

## Critical Behavior of the Magnetoresistive Pyrochlore $Tl_2Mn_2O_7$

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We report measurements of the ac susceptibility and dc magnetization of the colossal magnetoresistive pyrochlore  $Tl_2Mn_2O_7$  from which we determine the critical temperature  $T_c = 120.65 \pm 0.15$  K and critical exponents  $\delta = 4.65 \pm 0.15$  (from the critical isotherm),  $\gamma + \beta = 1.75 \pm 0.03$  (from the temperature dependence of the crossover line), and  $\gamma = 1.31 \pm 0.05$  (from the temperature dependence of the susceptibility along the same line). Unlike recently reported values for perovskite systems, these exponent values are very close to those predicted by the near-neighbor, 3D Heisenberg model. This pyrochlore system, however, exhibits a marked regular (i.e., noncritical) component in the response near  $T_c$ , which is unusual in view of the absence of  $Mn^{3+}$  ions in this system.

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The presence of colossal magnetoresistance (CMR) in mixed valence manganese oxides  $L_{1-x}A_xMnO_3$  ( $L$  = rare earth or Y and  $A$  = divalent alkaline earth) in the vicinity of a paramagnetic to ferromagnetic transition has been the subject of much recent interest [1]. The intimate connection between electrical transport and magnetic order displayed by these systems is generally ascribed to the presence of double exchange (DE), as a result of which the  $e_g$  holes at  $Mn^{4+}$  sites are inhibited from hopping to near neighbor  $Mn^{3+}$  when the core  $t_{2g}$  spins are antiparallel [2]. Thus the kinetic energy gained by these carriers in the transition from incoherent hopping in the high temperature paramagnetic insulating phase to the low temperature ferromagnetic metallic phase stabilizes the magnetic order. A quantitative understanding of CMR in these systems also requires strong Jahn-Teller effects [3], and is thus directly connected to the presence of  $Mn^{3+}$  ions induced by doping (as is DE).

Recently the pyrochlore  $Tl_2Mn_2O_7$  was reported to exhibit a CMR which appeared to arise from a different mechanism from that operating in the manganese perovskites [4]. This pyrochlore contains only  $Mn^{4+}$  ions, so that both Jahn-Teller effects and DE are precluded, and the onset of ferromagnetism (with  $T_c$  near 120 K) has been attributed to superexchange. Furthermore, not only are current explanations [5] of CMR in these two types of systems different but the attendant spin dynamics are also dissimilar. The magnetic correlation length diverges while the spin wave stiffness collapses as  $T_c$  is approached from above and below, respectively, in this pyrochlore in marked contrast to the doped manganites, particularly for Ca doping [6]. In the latter a quasielastic spin diffusion component, possibly associated with polaronic behavior, dominates the "critical" fluctuation spectrum. Here we focus on the quasistatic magnetic response of this pyrochlore in the critical regime and extract exponent values very close to those predicted by the near-neighbor, isotropic

three-dimensional Heisenberg model. This is in marked contrast to recently reported exponent estimates for the doped perovskite [7], thus suggesting that the basic interactions responsible for magnetic order may result in the doped perovskites and the pyrochlores being assigned to *different* universality classes.

Measurements of the ac susceptibility (at 2.4 kHz in a 30 mOe rms driving field) and the dc magnetization were carried out simultaneously in a Quantum Design Model PPMS 6000 magnetometer on a polycrystalline sample weighing 25.7 mg with approximate dimensions  $(5 \times 3 \times 3)$  mm<sup>3</sup>. At each temperature selected, an appropriate time interval was allowed to elapse prior to commencing measurements [7]. The sample preparation techniques have been detailed previously as have the structure and transport properties of similarly prepared specimens.

Figure 1 shows the ac susceptibility measured in various static biasing fields  $H_a$ ; the application of such fields of increasing strength progressively suppress the principal (Hopkinson) maximum evident in the zero-field response (inset), enabling the secondary, critical maxima to be resolved (as shown in the main body of this figure). The temperatures  $T_m$  of these critical maxima shift upward while their amplitudes decrease as  $H_a$  increases. As detailed previously [8], such maxima are a characteristic signature of critical fluctuations accompanying a continuous magnetic phase transition; their temperature and field dependence is consistent with the static scaling law description of such a transition, while the emergence of such peaks in finite field can be explained qualitatively on the basis of the fluctuation-dissipation theorem [8]. Furthermore, their appearance and field/temperature dependence agree with numerical solutions for the ferromagnetic phase of a Sherrington-Kirkpatrick-like model [8] (within which the peak evolution is governed—as expected—by mean field exponents). The locus of the critical maxima

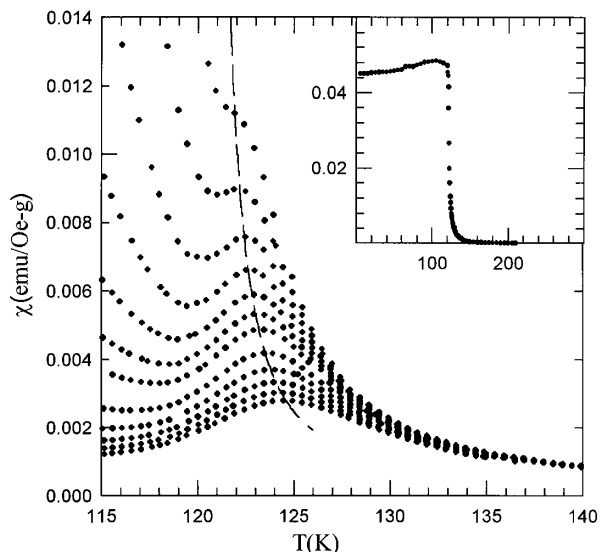


FIG. 1. The ac susceptibility (emu/g Oe-g), corrected for background and demagnetizing effects, as a function of temperature measured at static biasing fields of 400, 500, ..., 1000, 1200, ..., 2000 Oe, top to bottom, and clearly showing the emergence of the critical maxima. The dashed line denotes the crossover line. The inset shows the temperature dependence of the zero field ac susceptibility.

evident in Fig. 1 delineates the crossover line, above which the response is thermally dominated, while below it the response is field dominated. Of particular importance in the present investigation is the result that various critical exponents can be deduced *directly* from the maxima evident in Fig. 1; by contrast, estimates for the exponents  $\gamma$  (from the magnetization above  $T_c$ ) and  $\beta$  (from the spontaneous magnetization below  $T_c$ ) frequently involve extrapolation to zero field (to avoid the complications associated with regular, i.e., not critical, contributions to the low field response). The approach advocated here avoids such extrapolations (and any uncertainties inherent in them), as the following argument demonstrates. The scaling law equation of state (written in terms of the conventional linear scaling fields  $h \sim H_i/T_c$  and  $t = |T - T_c|/T_c$ ) expresses the magnetization ( $m$ ) and susceptibility ( $\chi$ ) in the vicinity of the ferromagnetic ordering temperature  $T_c$  as [9]

$$m = t^\beta F\left(\frac{h}{t^{\gamma+\beta}}\right); \quad \chi(h, t) = \frac{\partial m}{\partial h} = t^{-\gamma} G\left(\frac{h}{t^{\gamma+\beta}}\right), \quad (1)$$

where  $G$  is the derivative (with respect to its argument) of the (unknown) scaling function  $F$ . Assuming the Widom equality  $\gamma = \beta(\delta - 1)$  to be valid enables the susceptibility to be rewritten as

$$\chi(h, t) = t^{-\gamma} G\left(\frac{h}{t^{\gamma+\beta}}\right) = h^{1-1/\delta} H\left(\frac{h}{t^{\gamma+\beta}}\right), \quad (2)$$

where  $H(X) = X^{\gamma/(\gamma+\beta)} G(X)$ . The latter form in Eq. (2) indicates that measurements performed in fixed field (so that the prefactor  $h^{1-1/\delta}$  is constant) as a function of temperature reproduce the functional dependence of  $H(X)$ . Furthermore, if these (unknown) scaling functions  $H(X)$ ,  $G(X)$ , or  $F(X)$  are universal functions of their argument—as the scaling approach asserts—then any feature in, say,  $H(X)$ —such as the maxima evident in Fig. 1—will occur at the *same* value for the variable  $X$ . Denoting the reduced temperature of the maxima evident in this figure by  $t_m = (T_m - T_c)/T_c$ , this analysis leads directly to

$$\frac{h}{t_m^{\gamma+\beta}} = C; \quad t_m \propto H_i^{1/(\gamma+\beta)}, \quad (3)$$

and as the argument  $X$  of these scaling functions ( $H$ ,  $G$ , or  $F$ ) is a constant ( $X = C$ ) at such maxima, so are the functions themselves, when, from Eq. (1)

$$\chi(h, t_m) \propto t_m^{-\gamma}. \quad (4)$$

Equations (3) and (4) enable  $\gamma$  and  $(\gamma + \beta)$  to be estimated directly from such data, as the following shows. From Eq. (3), plots of the critical peak temperatures  $T_m$ , from Fig. 1, against  $H_i^{1/(\gamma+\beta)}$  should be linear with the intercept yielding  $T_c$  [the internal field,  $H_i = H_a - NM$  in the usual notation, was found using the measured magnetization  $M$  and the slope,  $N^{-1}$ , of the low field (shearing) curve]. Such plots have been made for a variety of exponent values, with the best fit obtained with  $\gamma + \beta$  values close to those predicted [10] by the isotropic, near-neighbor Heisenberg model ( $\gamma + \beta = 1.75$ ), yielding  $T_c = 120.65 \pm 0.15$  (slightly below the value found recently from neutron scattering data [6] on a similarly prepared sample). Figure 2(a) confirms both these exponent and  $T_c$  estimates; here the reduced peak temperatures,  $t_m$ , are plotted against the internal field,  $H_i$ , on a double logarithmic scale; the straight line drawn confirms the power-law prediction—Eq. (3)—with Heisenberg model exponents, viz.  $(\gamma + \beta)^{-1} = 0.57 \pm 0.01$ .

Having identified  $T_c$ , the exponent  $\delta$  is found directly from the field dependence of the magnetization measured along the critical isotherm, Fig. 2(b). These data yield

$$\delta = 4.65 \pm 0.15$$

in agreement with the Heisenberg model value of 4.80, within experimental uncertainty. The exponent  $\gamma$  is found from the data summarized in Fig. 1 utilizing Eq. (4). Figure 3 shows the susceptibility maxima evident in the first figure (corrected for background and demagnetizing effects) plotted against the reduced peak temperature,  $t_m$ , on a double logarithmic scale. These data confirm the power-law prediction—Eq. (4)—and yield

$$\gamma = 1.31 \pm 0.05,$$

marginally lower than the Heisenberg model value of 1.386. A final and convincing test of the applicability of

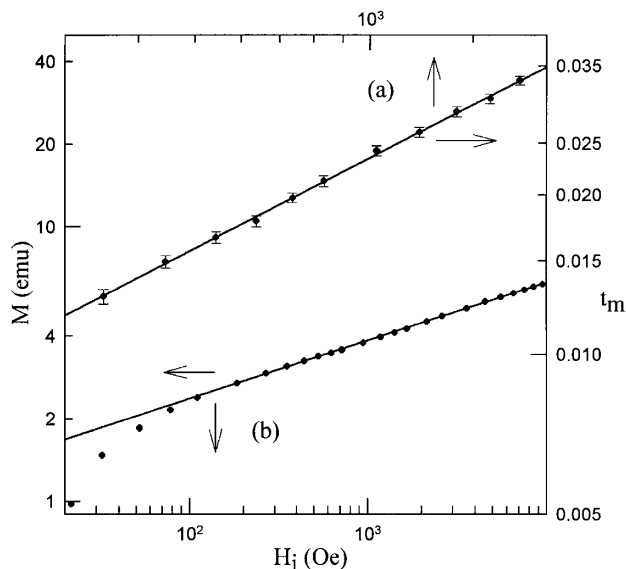


FIG. 2. (a) The reduced peak temperature,  $t_m$ , versus the internal field,  $H_i$  (kOe), on a double logarithmic plot. The straight line fit yields a value for the crossover exponent,  $(\gamma + \beta)^{-1}$ , of 0.57. (b) The sample magnetization,  $M$  (emu), as a function of the internal field,  $H_i$  (Oe), measured along the critical isotherm and plotted on a double logarithmic plot. The straight line fit yields  $\delta = 4.65$ .

Heisenberg model exponents to this system is provided in Fig. 4. The latter expression for  $\chi(h, t)$  shown in Eq. (2) indicates that each constant field scan or isokap of Fig. 1 corrected for background and demagnetizing effects and normalized to its peak value, viz.

$$\chi(h, t)/\chi(h, t_m) = H(X)/H(X = C), \quad (5)$$

should scale onto a single curve when plotted against the argument  $X$  of the scaling function [actually the inverse  $t/H_i^{1/(\gamma+\beta)}$  of this argument to preserve the structure evident in Fig. 1]. Figure 4 verifies such a scaling hypothesis, and from data contained in Figs. 2–4 it is concluded that the CMR pyrochlore  $Tl_2Mn_2O_7$  exhibits static magnetic critical exponents consistent with those predicted by the isotropic, near-neighbor three-dimensional Heisenberg model. This contrasts with the conclusions reached from recent detailed measurements on Sr-doped manganese perovskites [7], thus raising the possibility that these two types of systems, in which ferromagnetic order results from superexchange and double exchange, respectively, may belong in different universality classes. Further theoretical work is necessary to clarify the origin of such differences.

Despite the validity of Heisenberg model exponents demonstrated above, the response of this pyrochlore displays some unusual characteristics, specifically in the low field region near  $T_c$ . This can be seen directly from Fig. 1, in which fields in excess of 400 Oe are necessary to first resolve critical peak structure. Such a situation reflects the presence of a substantial regular component in this response (viz. a noncritical component, often attributed [11] to “technical” sources such as coherent rotation, domain wall motion, etc.). These regular components are clearly not driven to saturation in low fields ( $\leq 400$  Oe) near  $T_c$ , so that this pyrochlore system displays features normally associated with technical hardness. This result is difficult to understand as previous detailed analyses have

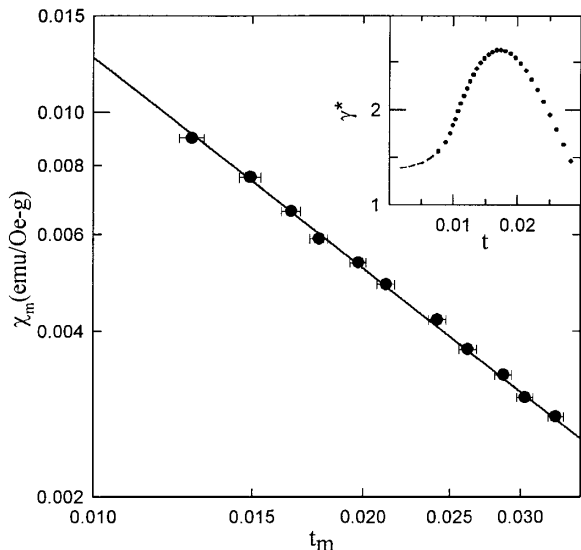


FIG. 3. The amplitude of the susceptibility maxima (emu/gOe) (shown in Fig. 1) versus the reduced peak temperature,  $t_m$ , on a double log plot. These data yield a value of  $\gamma = 1.31 \pm 0.05$ . The inset shows the temperature dependence of the effective Kouvel-Fisher susceptibility exponent,  $\gamma^*$ .

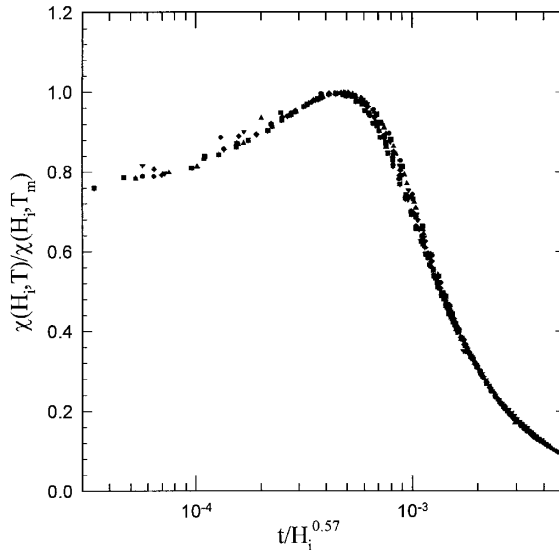


FIG. 4. The “scaling plot” for the isokaps shown in Fig. 1. The susceptibility normalized to the respective peak amplitudes is plotted against the (inverse) argument  $(t/h^{1/(\gamma+\beta)})$  of the scaling function. The data in Fig. 1 collapse onto a single curve providing convincing evidence of the validity of Heisenberg model exponents to this pyrochlore system.

convincingly demonstrated that this pyrochlore is devoid of  $\text{Mn}^{3+}$  ions, so that  $\text{Ti}_2\text{Mn}_2\text{O}_7$  displays neither mixed valent ( $\text{Mn}^{3+}$ - $\text{Mn}^{4+}$ ) mediated DE nor associated Jahn-Teller effects [4]. The latter is particularly important in the present context since the observation of technical “hardness” in a variety of other systems has been attributed to the presence of single ion anisotropy resulting from spin-orbit coupling [11]. The absence of a Jahn-Teller ion, such as  $\text{Mn}^{3+}$ , precludes such a coupling in the present system, so that the origin of this apparent hardness remains unclear.

The presence of a regular component in the low field response is also confirmed indirectly by the behavior of the effective Kouvel-Fisher susceptibility exponent [12]

$$\gamma^*(t) = d(\ln \chi(0, t))/d \ln(t),$$

deduced from the zero field susceptibility (inset, Fig. 1) and reproduced in the inset of Fig. 3. While the *asymptotic* ( $t \rightarrow 0$ ) behavior of  $\gamma^*(t)$  is consistent with the Heisenberg model value of  $\gamma = 1.386$ , the temperature variation of the *effective* exponent displays features frequently ascribed to the occurrence of a variance in the distribution of magnetic interactions [8,13] [viz. a maximum in  $\gamma^*(t)$  above  $T_c$ ]. Specifically in the doped manganese perovskites the inherently inhomogeneous mixed valent state prevalent in them could lead to spatially inhomogeneous magnetic interactions (i.e., a relative enhancement of ferromagnetic DE in regions statistically rich in the dopant ions, competing with the antiferromagnetic superexchange characteristic of the host  $\text{LaMnO}_3$ ), which could be modeled by such a distribution. This explanation is not appropriate here, and we contend that the temperature dependence displayed by  $\gamma^*(t)$  deduced from the “zero” field susceptibility results from an anomalous regular component in the low field response, directly evident in Fig. 1.

Further evidence of the anomalous character of this low field contribution is provided by measurement of the coercive field  $H_c$ , which, even at 4.2 K (i.e., well below  $T_c$ ), is only some 2 Oe. In general  $H_c$  is taken as a measure of technical hardness, and fields on the order of  $H_c(T \leq T_c)$  are generally sufficient to saturate the regular component arising from technical sources. This low value for  $H_c$  is clearly qualitatively consistent with the absence of an orbital component in the total moment at Mn sites in this pyrochlore. Nevertheless, we plan to investigate the spontaneous resistive anisotropy—the presence of which relies on the presence of such an orbital component

[14]—as a way of providing further confirmation of the absence of  $\text{Mn}^{3+}$  ions in this pyrochlore.

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