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Magnetic Polarons in Doped $La_{0.7}Ca_{0.3}MnO_3$, $La_{0.7}Ba_{0.3}MnO_3$, and $La_{0.7}Sr_{0.3}MnO_3$ Manganites

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The characteristics of the paramagnetic state of doped manganites containing 30% Mn^{4+} ions are studied. It is shown that the ferromagnetic Curie temperature for the materials with chemical composition $La_{0.7}A_{0.3}MnO_3$ (A = Ca and Ba) characterized by semiconductor conductivity at $T > T_C$ can be determined from the measured $\chi^{-1}(T)$ dependence. In the conducting $La_{0.7}Sr_{0.3}MnO_3$ compound, the nonlinear behavior of $\chi^{-1}(T)$ is interpreted as a result of summation of different contributions related to individual Mn ions, as well as to the paramagnetic and ferromagnetic polarons with enhanced magnetic moments. The order (first or second) of the magnetic transition and the crystal lattice symmetry do not affect the formation of correlated polarons in the paramagnetic range.

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Perovskite manganites are strongly correlated electron systems, in which an interplay between the magnetic and electron subsystems leads to the formation of nanoscale inhomogeneities of different types. The magnetic properties of manganites in the high-temperature range far exceeding T_C were studied only in a few works [1–4]. The stoichiometric $LaMnO_3$ compound is an antiferromagnet with the Néel point $T_N \approx 140$ K. The existence of vacancies in cation sublattices or the substitution of bivalent Ca^{2+}, Ba^{2+}, and Sr^{2+} ions for La^{3+} ions gives rise to Mn^{4+} ions and to the ferromagnetic order owing to superexchange between the ions of different valences, $Mn^{3+}(t_{2g}^3e_g^1)$–$Mn^{4+}(t_{2g}^3)$, and to the double exchange related to the transfer of e_g electrons [5]. Semiconductor conductivity in $LaMnO_{3+\delta}$ (LMO) compounds with vacancies in the cation sublattice exists at all temperatures [6]. A metal–insulator transition near T_C is observed in $La_{0.7}Ca_{0.3}MnO_3$ (LCMO) and $La_{0.7}Ba_{0.3}MnO_3$ (LBMO) compounds [7]. The $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) compound has metallic conductivity at $T > T_C$ [8, 9]. To determine the order (first or second) of the magnetic transition, the Banerjee criterion is often used (based on the $H/\sigma = f(\sigma^2)$ dependence) [10]. The magnetic transitions in LBMO and LSMO are second-order phase transitions, whereas LCMO undergoes the first-order magnetostructural transition [11–13].

In this work, we study the effect of itinerant charge carriers, order of phase transitions, and lattice symmetry on the characteristics of the doped $La_{1-x}A_xMnO_3$ manganites in the paramagnetic state. The manganites under study have the same content of Mn^{4+} ions and the maximum value of T_C. The previous discussion of the anomalous magnetic characteristics of manganites and of the applicability of the Griffiths phase models or of the magnetic polarons was mainly focused on the temperature range $T < 1.2T_C$. We discuss the temperature dependence of the paramagnetic susceptibility at high temperatures, $T > 400$ K, at which the Curie–Weiss law should be satisfied for homogeneous ferromagnets.

Polycrystalline LMO, LCMO, LBMO, and LCMO samples were prepared by the solid-phase synthesis using such precursors as La_2O_3, Mn_3O_4, CaO, $BaCO_3$, and $SrCO_3$. Preliminary annealings were performed at 1000–1200°C with intermediate grinding of the samples. The powders were pressed into tablets and sintered at $T = 1300$°C for 24 h. Then, all samples were annealed at 600°C in air for 10 h and were

Structural and magnetic characteristics of the $La_{0.7}A_{0.3}MnO_3$ samples

Chemical composition	LMO	LCMO	LBMO	LSMO
V/formula unit, Å^3	58.69	57.73	5983	58.42
Lattice type	$R\bar{3}c$	*Pnma*	$R\bar{3}c$	$R\bar{3}c$
T_C, K	162	259	340	345
T_0, K	157	252	346	343
C_∞, cm^3 K/g	0.0085	0.0084	0.0058	0.67
B, cm^3 K^2/g	4.58	4.46	3.20	–260

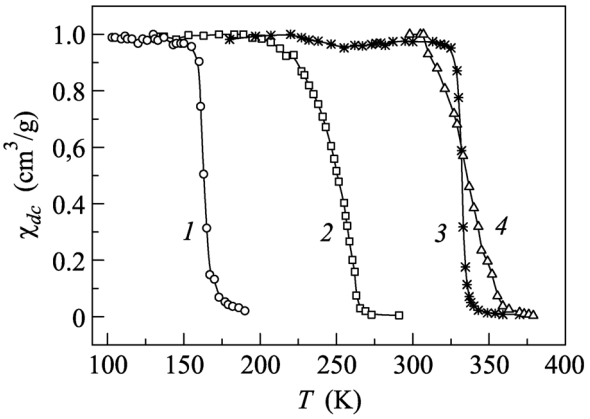

Fig. 1. Temperature dependence of $\chi_{dc}(T)$ in magnetic field $H = 90$ Oe for (*1*) $LaMnO_{3+\delta}$, (*2*) $La_{0.7}Ca_{0.3}MnO_3$, (*3*) $La_{0.7}Ba_{0.3}MnO_3$, and (*4*) $La_{0.7}Sr_{0.3}MnO_3$ samples.

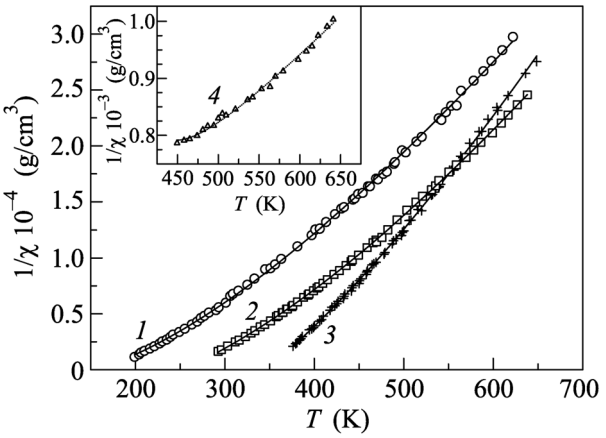

Fig. 2. Temperature dependence of the inverse magnetic susceptibility for (*1*) $LaMnO_{3+\delta}$, (*2*) $La_{0.7}Ca_{0.3}MnO_3$, (*3*) $La_{0.7}Ba_{0.3}MnO_3$, and (*4*) $La_{0.7}Sr_{0.3}MnO_3$ samples. Solid lines correspond to the calculations by Eq. (3).

quenched. The X-ray diffraction studies were performed at room temperature using a DRON-2.0 diffractometer. The LCMO sample has the orthorhombic *Pnma* structure, whereas three other samples are rhombohedral and are described by the $R\bar{3}c$ space group. An increase in the dopant ionic radius in comparison to $r = 1.36$ Å characteristic of La^{3+} ions leads to the growth in the crystal lattice volume (see table). The dc magnetic susceptibility $\chi_{dc}(T)$ was measured within the temperature range of 80 K $< T <$ 600 K at $H <$ 10 kOe using the magnetic balance technique characterized by a sensitivity of 10^{-8} cm^3/g. The ferromagnetic Curie temperature was determined by the position of the derivative susceptibility peak at a low applied magnetic field.

In Fig. 1, we illustrate the $\chi_{dc}(T)$ temperature dependence at $H = 90$ Oe. The values of the ferromagnetic Curie temperature T_C are listed in the table. They agree with the data reported in [1, 3, 4, 11, 13–19], according to which the Curie temperature varies from 218 to 270 K for LCMO, from 310 to 340 K for LBMO, and from 352 to 378 K for LSMO. A significant scatter in the values of the ferromagnetic Curie temperature in manganites can be related to the deviations from stoichiometry, to the inhomogeneous ferromagnetic state, and to the different techniques used for determining T_C (from magnetic measurements, neutron diffraction, and specific heat).

One type of nanoscale inhomogeneities is related to magnetic polarons, which can exist in the vicinity of the Curie temperature both at $T < T_C$ and at $T > T_C$ [20]. The temperature dependence of the inverse paramagnetic susceptibility for the $La_{1-x}A_xMnO_3$ samples under study is presented in Fig. 2. The curves are convex toward the T axis, having the shape characteristic of ferromagnets in the region of short-range order [21]. The nonlinear $\chi^{-1}(T)$ behavior could be a signature of an inhomogeneous paramagnetic state or of a change in the parameters of exchange near the magnetic transition temperature [15, 22–24]. For the homogeneous paramagnetic state, the Curie–Weiss law

$$\chi = C/(T-\theta) = N\mu_{eff}^2\mu_B^2/3k_B(T-\theta), \qquad (1)$$

should be satisfied, where N is the number of magnetic ions, μ_{eff} is the averaged effective magnetic moment of isolated Mn ions, μ_B is the Bohr magneton, k_B is the Boltzmann constant, and θ is the paramagnetic Curie temperature. In doped manganites, the temperature-independent effective magnetic moment is given by the expression

$$\mu_{eff}^2 = (1-x)g^2S_1(S_1+1)\mu_B^2 + xg^2S_2(S_2+1)\mu_B^2, \quad (2)$$

where x is the density of Mn^{4+} ions, $g \approx 2$ [18, 25], and $S_1 = 2$ and $S_2 = 3/2$ are the spins of Mn^{3+} and Mn^{4+}, respectively. If the relative number of Mn^{4+} ions equals 30% of the total number of manganese ions, the effective magnetic moment should not exceed $\mu_{eff} = 4.62\mu_B$. The measured temperature dependence of the inverse susceptibility demonstrates that, within the range $T_C < T < 600$ K, the values of μ_{eff} determined from the slope of the tangent to the $\chi^{-1}(T)$ curve exceed the calculated value and decrease gradually with increasing temperature. In LMO, the effective magnetic moment varies from $6.44\mu_B$ to $4.81\mu_B$ within the temperature range $T = 210$–600 K. In LCMO, μ_{eff} decreases from $6.0\mu_B$ to $4.99\mu_B$ within the temperature range $T = 290$–600 K, whereas the effective magnetic moment in LBMO decreases from $5.21\mu_B$ to $4.72\mu_B$ within the temperature range $T = 380$–500 K. The LSMO conducting sample exhibits much higher values of the effective magnetic moment: $\mu_{eff} \approx 57\mu_B$ at $T \approx 370$ K and $\mu_{eff} \approx 33\mu_B$ at $T \approx 600$ K. The deviations from the Curie–Weiss law were observed in LCMO at

$T < 705$ K and in LSMO at $T < 900$ K [1, 3]. In $LaMnO_{3+\delta}$ manganites with different contents of Mn^{4+} ions, the temperature dependence of the inverse susceptibility is also nonlinear up to temperatures of the order of $4T_C$ [2]. The nonlinear behavior of $\chi^{-1}(T)$ is related to the changes in the effective magnetic moment. It stems from the inhomogeneous paramagnetic state [20, 26] (a mixture of individual Mn ions and magnetic polarons with enhanced magnetization near Mn^{4+} ions). With the growth of the temperature, the spin correlations in polarons become weaker and the magnetic moments of polarons decrease.

In several papers [14, 15, 27], the specific features of magnetic properties in doped manganites above T_C (magnetic field dependence of χ, nonlinear behavior of $\chi^{-1}(T)$, and large values of μ_{eff}) are treated as signatures of the Griffiths phase. Rather hot recent debates concern the mechanisms underlying the features of the paramagnetic characteristics, whether they are related to the Griffiths phase or to the formation of magnetic polarons [4, 28, 29]. Griffiths considered the nonanalytical dependence of the magnetization $M = \chi H$ above the ferromagnetic Curie temperature for the randomly diluted Ising ferromagnet. However, in 3D Heisenberg doped manganites, there is no magnetic dilution, because the number of magnetic ions is conserved and only the spin of some ions changes. At a nonuniform distribution of dopant ions, the indications of the Griffiths phase can manifest themselves in the temperature range below the maximum value of T_C characteristic of the system under study. In each $La_{1-x}A_xMnO_3$ family, the highest values of the Curie temperature occur for the samples containing about 30% of Mn^{3+} ions. For such chemical compositions, the values of T_f and T_C should coincide; i.e., the Griffiths phase should not exist in the paramagnetic range [15].

Analyzing the magnetic susceptibility of LCMO within a wide temperature range ($T_C < T < 700$ K), the authors of [4] suggested that the anomalous physical characteristics such as a pronounced negative magnetoresistance and the pressure effect on T_C could be related to the Griffiths phase. However, at $T > 1.1T_C$, magnetic polarons play the dominant role. The magnetic transition at T_C is the phase transition from the ferromagnetic state to the polaronic one. The observed behavior of $\chi^{-1}(T)$ is interpreted in [4] as a result of the competition between the paramagnetism of individual Mn ions and the formation of dimers in the orthorhombic phase. Note that the ferromagnetic coupling in dimers implies the Curie law for the susceptibility, $\chi = C/(T - T_C)$ [30].

The nonlinear temperature dependences of the inverse susceptibility in doped manganites at $T > 1.2T_C$ imply changes in the effective magnetic moment. Assuming that both individual Mn ions with the fixed magnetic moment and magnetic polarons with the temperature-dependent magnetic moment contribute to μ_{eff}, we described the behavior of $\chi^{-1}(T)$ in nonstoichiometric LMO manganites using the formula [2]

$$\chi^{-1}(T) = \frac{T - T_0}{C_\infty + B/T}. \quad (3)$$

Here, the values of T_0 should be close to the Curie temperatures (T_C or θ), C_∞ is the Curie constant for separate Mn ions at $T \to \infty$, and the term B/T is related to the changes in the effective magnetic moment of polarons.

In this work, we use Eq. (3) to describe the temperature dependence of the inverse susceptibility in doped $La_{0.7}A_{0.3}MnO_3$ manganites. The parameters T_0, C_∞, and B are determined by fitting the $\chi^{-1}(T)$ curve to the experimental data (see table). In Fig. 2, we can see that the calculated curves agree well with the measured $\chi^{-1}(T)$ dependence for LMO, LCMO, and LBMO. The contribution B related to the magnetic polarons is positive and far exceeds the values of C_∞. The calculated T_0 values are close to the measured values of T_C. Taking into account the shape of the $\chi^{-1}(T)$ curves, we can suppose that the paramagnetic Curie temperature θ in these compounds is much higher than T_C. The difference $\theta - T_C \approx 100$ K was observed in Ca- and Sr-doped manganites [1, 3, 4].

A small difference between T_C and T_0 could arise because we disregarded small contributions to the measured χ values. The magnetic susceptibility can be written in the general form

$$\chi = C/(T - \theta) + \chi_{core} + \chi_{VV} + \chi_{Pauli}. \quad (4)$$

The diamagnetic contribution χ_{core} from the closed atomic shells is usually small and is independent of the temperature. In the samples under study, we have $\chi_{core} = -(0.26–0.30) \times 10^{-6}$ G cm^3/g [3], which is less than 0.7% of the measured values $\chi = (1026–36.2) \times 10^{-6}$ G cm^3/g at $T < 600$ K. The paramagnetic Van Vleck contribution from the excited states, $\chi_{VV} = 0.22 \times 10^{-6}$ G cm^3/g, is also independent of the temperature and is comparable to χ_{core}. In the first three samples, the density of itinerant charge carriers is very low. Therefore, we can neglect the χ_{Pauli} term. In LSMO, the number of itinerant charge carriers is larger; i.e., this compound is characterized by metallic conductivity. However, analyzing the data on $\chi^{-1}(T)$ in the range $T > 700$ K, where the Curie–Weiss law with the theoretically expected value μ_{eff} is satisfied, the authors of [3] concluded that the contribution of χ_{Pauli} can be neglected for $La_{1-x}Sr_xMnO_3$ at $x \le 0.35$.

Currently, there exist two models explaining the formation of magnetic polarons in manganites, namely, that based on the Mn^{4+}–Mn^{3+} superexchange [31] and another one implementing the double

exchange related to the delocalization of e_g electrons [32]. In the Varma model [31], we have

$$\chi \propto (T - T_C)^{-1}, \quad (5)$$

and the electron hoppings occur only between the nearest Mn ions having different valences. At $T > T_C$, such a situation can take place in LMO, LCMO, and LBMO. At the concentration x of Mn^{4+} ions, the effective magnetic moment corresponding to an inhomogeneous system is given by the expression

$$\mu_{eff}^2 = [x(S_1 + PS_2)(S_1 + PS_2 + 1) + (1 - x - Px)S_2(S_2 + 1)]g^2\mu_B^2. \quad (6)$$

Here, $0 \le P \le 6$ is the number of the polarized spins of the Mn^{3+} ions that are the nearest neighbors of a Mn^{4+} ion, $S_1 = 3/2$ (Mn^{4+}), $S_2 = 2$ (Mn^{3+}), and $S_1 + PS_2$ is the polaron spin. Such polarons can have the size of a doubled unit cell. For $La_{0.7}A_{0.3}MnO_3$, the estimates of μ_{eff} within the Varma model give $\mu_{eff} = 5.34\mu_B$ at $P = 1$ and $\mu_{eff} = 14.44\mu_B$ at $P = 6$. Note that not all Mn^{4+} ions polarize the nearest-neighbor Mn^{3+} ions. At large concentrations x, one polaron can contain more than one Mn^{4+} ion. If the antiferromagnetic Mn^{4+}–Mn^{4+} interaction exceeds the ferromagnetic exchange in a polaron, the contribution of such polarons to the susceptibility vanishes [26]. The observed nonlinear behavior of $\chi^{-1}(T)$ and large values of μ_{eff} suggest the existence of the paramagnetic Varma polarons at $T <$ 650 K.

A somewhat different situation is observed in the conducting $La_{0.7}Sr_{0.3}MnO_3$ compound. The temperature dependence of the inverse susceptibility is also nonlinear. Choosing the values of T_0, C_∞, and B, we can fit the experimental curve by Eq. (3) within the temperature range T = 450–600 K. However, this leads to very large negative values of the parameter B. Such calculations were performed for T_0 = 350–380 K. The magnetic moment of polarons cannot be negative. In addition, the measured values of the magnetic moment within the temperature range 360–650 K far exceed $\mu_{eff} = 14.44\mu_B$ at $x = 0.3$ and $P = 6$ characteristic of the system consisting of paramagnetic Mn ions and the Varma polarons. It seems that the Varma model is not applicable to LSMO.

The neutron scattering studies of LSMO demonstrate that the spin wave energy is much higher than T_C [19]. The magnetic polarons include a large number of ordered spins. As we have already mentioned, LSMO retains metallic conductivity in the paramagnetic state since the charge transfer energy for e_g electrons in the d band is rather high. Near the Curie temperature, the critical parameters characterizing the magnetization and susceptibility at $T > T_C$ and $T < T_C$ differ from each other. We can suggest that the inhomogeneous magnetic state in LSMO above T_C is formed by the ferromagnetic polarons embedded into the paramagnetic host and the magnetic order in these polarons results from the double exchange [3, 19, 20, 24].

The formation of correlated polarons in manganites owing to the transfer of e_g electrons of Mn^{3+} via oxygen ions was considered by Wang and Freeman [32]. As criteria for the formation of ferromagnetic polarons, they chose the minimization of the size of ordered domains leading to the energy lowering with respect to the homogeneous paramagnetic state and the absence of overlapping between polarons. With a decrease in T, the spin polarons grow in size. Therefore, the change in susceptibility obeys the law

$$\chi \propto T^{-3/5}(T - T_C)^{-1}. \quad (7)$$

In the high-temperature range, $kT \approx zJ$ (where z is the number of interacting spins and J is the exchange integral in polarons), the size of spin polarons stops changing, and the susceptibility behaves according to the Curie–Weiss law. The authors of [32] did not present any explicit form of the temperature dependence for such a magnetic system. Our attempts to implement the expression

$$\chi = (C_\infty + BT^{-3/5})/(T - T_0) \quad (8)$$

similar to Eq. (3) were unsuccessful. As in the situation with formula (3), the description of the $\chi^{-1}(T)$ dependence in LSMO also leads to a negative B value and to a T_0 value significantly different from T_C. Probably, the $\chi^{-1}(T)$ dependence in LSMO has a more complicated form. In the vicinity of T_C, we observe a gradual transition from the homogeneous ferromagnetic state to the inhomogeneous polaron state. Within the temperature range $T_C > T > 650$ K, the ferromagnetic polarons (similar to the short-range order) and paramagnetic polarons can coexist. With a further increase in the temperature up to 900 K, only the paramagnetic Varma ions survive.

To summarize, our studies of the magnetic characteristics of $La_{1-x}A_xMnO_3$ manganites containing 30% Mn^{4+} ions have demonstrated that the paramagnetic state is inhomogeneous within the temperature range $T_C < T < 650$ K. The LMO, LCMO, and LBMO manganites with semiconductor conductivity at $T > T_C$ exhibit a nonlinear temperature dependence of the inverse susceptibility, which can be fitted by the Curie–Weiss law with the temperature-dependent effective magnetic moment. In these compounds, the magnetic polarons are due to superexchange between the nearest neighbors, Mn^{3+}–O^{2-}–Mn^{4+}. Here, we observe a correlation between the lattice volume and the magnetic moments of paramagnetic polarons. The LBMO sample with the large unit cell volume has a smaller value of parameter B. At the same time, the crystal lattice symmetry (orthorhombic or rhombohedral) does not produce any pronounced effect on the magnetic moment of polarons. We have fitted the

measured $\chi^{-1}(T)$ for manganites with semiconductor conductivity in the far paramagnetic range using an empirical formula allowing us to determine the value of T_C.

In the conducting $La_{0.7}Sr_{0.3}MnO_3$ compound, the Curie temperature can be treated as the temperature of the transition from the long-range ferromagnetic order to the polaronic state. Above T_C, ferromagnetic polarons (similar to the short-range magnetic order), paramagnetic polarons with an increased μ_{eff} value, and individual Mn ions exist. The presence of magnetic polarons in the far paramagnetic range ($T > 2T_C$) is a characteristic feature of classical magnetic semiconductors.

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