Anomalous low-field magnetization in $La_{2/3}Ca_{1/3}MnO_3$ near the critical point: Stable clusters?

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The magnetic behavior of bulk $La_{2/3}Ca_{1/3}MnO_3$ ($T_C=267$ K) at low fields in the paramagnetic phase was studied. Near $T_C(T-T_C<30$ K) we find a sequence of steplike features in the effective Curie constant $C(T)=M(T-T_C)/H$ at well defined temperatures and intermediate plateaus, accompanied by temperature hysteresis. On approaching T_C, the C values at each plateau follow a geometrical progression, with the effective spin S doubled at each step. The first plateau gives $S=5.5$, corresponding to a cluster of three Mn^{3+} ions sharing one extra hole. This suggests that close to T_C short range magnetic order at low fields develops hierarchically through a series of most stable cluster states. [S0021-8979(98)52311-0]

I. INTRODUCTION

The doped manganites $Ln_{1-x}A_xMnO_3$ (where Ln and A are trivalent lanthanide and divalent alkali-earth, respectively) are of great interest now due to the colossal magnetoresistance effect (CMR).[1] Although the basic mechanism for the onset of uniform ferromagnetism, the Zener's double exchange (DE) interaction, was recognized long ago,[2] it does not provide a satisfactory description of the magnetic state close to the transition temperature T_C.[3] It was already noted in the previous authors' work[4] that certain features observed in the critical behavior of MR disagree with the classical concept of electron spin scattering by thermodynamic fluctuations of localized Mn spins. A possible explanation was proposed through coexistence of thermodynamic and static fluctuations, the latter being due to spontaneous formation of spin clusters by local DE in the random potential of chaotically distributed dopants. Also it was evidenced[5] that in these materials the magnetization per manganese atom $M(T)$ at higher temperatures T (up to about three times T_C) and applied field H does not follow the classical Curie–Weiss law $M_{\mathrm{CW}}=C\mu_B{}^2H/k_B(T-T_C)$. In particular, the apparent Curie constant (for $T-T_C$ up to ~ 100 K), obtained from the data of Ref. 5 on $La_{2/3}Ca_{1/3}MnO_3$, is $C\approx 11.4$, much higher than the simple weighted sum $\bar{C}=xC_{3/2}+(1-x)C_2$ of Brillouin contributions $C_S=4/3S(S+1)$ from $Mn^{4+}(S=3/2)$ and $Mn^{3+}(S=2)$; for $x=1/3$ we have $\bar{C}=7$. There is a general consensus about the relation of this effect to the formation of composite cluster spins,[6,7] for instance, a spin-coupled pair of Mn^{4+} and Mn^{3+} will contribute $C_{7/2}=21$ which is ≈ 1.6 times greater than the sum $C_{3/2}+C_2$ for two uncoupled spins, and such enhancement must be even stronger for greater clusters. The same data show that at sufficiently high temperatures the Curie–Weiss law with $C\approx\bar{C}$ is restored (but with modified $T_C'>T_C$). This suggests that cluster formation is favored closer to the transition temperature. But, like the usual ferromagnetic transition, a strong enough external field will suppress the critical spin fluctuations and spontaneous cluster structure can be smeared. In the present work we study the deviations from uniform paramagnetic behavior of $La_{2/3}Ca_{1/3}MnO_3$ with approaching T_C, at as low applied fields as possible. Besides confirming the difference between the Curie constants close and far from T_C at fields ranging above some kOe, we found some essentially new effects close to T_C at fields below ~ 50 Oe. Particularly, a sequence of steplike features observed at well-defined temperatures and accompanied by temperature hysteresis suggests a discontinuous dynamics of spin clustering with possible hierarchical structure.

II. EXPERIMENT

A bulk ceramic sample of composition $La_{0.67}Ca_{0.33}MnO_3$ was prepared by standard solid-state methods from oxides and carbonates, with three intermediate grindings and final sintering at 1300 °C for 50 h and very slow cooling to room

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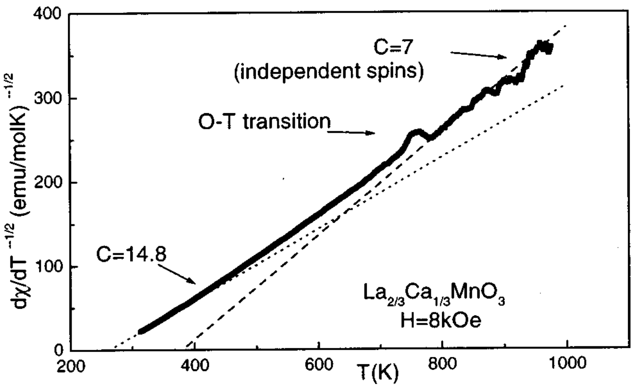

FIG. 1. $(dM/dT)^{-1/2}$ from high temperature measurements at field 8 kOe. The arrow indicates the orthorhombic-trigonal structural transition at T_{O-T} ≈ 750 K.

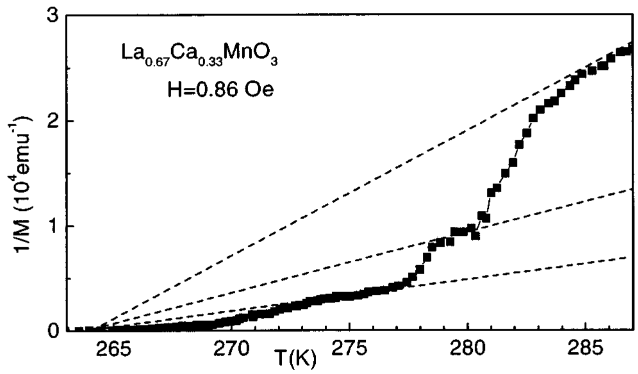

FIG. 2. Inverse magnetization close to T_C. Instead of a continuous decrease, we find a sequence of steps and intermediate regions were a Curie-like type of dependence seems valid (lines).

temperature within 20 h. Powder diffraction showed a single phase orthorhombic structure (P_{bnm}), and scanning electron microscopy revealed that the samples have very small porosity and 10 μm average grain size. High resolution electrical resistivity and magnetoresistance measurements confirmed the characteristic behavior of these ferromagnetic ceramics.[8]

The low field magnetization of the sample was measured with a Quantum Design superconducting quantum interference device (SQUID) magnetometer. In order to reduce the effect of frozen magnetic fields in the superconducting coil and ensure a better field homogeneity, prior to these measurements the coil was heated to room temperature. During the measurement of these low field data, the maximum magnetic field did not exceed 30 Oe. The measurements at constant magnetic field were taken on cooling the sample from high temperatures (320–380 K), down to 20 K and then on heating back to the initial temperature. On the first run, at 1.36 Oe, a zero-field cooled curve was also measured. High temperature (300–1000 K) magnetic measurements were taken in an Oxford Instruments vibrating sample magnetometer (VSM) with a constant applied field of 8 kOe.

III. RESULTS AND DISCUSSION

Well above T_C where the sample magnetization $M(T)$ is small, we separated the paramagnetic term from the diamagnetic background by means of the derivative dM/dT to evaluate the function $1/\sqrt{dM/dT}$. For $M=M_{\mathrm{CW}}$ it should be linear in temperature: $(T-T_C)/\mu_B\sqrt{CH/k_B}$, but from our measurements up to 1000 K this function is slightly nonlinear (Fig. 1). Hence, either C or T_C (or both) are not exactly constants, and therefore the effective cluster spin $S_{\mathrm{eff}}=3C/4S-1$ (note that C is defined per one Mn spin, and the mean spin value $\bar{S}=x3/2+(1-x)2=11/6$ provides $C_{\bar{S}}\approx\bar{C}$) and its coupling to neighbor spins (clusters) $J_{\mathrm{eff}}\approx 4T_C/C$ are temperature dependent. We found the experimental value of the Curie ''function'' $C(T)$ to increase from $\approx\bar{C}$ at $T>800$ K to ≈ 14.8 at 300–350 K (from the two linear asymptotes far and close to T_C), in agreement with known data.[6–8] The same $C(T)$ value at 300 K is obtained with SQUID and VSM measurements. The hump at the orthorhombic-trigonal structural transition $T_{O-T}\approx 750$ K (shown in Fig. 1), can be explained by the increase of exchange at shrinking lattice parameters. To our knowledge, this is the first report of the $O-T$ transition through magnetic measurements. Resistivity measurements showing a kink at T_{O-T} were reported in literature.[9]

To understand the high-temperature behavior of $C(T)$, we calculated the spectrum of spin states for the simplest cluster model of two Mn^{3+} atoms, sharing one extra hole with hopping amplitude t. Apart from the splitting between bonding and antibonding states, known already from the semiclassical approach,[2] the spectrum is characterized by equal separation $t/4$ between levels which is not exactly equivalent to isotropic Heisenberg exchange. With decreasing temperature the calculated Curie function rapidly grows from the asymptotic value $C_{3/2}+C_{3/2}+C_{1/2}$, for fully independent components, to the limit $C_{7/2}$ for the fully aligned cluster spin.

Closer to T_C, where the diamagnetic contribution can be neglected, $C(T)$ can be defined directly as $M\ k_B\ (T-T_C)/\mu_B{}^2H$ where $T_C=263.5$ K fits best. For magnetic fields above 50 Oe, $C(T)$ displays even faster growth, which can be associated with a rapid continuous increase of effective cluster spin S_{eff}. Similar behavior for $(La_{1-x}Tb_x)_{2/3}Ca_{1/3}MnO_3$ was already reported.[10] In addition to this, in lowest fields (<50 Oe) some discrete steplike features appear in the magnetization data. In Fig. 2 we show the inverse magnetization as a function of temperature. It is seen that between steps a Curie-like behavior is observed (lines). The Curie function $C(T)$ is represented in Fig. 3 for several fields. Here these anomalies are more clear, with steps at well-defined temperatures and intermediate plateaus, and lower is the field better resolved are these features. This effect is new and it shows that intrinsic short range magnetic order in the considered material develops through a series of more or less stable intermediate states (clusters). We plotted the logarithms of plateau heights of $C(T)$ at different fixed fields and found them to grow almost linearly with the plateau number ($n=0,1,2,...$) (Fig. 4). The case $n=0$ is taken as the limiting value for independent spins measured at high temperatures: $\log C_{\mathrm{step}}(n)\approx\log\bar{C}+\gamma n$, with $\gamma\approx\log(2.1\pm 0.1)$. This can be interpreted as if the typical cluster spin S_{eff} is doubled each time as the corresponding temperature

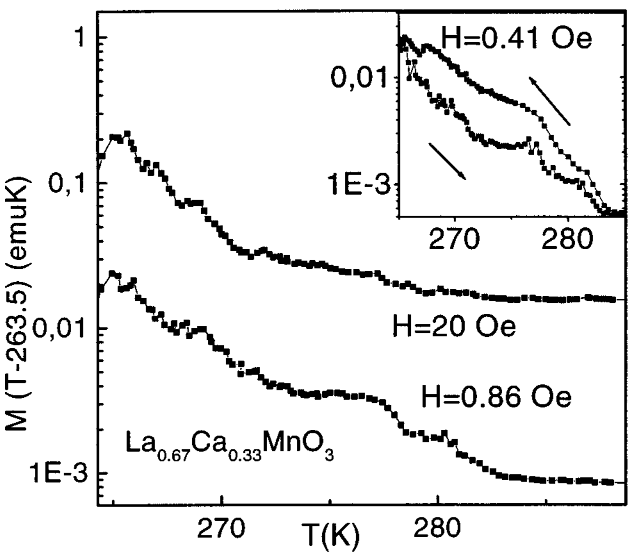

FIG. 3. Steplike behavior of the Curie function at low magnetic fields close to T_C. Inset: Temperature irreversibility effects.

T_n is reached. The first plateau around $T_1 \approx 290$ K with $C_1 \approx 15$ relates to $S_{eff} \approx 5.5$, which fits to a cluster of *three* Mn^{3+} ions sharing one extra hole, in coherence with the stoichiometric Mn^{3+}/Mn^{4+} ratio. The consecutive plateaus around $T_2 \approx 280$ K, $T_3 \approx 276$ K, $T_4 \approx 269$ K, and $T_5 \approx 266$ K (observed in fields down to 0.5 Oe) can correspond to condensation of clusters with $S_{eff} \approx 11$, 22, 44, 88.

It is noteworthy that neither the temperature intervals between the steps nor their stability against the applied field are equal. For instance, the feature at $T_3 \approx 276$ K (supposedly 12 Mn^{3+} ions coupled by four extra holes) looks particularly stable. Also a considerable temperature hysteresis of magnetization $M(T)$, confined just to the range of steplike behavior, suggests that the steps can be compared to a series of first kind phase transitions in the spin subsystem (inset to Fig. 3).

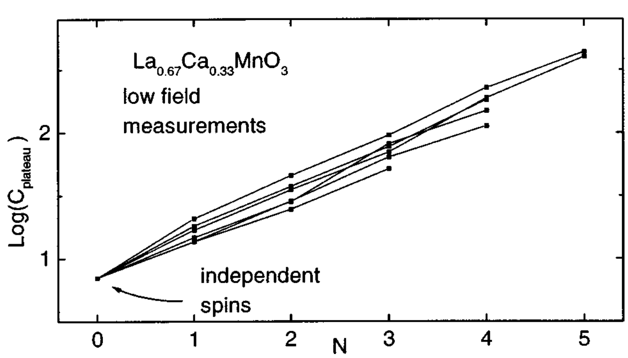

FIG. 4. Approximate linearity of logarithms of the plateau C values vs plateau number, indicating that these follow a geometrical progression, with the effective spin S doubled each time as a step occurs. The point for plateau 0 is obtained at high temperatures.

The sequence of cluster states for this sample can consist of: a triplet of Mn^{3+} ions sharing one extra hole, in line, six Mn^{3+} ions sharing two extra holes, possibly in a 2×3 rectangle, twelve Mn^{3+} ions sharing three extra holes possibly in a $2\times2\times3$ paralelepiped (two cubes) and so on. The calculation of the lowest energy level for clusters in a cubic lattice containing three Mn^{3+} ions for each hole in the double exchange Hamiltonian gives the following values: $E/t = -1.41$, -1.71, -1.89, -2.06, -2.08, and -2.20 for the cases of 1, 2, 3, 4, 6, and 9 holes in a cluster. Some of these values were recently reported by Gehring and Coombes.[11] It can be seen that the formation of clusters with more than four holes (12 ions) does not lead to a considerable energy reduction, while loosing in entropy. This may serve as an explanation for the above-indicated stability of the feature at $T_3 \approx 276$ K.

For comparison, the same measurements were also done on a less doped sample of $La_{0.75}Ca_{0.25}MnO_3$. Here the effect of strong enhancement of the Curie constant and hysteresis at low fields are also observed close to the transition temperature ≈ 232 K, however, no clear fine structure was seen even at lowest fields.

ACKNOWLEDGMENTS

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