

Evidences for Tsallis non-extensivity on CMR manganites

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Abstract. – We found, from the analysis of M vs. T curves of some manganese oxides (manganites), that these systems do not follow the traditional Maxwell-Boltzmann statistics, but the Tsallis statistics, within the *normalized* formalism. Curves were calculated within the mean-field approximation, for various ferromagnetic samples and the results were compared to measurements of our own and to various other authors's published data, chosen at random from the literature. The agreement between the experimental data and calculated M_q vs. T^* curve, where T^* is an effective temperature, is excellent for all the compounds. The entropic parameter, q , correlates in a simple way with the experimental value of T_c , irrespective of the chemical composition of the compounds, heat treatment or other details on sample preparation. Examples include $q < 1$ (superextensivity), $q = 1$ (extensivity) and $q > 1$ (subextensivity) cases.

Manganese oxides, or simply manganites, have, to a great extent, dominated the literature on magnetism for the last five years [1]. The number of yearly published papers on the subject since 1993 to present date, amounts to over 2000. All this interest lies on at least three different reasons: i) the rich phase diagram of manganites exhibits a variety of transport, structural and magnetic phenomena [1, 2], which stimulates new models in condensed matter [3–14]; ii) manganites can present the so-called *colossal magnetoresistance* (CMR), and therefore are interesting systems for industrial applications [15]; and iii) samples are relatively easy to prepare [1].

In the literature of manganites, various models have appeared in different attempts to reproduce the electric and magnetic properties of these systems. Krivoruchko *et al.* [3], Nunez-Regueiro *et al.* [4] and Dionne [5] are interesting examples of multiparameter models, but which failed to achieve full agreement to experimental data. Ravindranath *et al.* [6] compare resistivity data in $\text{La}_{0.6}\text{Y}_{0.1}\text{Ca}_{0.3}\text{MnO}_3$ to different two-parameter models which do not agree

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to each other in the low-temperature range. Other interesting attempts can be found in Rivas *et al.* [7], Hueso *et al.* [8], Heremano *et al.* [9], Pal *et al.* [10], Philip *et al.* [11], Szewczyk *et al.* [12], Viret *et al.* [13] and Tkachuk *et al.* [14]. None of these obtained plain agreement between experiment and theory, irrespective of their number of adjusting parameters and approach.

Another rather different area which has been growing at an analogous rate is the Tsallis generalized statistics [16], and its applications [17, 18]. This is based on the definition of the generalized entropy [16, 17]:

$$S_q = k_B \frac{1 - \sum_i p_i^q}{q - 1}, \quad (1)$$

where q is the *entropic index* and p_i are probabilities satisfying $\sum_i p_i = 1$. The above formula converges to the usual Maxwell-Boltzmann definition of entropy in the limit $q \rightarrow 1$ [16, 17].

Applications of eq. (1) to condensed matter include: Ising ferromagnets [19], molecular field approximation [20], percolation problems [21], Landau diamagnetism [22], electron-phonon systems and tight-binding-like Hamiltonians [23], metallic [24] and superconductor [25] systems, etc.

Maximization of eq. (1) subjected to the normalized q -expectation value of the Hamiltonian [26]

$$U_q = \frac{\text{Tr} \{ \mathcal{H} \rho^q \}}{\text{Tr} \{ \rho^q \}} \quad (2)$$

and the usual normalization of the density matrix $\text{Tr} \{ \rho \} = 1$, yields the following expression for the density matrix ρ :

$$\rho = \frac{1}{Z_q} [1 + (1 - q) \tilde{\beta} (\mathcal{H} - U_q)]^{1/(1-q)}, \quad (3)$$

where $Z_q = \text{Tr} [1 + (1 - q) \tilde{\beta} (\mathcal{H} - U_q)]^{1/(1-q)}$ is the partition function, $\tilde{\beta} = \beta/c_q$ and $c_q = \text{Tr} \{ \rho^q \}$. The magnetization of a specimen is, accordingly, given by

$$M_q = \frac{\text{Tr} \{ \mu \rho^q \}}{\text{Tr} \{ \rho^q \}}. \quad (4)$$

Note that eqs. (2) and (4) need to be solved self-consistently, since the density matrix ρ (eq. (3)) depends on the Hamiltonian $\mathcal{H} = -\mu[B_0 + \lambda M_q]$ and its q -expectation value, U_q . In the Hamiltonian above, B_0 represents the external magnetic field, and λ the molecular field parameter. Similar calculation in the context of many-particle system employing the normalized approach has been done for the quantum statistics [27, 28].

Equation (3) can be written in a more convenient form in terms of β^* , defined as $\beta^* \equiv \tilde{\beta}/(1 + (1 - q)\tilde{\beta}U_q)$ [26]. In particular, to analyze the physical system described here, the quantity $1/k_B\beta^* \equiv T^*$ represents a temperature scale against which this quantity M_q will be compared to experimental results. A discussion about the concept of temperature and Lagrange parameters in Tsallis statistics can be found in the literature [26, 27, 29, 30].

In this letter we argue, based on published experimental results, that manganites are non-extensive objects. This property appears in systems where long-range interactions and/or fractality exist, and such features have been invoked in recent models of manganites, as well as in the interpretation of experimental results. In a recent review [31], Dagotto and co-workers emphasize the role of the competition between different phases to the physical properties of these materials. Various authors have considered the formation of micro-clusters of competing

phases, with *fractal* shapes, randomly distributed in the material [32, 33], and the role of *long-range interactions* to phase segregation [34, 35]. Important experimental results in this direction have also been reported by Marethew *et al.* [36], and Fiebig *et al.* [37]. Particularly insightful is the recent paper of Satou and Yamanada [38] who derived a *Cantor* spectrum for the double-exchange Hamiltonian, basis of theoretical models of manganites. In spite of these evidences, Tsallis statistics, to the best of our knowledge, has never been used in the context of manganites.

Bulk samples of $\text{La}_{0.89}\text{Sr}_{0.11}\text{Mn}_{1-x}\text{Cu}_x\text{O}_3$ ($x = 0; 0.07$) were produced by standard solid-state reaction of high-purity La_2O_3 , SrCO_3 , MnO_2 and CuO powders mixed in stoichiometric proportions. The mixed powder was pressed into pellets and heat-treated at 930°C in atmospheric air during four days with three crushing/pressing procedures intermediating the treatment. Then, the pellets were heat-treated at 1350°C under oxygen flow during 48 h, with one intermediate crushing and pressing. X-ray diffraction (XRD) indicated the formation of single-phase samples (rhombohedral cell). Scanning electron microscopy (SEM) showed the formation of crystals with dimensions around 2 microns and energy-dispersive X-ray (EDS) analysis indicated a nearly homogeneous composition, close to the stoichiometric one. Field-cooled magnetic measurements were held in a SQUID magnetometer under a 10 kOe applied field, in order to sweep out domain walls contribution to the magnetization curve.

Table I displays the various compounds analyzed in the present work, and the respective reference. Most of them were taken from the literature. The choice was made such as to cover a wide range of T_c values (within the ferromagnetic region, roughly between 100 and 400 K), but was random in any other aspect. It is important to emphasize some differences between the compounds, such as the $\text{Mn}^{3+}/\text{Mn}^{4+}$ concentration, distinct preparation processes, different ionic radii of divalent ions, etc. Experimental details can be found in the list of references.

The experimental results from the samples listed in table I were compared to the calculated total magnetization, M_q , given by

$$M_q = (1 - x)M_q^{3+} + xM_q^{4+}, \quad (5)$$

where $1 - x$ and x are, respectively, Mn^{3+} and Mn^{4+} concentrations. This equation, along with eqs. (2) and (4) are solved simultaneously and self-consistently in the mean-field approx-

TABLE I – *Manganites compounds analyzed in the present work and the respective references. The choice of compounds was made such as to cover a wide range of T_c values within the ferromagnetic phase, but it was random in any other aspect.*

Compound	Reference
$\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{0.9}\text{Ru}_{0.1}\text{O}_3$	[39]
$\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$	[40]
$\text{La}_{0.83}\text{Sr}_{0.17}\text{Mn}_{0.98}\text{Fe}_{0.02}\text{O}_3$	[41]
$\text{La}_{0.62}\text{Y}_{0.07}\text{Ca}_{0.31}\text{MnO}_{3+\delta}$	[42]
$\text{La}_{0.875}\text{Sr}_{0.125}\text{MnO}_{3+\delta}$	[43]
$\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_3$	[44]
$\text{La}_{0.75}\text{Ba}_{0.25}\text{MnO}_3$	[44]
$\text{La}_{0.89}\text{Sr}_{0.11}\text{MnO}_{3+\delta}$	Present work
$\text{La}_{0.89}\text{Sr}_{0.11}\text{Mn}_{0.93}\text{Cu}_{0.07}\text{O}_{3+\delta}$	Present work

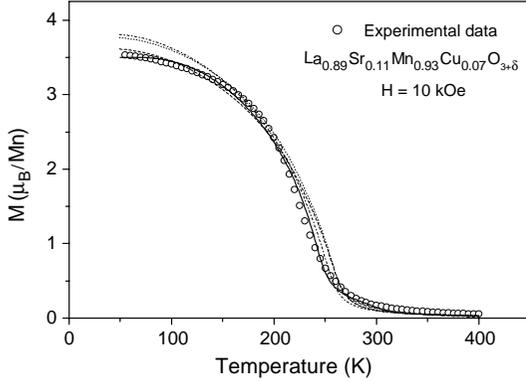


Fig. 1

Fig. 1 – Experimental and calculated magnetization curves for $\text{La}_{0.89}\text{Sr}_{0.11}\text{Mn}_{0.93}\text{Cu}_{0.07}\text{O}_{3+\delta}$. Dashed lines: *approach 1*; dotted: *approach 2*; dash-dotted: *approach 3* and solid line: Tsallis statistics result. See text for details.

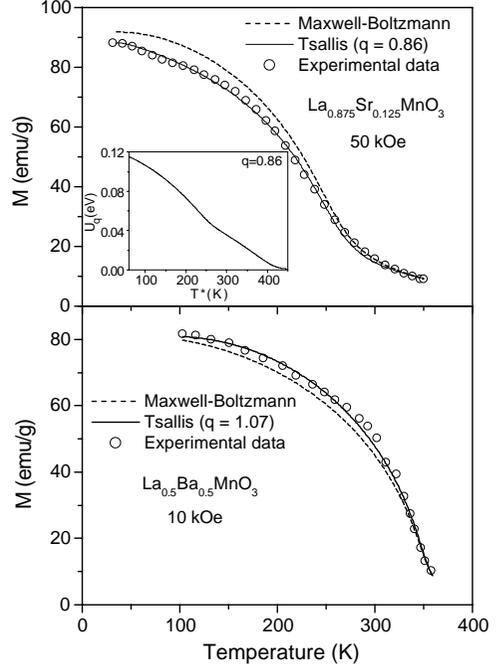


Fig. 2

Fig. 2 – Experimental and calculated ($q=1$ and $q \neq 1$) magnetization curves for $\text{La}_{0.875}\text{Sr}_{0.125}\text{MnO}_{3+\delta}$ reprinted from [43] (upper panel), and $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_3$, reprinted from [44] (lower panel). The inset displays the U_q value (eq. (2)), as a T^* function. See text for details.

imation, where the magnetic fields action on the 3+ and 4+ ions is given, respectively, by $B^{3+} = B_0 + \lambda^{3+} M_q^{3+}$ and $B^{4+} = B_0 + \lambda^{4+} M_q^{4+}$, where B_0 is the external field. The molecular field parameters λ^{3+} and λ^{4+} are, with the value of q , input quantities which are varied to seek the best agreement between the experimental and calculated results. It is also important to mention that the analysis was carried on exactly the same data as they appear in the original papers, and no normalization, re-arranging or any kind of data treatment, such as smoothing, filtering, etc., took place.

Figure 1 displays the experimental and calculated data for the magnetization in $\text{La}_{0.89}\text{Sr}_{0.11}\text{Mn}_{0.93}\text{Cu}_{0.07}\text{O}_{3+\delta}$ compound. The various curves appearing correspond to different attempts of using the Maxwell-Boltzmann, (*i.e.* $q = 1$) statistics to reproduce experimental data. These were: *approach 1*: only Mn moments, without inter-lattice interaction; *approach 2*: Mn and Cu moment [45], with the same intra-lattice interaction as in 1; *approach 3*: Mn and Cu moment, with inter- and intra-lattice interaction. The best agreement, however, is obtained in *approach 4*: only Mn moment, with the same interaction parameters of approach 1, and $q = 1.09$. Besides these attempts, we also tried extensive models which consider the statistical distribution of Mn and Cu ions in the crystal sites, but they all failed to explain the experimental curve.

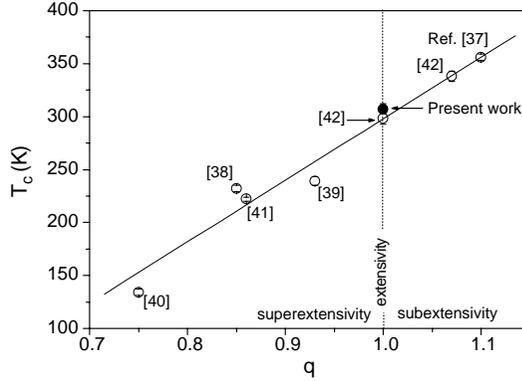


Fig. 3 – Correlation between T_c and q . The straight line is only a guide to the eyes.

The above results clearly indicate a non-extensive behavior in these compounds and, although the difference of the curves for $q \neq 1$ and $q = 1$ is not too big, it served to us as a motivation to seek for further examples. Therefore, we look up other M vs. T curves in the literature. In fig. 2 (upper panel) we show a magnetic measurement, taken at 50 kOe, in $\text{La}_{0.875}\text{Sr}_{0.125}\text{MnO}_{3+\delta}$, reproduced from ref. [43], and the calculated M_q curve for $q = 0.86$ (superextensive case). We also show the $q = 1$ curve. In fig. 2 (lower panel) the M vs. T curve reproduced from ref. [44] is shown for $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_3$. The experiment was taken at 10 kOe. The best curve was obtained for $q = 1.07$ (subextensive case). Again, the $q = 1$ case is shown for comparison. The analysis of the other compounds shown in table I follows in an analogous way.

In order to correlate the magnetic properties of manganites to the value of the entropic parameter q , we show in fig. 3 the experimental value of T_c , plotted against q . The error in the values of q are less than 2%. Perhaps the most striking feature of this curve is its simplicity: the data tend to fall on a straight line. This simplicity very much contrasts with the usual complexity of physical behaviors observed in manganites.

One can have a clue about the correlation between T_c and q shown in fig. 3 using a integral representation of the density matrix [46] and making $B \rightarrow 0$. For the case of a single magnetic lattice, an expression for the q -dependent magnetic susceptibility can be derived: $\chi_q = \partial M_q / \partial B_0 = C^{(q)} / (T^* - T_c^{(q)})$, where $T_c^{(q)} = T_c^{(1)} q = C \lambda q$ and $C^{(q)} = C^{(1)} q$, revealing the linearity between T_c and q , still observed in our case.

In summary, we have found that the magnetic properties of manganites are better described by the generalized statistics of Tsallis, instead of the traditional Maxwell-Boltzmann statistics. The entropic parameter q is a “measure” of the degree of non-extensivity in the system, caused by fractality and/or long-range interactions. These features have been invoked in very recent works (references from [31] to [38]) and recognized as essential aspects for the understanding of the magnetic and transport properties of these materials, although no attempt has been made to apply Tsallis formalism before the present work. At the moment, q must be regarded as a “phenomenological” parameter and its deviation from unit is a confirmation of those features leading to non-extensivity in these materials, and therefore in accordance to current models. In short, the use of Tsallis statistics to analyze manganites can guide the development of new models where the entropic parameter is identified to other fundamental quantities of the problem.

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