Nature of short-range order in the paramagnetic state of manganites

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We study the nature of short-range magnetic interactions observed in the paramagnetic phase of colossal magnetoresistance compounds. Our results reveal that ferromagnetic-like interaction between Mn ions cannot be explained by the conventional double exchange mechanism. The results show evidence that the eg electrons are localized in Mn3+ ions regardless the introduction of holes leading to ferromagnetic/antiferromagnetic superexchange-like interactions.

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Doped transition metal oxides are of fundamental importance for interesting electronic and magnetic properties such as high-temperature superconductivity, colossal magnetoresistance (CMR), and ferroelectricity observed in several types of systems [1–3]. A general idea that is relevant for many of these families is the observation of short-range correlations at high temperature whose nature is little understood. Magnetic and electronic correlations are also revealed theoretically in computational models [4].

The CMR effect, i.e., a decrease in the electrical resistance of several orders of magnitude when a magnetic field is applied, starts to be pronounced above the ferromagnetic (FM) transition temperature (Tc) [5]. At high temperatures (T > Tc) an unconventional paramagnetic (PM) phase suggested to be due to magnetic correlations has been found in the majority of CMR compounds. Several works have revealed the presence of FM short-range order (SRO) embedded in either paramagnetic or charge/orbital matrix [6,7]. Short-range FM regions in the PM phase of La2/3Ca1/3MnO3 compound is shown – the correlation length increases with the magnetic field, suggesting that the FM clusters increase in size [8–12]. It is suggested therefore that those correlations above Tc are the precursor of CMR effect. On the other hand, magnetic-susceptibility measurements above 400 K are scarce in the literature. It is difficult with the available data to learn about the contributions to the paramagnetic susceptibility and the nature of the precursors of long-range-ordered states at low T.

A simulation of magnetic susceptibility curves illustrating short-range FM order embedded in a PM matrix is depicted in Fig. 1 [13]. Two ferromagnetic phase transitions are simulated. The first curve was simulated by using the Curie–Weiss law, i.e., a conventional paramagnetic state where the inverse of magnetic susceptibility has a linear temperature dependence (χ = C/(T – θ)), where θ is the Weiss temperature and C the Curie constant which values were chosen arbitrarily. The second curve represents the scenario above where short-range order (SRO) appears at high temperature T > Tc. In this case, the Curie constant has a temperature dependence as (χ = C(T)/T – θ, with also arbitrary value of θ) due to the coupling of ions as temperature decreases. According to this scenario, these interacting magnetic moments forming a cluster can be thought of as giant spins with large magnetic susceptibility (see inset of Fig. 1). Thus, the CMR effect will occur due to percolation of these FM entities. In this picture, the magnetic interaction within these clusters is described by the double exchange (DE) mechanism where the eg electrons are delocalized. The DE is widely used in variety of magnetic behavior in doped transition metal compounds. The origin of the DE interaction comes from the intra-atomic coupling of the spin of the itinerant electrons with localized spins belonging to the same atomic shell. In spite of recent advances on DE model below Tc [4], our understanding of spin interaction and the short-ranged magnetic structure of the clusters above Tc is still incipient. This knowledge is the essence to understand not only the CMR effect but also the order parameter claimed to be much more complex than the solely magnetization in this system.

In this work, we have studied the magnetic correlations present in the paramagnetic phase of the well-know La1−xCaxMnO3 compounds, with x = 0.20, 0.25, 0.30, 0.34, 0.40, and 0.45, at high T where precursor magnetic phases of CMR are formed. Also, this
family shows a structural phase transition \cite{5} from rhombohedral \((R/C_{22}^3c)\) to orthorhombic \((Pnma)\) at \(T_{RO}\) well above \(T_C\). Several neutron and X-ray scattering works show strong magnetic correlations in the \(Pnma\) phase and disappear in the \(R/C_{22}^3c\) one of several manganite compounds \cite{9,14–17}. Therefore, this family provides an ideal scenario to study the evolution of these magnetic correlations as a function of charge carriers and temperature. The existence of strong short-range magnetic interactions can be inferred from the magnetization measurements. The nature of the magnetic interaction to establish a magnetic cluster at high \(T\) and its evolution with both temperature and charge carriers have been discussed in detail. Our results are different from those shown in Fig. 1, instead they strongly suggest that the magnetic interaction is not described by the double exchange mechanism in PM state as claimed by many well-know studies in the literature. We suggest that the orthorhombic lattice lowers the elastic energy for spin–lattice–charge correlations leading to antiferromagnetic and ferromagnetic superexchange-like magnetic interactions. Only at \(T_C\), the system becomes ferromagnetic via double exchange mechanism.

Polycrystalline samples of \(La_{1-x}Ca_xMnO_3\), with \(x = 0.20, 0.25, 0.30, 0.34, 0.40, \) and 0.45, were prepared by sol–gel method. The X-ray powder diffraction confirmed the single-phase nature for all samples. Magnetization measurements (from 10 K up to 900 K with an applied field of \(H = 1\) kOe) were performed using a standard vibrating sample magnetometer (VSM) oven option from Quantum Design. In Fig. 2 we show the inverse of magnetic susceptibility as a function of temperature for all samples. At low temperatures a magnetic phase transition from PM to FM state is observed. The \(T_C\) as a function of Ca concentration is shown in the inset of Fig. 2d and is in agreement with the phase diagram \cite{5}. The magnetic susceptibility in the insulating-paramagnetic state of localized ions can be written as \(\chi(T) = \chi_{CW} + \chi_{VV}\) \cite{18}. The temperature dependence term \(\chi_{CW}\) is the Curie–Weiss law from the molecular field theory. The magnetic susceptibility is given by \(\chi(T)_{CW} = C/(T - \theta_W)\) where \(C\) is the Curie constant and \(\theta_W\) is the Weiss temperature. If \(\theta_W > 0\), the material is ferromagnetic and we expect \(\theta_W = T_C\); if \(\theta_W < 0\), the material is antiferromagnetic.

**Fig. 1.** Simulated magnetic susceptibility and its inverse as a function of temperature. The black curve indicates a conventional FM transition where the Curie–Weiss law is obeyed. The red curve simulated also a FM phase transition, but with the presence of SRO formed via DE \cite{13} appearing at high temperature \(T^*\) causing deviation in the Curie–Weiss law. If the magnetic SRO has higher effective magnetic moment, the magnetic susceptibility will increase as shown in the inset and \(T_C > \theta_W\). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

**Fig. 2.** The inverse of magnetic susceptibility as a function of temperature measured in the presence of a magnetic field of \(H = 1\) kOe for the samples. The derivative of \(d\chi^{-1}/dT\) confirms that the slope \(A(T)\) is temperature dependent below \(T_{GR}\). The inset of \(x = 0.30\) shows the behavior close to \(T_C\). The inset of \(x = 0.34\) shows \(T_C\) and \(\theta_W\) as a function of Ca.
Fig. 2 is very different from that Fig. 1. First, the 1/electron doped systems [22]. However, the behavior observed in interpreted as due to spin canted interactions, through DE, in the electrons within clusters involves a local double-exchange process exchange mechanism [4]. This deviation in CW law has also been of short-range FM clusters that would originate from the double exchange mechanism [23].

The Curie–Weiss law predicted that the inverse of magnetic susceptibility in the PM state should have a linear dependence with temperature as simulated in Fig. 1. As clearly displayed in Fig. 2, a linear behavior is observed only above the structural phase transition for all samples. This result suggests that the Mn⁴⁺ and Mn³⁺ ions are totally free in the rhombohedral phase. The expected effective magnetic moment (\(\rho_{eff}\)) for non-interaction ions is given by Eq. (1) when \(n\) = 0. The values of \(\rho_{eff}\) obtained from the C are in excellent agreement with expected for spin-only ions Mn⁴⁺/Mn³⁺ for all samples (Fig. 3 (square symbols)). Below \(T_{Or}\) a pronounced curvature in \(\chi^ {-1}\) versus \(T\) deviating from the Curie–Weiss law is observed. This behavior reveals the existence of magnetic correlations between Mn ions. As already mentioned, this behavior has been extensively recognized as due to the formation of short-range FM clusters that would originate from the double exchange mechanism [4]. This deviation in CW law has also been interpreted as due to spin cantated interactions, through DE, in the electron doped systems [22]. However, the behavior observed in Fig. 2 is very different from that Fig. 1. First, the 1/\(\chi\) increases as the temperature decreases instead of decreasing due to the presence of entities with higher magnetic susceptibility as represented in Fig. 1. Second, the Curie temperature \(T_C\) is lower than the Weiss temperature \(\theta_W\). This result indicates that the molecular field strength, which measures the effect of ordering of the system due to the microscopic magnetic exchange interaction, has been decreased in completely contrast with that simulated in Fig. 1. As we shall see, the effect of the presence of magnetic SRO affecting the magnetic susceptibility as simulated in Fig. 1 is observed only close to \(T_C\) as shown in the inset of Fig. 2c.

Before going further in the analysis of the data, we explore the current understanding of magnetic clusters in PM phase suggested in the literature [4]. It takes into account that the trapping of electrons within clusters involves a local double-exchange process where the \(e_g\) electrons would be delocalized. For example, the magnetic structure would be composed of dimers Mn⁴⁺–O²⁻–Mn³⁺ [23], with \(S = 7/2\), effective magnetic moment given by \(\rho_{eff}(\mu_0) = g \sqrt{S(S + 1)} = 7.94\mu_0\), and higher magnetic susceptibility. Similar models have been proposed for explaining the short-range magnetic correlation observed in manganites [24,25]. Most important, in this picture, the effective magnetic moment must increase with the hole concentration, since that more Mn⁴⁺ ions will be available for the charge transfer from oxygen and/or Mn ions. In this picture, the number of Mn⁴⁺ coupled to Mn³⁺ ions or an optimal configuration (the ratio of Mn⁴⁺/Mn³⁺ pairs, 1/1, 1/2, 1/3) to establish a magnetic cluster and its evolution with temperature are at the heart of its conception. Following this idea, the equation below tells the expected effective magnetic moment produced by mixtures of ferromagnetic clusters formed via DE with different Mn³⁺ and Mn⁴⁺ configurations and the remaining free Mn³⁺ ions. We consider that Mn⁴⁺ ion nucleates a cluster formed by magnetic interaction via the double exchange mechanism:

\[
\rho_{eff} = g \sqrt{\chi(S_1 + nS_2)(S_1 + nS_2 + 1) + (1 - x)\chi S_2(S_2 + 1)}
\]

where \(S_1 = 3/2\) and \(S_2 = 2\) is the spin for Mn⁴⁺ and Mn³⁺, respectively, \(n\) is the number of Mn³⁺ coupled to Mn⁴⁺ forming a cluster, and \((S_1 + nS_2)\) is the new value of the spin of a FM cluster due to the double exchange interaction. The first term inside the square root is the magnetic cluster contribution while the second term corresponds to the contribution of remaining Mn³⁺ part. For example, when \(n = 0\) there is no cluster and the ions (Mn⁴⁺ and Mn³⁺) are free (standard definition); \(n = 1\) corresponds to clusters formed by dimers of Mn⁴⁺–Mn³⁺ with \(S = 7/2\); \(n = 2\) the clusters are formed by trimers of Mn³⁺–Mn⁴⁺–Mn³⁺, and so on. In Fig. 3 the values of \(\rho_{eff}\) (solid circles) calculated from the equation above for different configurations \((n = 0, 1, 2, 3)\) as a function of the hole concentration – Mn⁴⁺ – are presented. The effective magnetic moment increases with \(x\) for \(n \neq 0\) configurations, since more Mn⁴⁺ will be available to couple with Mn³⁺ and form a new entity with higher spin. One important result revealed in Fig. 3 is the very good agreement between the measured effective magnetic moment and the expected value for \(n = 0\) (free ions) in the rhombohedral phase.

Turning back to our results, Fig. 2 clearly shows a pronounced curvature in \(\chi^{-1}\) versus \(T\) below \(T_{Or}\) reflecting deviation from a conventional paramagnet. This behavior reveals that the Curie constant is temperature dependent \(C(T)\). Thus, in order to shield light on the magnetic interaction nature of the Mn ions in the orthorhombic phase, we empirically study the behavior of \(C(T)\). As far as this point is concerned and following the experimental data, we defined the magnetic susceptibility in the orthorhombic phase as \((1.17/T < T < T_{Or})\):

\[
\chi(T) = C(T) \frac{T}{T - \theta_W}
\]

As a consequence, this parameter is related with a global effective magnetic moment \((S')\), \(C(T) = nS'\gamma /3k_B\). It is important to emphasize that in this empirically defined the \(S'\) is not the conventional spin magnetic moment but a general magnetic moment which encloses all possible magnetic contributions/correlations from any nature. This general magnetic parameter is temperature dependent as experimentally imposed by \(C(T)\). The behavior of \(S'(T)\) along with its microscopic nature are important for the understanding of physical properties in this strong correlated system. Here, we study it empirically by using the experimental value of the angular coefficient \(A(T) = 1/C(T)\) of \(\chi^{-1}\) versus \(T\) as:

\[
S'(T) = \sqrt{\frac{3k_B}{n}} \sqrt{\frac{4}{A(T)}}
\]

where \(S'(T)\) is given in \(\mu_0\) unit and \(A(T)\) is empirically obtained by using \(A(T) = \lim_{T \to \infty} \frac{\partial \chi}{\partial T}\). The experimental results are shown in Fig. 4 where \(S'(\mu_0)\) as a function of both charge carrier concentration and temperature is illustrated. It is important to mention that above \(T_{Or}\), where the Curie–Weiss law is obeyed, \(S'(\mu_0) \neq \rho_{eff}(\mu_0)\), which is in very good agreement with expected for a mixture of free Mn⁴⁺/Mn³⁺ ions. We believe that this agreement gives further support for the analysis done below \(T_{Or}\).
The more important observation extracted from these experimental results, Fig. 4, is that $S^\prime$ decreases with increasing amount of Mn$^{4+}$ ions in the whole $T$ range. For instance, the value of $S^\prime(-T = 400 \text{ K})$ decreases from 5.69, 5.55, 5.45, 5.27, 5.10 down to 5.02 $\mu_B$ when Mn$^{4+}$ ions are introduced into the system (plotted in Fig. 3). This result reveals that any formed magnetic entity, at least with higher spin due to introduction of holes, is not present in the system. Instead, the evolution of $S^\prime$ follows the same trend as the free ions since Mn$^{4+}$ has smaller spin than Mn$^{3+}$ (see Fig. 3). Furthermore, the general values of $S^\prime$ are lower than the minimum value expected for a dimer formation. For example, the minimum value of a dimer formation $(n = 1)$ for $x = 0.25$ is 5.43 $\mu_B$ and 6.46 $\mu_B$ for a trimer. According to Fig. 4, these values are reached only at lower temperatures. We believe that this scenario takes place at $T^r$ which in this case is close to $T_c$, see inset of Fig. 2. If the dimer/trimer formation were the case, a feature in temperature would mark the ions coupling and one would observe a deviation in the data. This deviation is not observed in Fig. 4, instead a monotonically increase is observed when $T$ is decreased from $T_{c0}$ down to 1.1 $T_c$. The $S^\prime$ evolution of these prediction indicates and how they evolve as the temperature change should also depend on the charge carrier concentration. The value of the derivative of the slope $(d^2 S^\prime/dT^2)$ shown in the same inset of Fig. 2, decreases from 5.3, 4.8, 3.4, 3.3, and 2.6 $\times 10^{-4}$ as charge carriers are introduced indicating a short of weakness of magnetic strength. We naturally conclude that the deviation from Curie–Weiss law cannot be explained through the existence of short-range ferromagnetic clusters due to double exchange mechanism. An envisaged interaction for explaining this result must be superexchange-like where the $e_g$ electron is fully localized on the Mn$^{3+}$ ions regardless the presence of Mn$^{4+}$. Anderson [26] introduced the covalent character of the cation–anion bond where it is taken into account the hybridization of the localized 3d orbitals and p orbitals. According to the rules [27], the resultant superexchange interaction will be ferromagnetic (antiferromagnetic) for the Mn$^{3+}$–O$^2$–Mn$^{3+}$ bonds when the angle between Mn–O–Mn is 180° (90°). When the Mn–O–Mn bond angle is 90° (180°), the superexchange interaction will also be ferromagnetic (antiferromagnetic) in the Mn$^{3+}$–O$^2$–Mn$^{4+}$ and Mn$^{4+}$–O$^2$–Mn$^{3+}$ bonds. In this case, any effective magnetic moment will decrease as the concentration of the Mn$^{4+}$ ions increases in an agreement with the results shown in Figs. 3 and 4 since $S$ of the Mn$^{3+}$ is lower than the spin of Mn$^{4+}$. Bozin et al. [28] suggested that the PM state of La$_{0.8}$Ca$_x$MnO$_{3+y}$ with $0 < x < 0.50$, cannot be interpreted in a simple static polaron picture. Their results were explained in a homogeneous picture where the electron density is uniformly distributed over all Mn sites. We assert that the double exchange mechanism starts to operate forming short range order (dimers, trimmers and so on) at $T^r$ around 20 $\text{K}$ above $T_c$ (see inset of Fig. 2) and is achieved only at $T_c$ where $e_g$ electrons become itinerant as observed experimentally [26].

In summary, we have performed a systematic analysis of the magnetic entities susceptibility data in the PM phase. The analysis indicates that the deviation of Curie–Weiss law cannot be explained in the picture of ferromagnetic-like clusters formed by double exchange mechanism. Urged by experimental results we have empirically defined a general effective magnetic moment $S^\prime$ which decreases continuously with increasing hole doping, in agreement with the fact that the spin of the Mn$^{4+}$ is lower than the spin of Mn$^{3+}$. Below $T_{c0}$ and down to $T^r$, the results can be described by ferromagnetic/anti-ferromagnetic superexchange-like interactions due to the localized nature of $e_g$ electrons. This will lead to a homogeneous macroscopic electronic state picture which is in contrast with the canonical understanding where ferromagnetic metallic clusters containing electrons free to move via double exchange, coexists with insulating regions in the PM state of manganites. We believe that these experimental results and will impose constraints on any microscopic magnetic structure of short-range order in the high temperature PM phase of manganites.

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References


Fig. 4. $S^\prime$ as a function of the temperature and charge carrier concentration. The arrow indicates the decreasing of $S^\prime$ at $T = 400 \text{ K}$ and dashed lines the supposed values for dimers and trimmers formation.