.9) is obtained. Here, such a variance might be a consequence of the substitutional process, which produces both antiferromagnetic (as between Mn^{3+} ions in the undoped system) and ferromagnetic (Mn^{3+}-Mn^{4+}) double exchange; indeed the appearance of spin-glass-like features in some perovskites[5] demands such a variance (but with somewhat different characteristic parameters). A second point that should be made regarding the data in Figs. 1 and 2 is that these critical peaks cannot be resolved in fields below ~180 Oe, a field over two orders of magnitude larger than that reported in the softest metallic alloys.[11] Such behavior is not fully understood at present as ''butterfly'' loop measurements [$\chi(H,T)$ versus H_a at fixed T] indicate coercive fields of only 3.4 Oe in this system at 77 K, these fields being responsible for the retention of the significant technical/regular contributions to $\chi(H,T)$, which generally obscure emerging critical behavior.[8,11] Nevertheless, the low-field data in Fig. 2(a) [which provide the most appropriate comparisons with scaling law predictions, the latter being asymptotic ($h\rightarrow 0$, $t\rightarrow 0$) in nature] are, despite these complications, consistent with the Heisenberg model value of δ=4.8.

Similar comments apply to the data in Figs. 2(b) and 3. Figure 2(b) reproduces a plot of the (reduced) critical peak temperature against the internal field H_i; the line drawn verifies the power-law relationship between these two quantities summarized by Eq. (2), and the slope of this line is consistent with the 3d-Heisenberg model value for the crossover exponent $(\gamma+\beta)^{-1}$ of 0.571. The temperature dependence of the effective zero-field susceptibility exponent is summarized in Fig. 3 using a combination of the Kouvel-Fisher exponent[12]

$$\gamma^*(T)=d\ln(\chi(0,t))/d\ln(t) \tag{3}$$

in the range $t\geqslant 0.1$, and the relationship

$$\chi(H,t_m)\propto t_m^{-\gamma} \tag{4}$$

[a power law based on the assumption of the validity of the Widom equality, $\gamma=\beta(\delta-1)$ and a combination of Eqs. (1) and (2)] in the range $\pm<0$ where Eq. (3) becomes unreliable.[8,9,11]

The asymptotic ($t\rightarrow 0$)value for $\gamma^*(t)$ is again consistent with the 3d-Heisenberg model prediction of γ=1.386.

A temperature-dependent $\gamma^*(t)$—specifically one that increases with increasing temperature above T_c—is also a characteristic of systems with a distribution of exchange coupling strengths.[8,13] Indeed the early observation[14] of a rapid decrease in the spontaneous magnetization in Pb substituted perovskites (which also raised the possibility of a first-order magnetic transition) fitted with a large (average) value of $\beta^*\simeq 0.57$, and the distribution of β value reported for $La_{0.67}Sr_{0.33}MnO_3$ (Ref. 7) support the presence of such a distribution. Specifically as discussed extensively for a variety of metallic systems where such distributions frequently exist,[13] effective exponents often vary with the range of re-

duced temperature over which appropriate fits are attempted. Having discussed the experimental evidence identifying a second-order paramagnetic-to-ferromagnetic transition, we present a brief summary of the transport properties.

Figure 4 displays the zero-field resistivity $\rho(0,T)$ measured using a four probe technique (absolute values for ρ are uncertain to typically 10% arising principally from shape factor uncertainties) as a function of temperature for $70<T\leqslant 120$ K. Below 60 K ρ became too large to be measured, exceeding 10^9 Ω cm in fields up to 8.4 T. Thus we conclude that this system displays an insulating/semiconducting response over the entire temperature range examined ($60<T\leqslant 300$ K); in particular, there is no evidence for a metal/insulator transition at or below T_c. While such a change in the conducting properties of this system are absent, the magnetoresistance is, nevertheless, substantial. Figure 5 reproduces the field induced change in the resistivity at 73.4 and 110 K, as the field is cycled to ± 8.4 T. The largest (fractional) changes occur in the immediate vicinity of T_c despite the absence of an associated metal-insulator transition, as the inset in Fig. 5 shows. At 88 K the field-induced change $[\rho(0)-\rho(H)]/\rho(0)$ approaches 83% (so that $[\rho(0)-\rho(H)]/\rho(H)$ exceeds 500%), comparable to systems often classified as displaying colossal magnetoresistance. It is thus clear that neither a first-order paramagnetic-to-ferromagnetic transition nor a metal-insulator transition is a prerequisite for cmr effects.

The data in Fig. 5 reveal a further interesting feature displayed by (among others) perovskite and multilayer systems, namely, an inability to return to a virgin state following field cycling; a probable cause is the (as yet) undetermined domain structure in this system and its field and temperature variation. Such structure can be a cause of metastability and time dependent/relaxation behavior, a feature also occurring here.

In conclusion, the implications of the present results on models of perovskite systems can be summerized as follows. While the influence of lattice distortion generated by *A*-site substitution on the overlap between the Mn (*B* site) *d* orbitals and the oxygen *p* orbitals forming the electronically active band has been stressed previously,[4–6] the current data indicate that reductions in $r<1$ resulting from divalent cation substitution can produce even more marked effects. The counterintuitive reduction in the Mn to Mn electron hopping matrix elements *b* accompanying reductions in the Mn-O-Mn bond angle completely suppress the metal-insulator transition here,[15] and the double-exchange coupling J_{DE} (which determines the magnetic transition temperature) is also reduced. Furthermore, the changes in *b* induced by this latter transition are essentially nonexistent, in contrast to the catalogued behavior for the majority of substituted perovskites.

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