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Paramagnet-to-ferromagnet and insulator-to-metal phase transitions in $La_{0.88}MnO_{2.95}$

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Results of structural neutron diffraction study and data on the transport and magnetic properties (the linear and nonlinear (second and third order) susceptibilities) are presented for the metallic polycrystal $La_{0.88}MnO_{2.95}$. This above compound exhibits the paramagnet-ferromagnet (P-F, $T_C \approx 244$ K) and insulator-metal (I-M, $T_{IM} \approx 253$ K $> T_C$) phase transitions, and reveals a colossal magnetoresistance near T_{IM}. An analysis of the diffraction data is performed using the rhombohedral space group (*R3c*) in the temperature range 4–300 K. Below $T^* \approx 258$ K, the FM clusters appear in the PI matrix undergoing a second-order transition. In contract to the traditionally doped analogs, this compound reveals the clustered state in the high symmetrical rhombohedral phase. The concentration of FM clusters increases under cooling, so that it exceeds the percolative threshold value below T_{IM}, and the sample exhibits a metallic behavior. The T-evolution of the clustered state is unexpectedly found to be very close to that of the insulating $La_{0.88}MnO_{2.91}$ with the F ground state. It is shown that this leads to a certain restriction on a structure of a FM percolative network forming at T_{IM}. The critical behavior of this system has a complicated character due mainly to the origination of the FM infinite cluster below T_{IM} and its interaction with the PI matrix.

Результаты структурных нейтронно-дифракционных исследований и данные о транспортных и магнитных свойствах (линейной и нелинейных (второго и третьего порядка) восприимчивостей) представлены для поликристаллического металлического $La_{0.88}MnO_{2.95}$. Это соединение испытывает фазовые переходы парамагнетик-ферромагнетик (П-Ф) ($T_C \approx 244$ K) и изолятор-металл ($T_{IM} \approx 253$ K $> T_C$) и проявляет колоссальное магнитосопротивление вблизи T_{IM}. Анализ дифракционных данных выполнен с использованием ромбоэдрической пространственной группы (*R3c*) в температурной области 4–300 K. Согласно данным $M_2(H,T)$, ниже $T^* \approx 258$ K ФМ кластеры появляются в ПИ матрице, претерпевающей переход второго рода. В отличие от традиционно допированных аналогов, это соединение проявляет кластерное состояние в высоко симметричной ромбоэдрической фазе. Концентрация ФМ кластеров возрастает при охлаждении, так что при температуре ниже T_{IM} она выше, чем порог протекания, и образец испытывает металлическое поведение. T-эволюция этого кластерного состояния неожиданно оказывается очень близкой к эволюции этого состояния в изоляторном $La_{0.88}MnO_{2.91}$ с Ф основным состоянием. Показано, что это приводит к определенным ограничениям на структуру ФМ перколяционной сети, формирующейся при T_{IM}. Критическое поведение этой системы имеет сложный характер в основном из-за возникновения бесконечного ФМ кластера ниже T_{IM} и его взаимодействия с ПИ матрицей.

1. Introduction

The interest in the study of the perovskite manganite oxides is due to their unusual electron and magnetic properties. Some important aspects of their behavior in a hole doped region are not yet well understood. The peculiarities of the paramagnet (P) to ferromagnet (F) phase transitions and formation of an inhomogeneous state above T_C with the ferromagnetic clusters in a paramagnetic matrix are among the central open problems in the field of Mn oxides. They are closely related to the nature of insulator (I) to metal (M) phase transition and colossal magnetoresistance (CMR) [1]. This work continues the comprehensive investigation of these questions. Recently, the study of a nonlinear response to a weak *ac* magnetic field for $Nd_{1-x}Ba_xMnO_3$ (x = 0.23, 0.25) single crystals of a pseudocubic structure and the FI ground state has revealed an unusual scenario of the P-FI phase transition [2, 3]. Above T^* ($\approx T_C + 20$ K), the critical behavior corresponded to that of a 3D isotropic ferromagnet. Below T^*, an anomalous behavior was observed. It was characterized by the appearance of a new phase with strong nonlinear properties in the weak magnetic fields that are due to the F clusters. A similar behavior above T_C was also found in $La_{0.88}MnO_{2.91}$ manganite with the FI ground state where the doping is due to variation in the oxygen content [4]. These facts support an assumption on universal character of this P-F phase transition scenario. This new class of the manganites, $La_{0.88}MnO_x$ (x = 2.82–2.95), synthesized recently has the phase diagram, magnetic and transport properties similar to those of the traditionally doped manganites [5]. The x = 2.82 compound, for instance, is a counterpart of $LnMnO_3$, and the x = 2.95 system reveals the I-M transition at $T_{IM} > T_C$ accompanied by a CMR. Here, presented are the results of the careful investigation of the P-F and I-M phase transitions in polycrystalline $La_{0.88}MnO_{2.95}$. The studies include an analysis of the crystal structure (neutron diffraction), as well as the data on the transport and magnetic properties (the linear and nonlinear (second and third order) susceptibilities). The main task is to elucidate the metallization scenario of these materials by comparing the data for x = 2.91 (FI) and 2.95 (FM) compounds. This refers first of all to the properties of the second harmonic of magnetization in the parallel *ac* and *dc* magnetic fields that provides the T-evolution control of the clustered state.

2. Experimental

The preparation and testing of polycrystalline $La_{0.88}MnO_{2.95}$, as well as the corresponding equipment and measurement protocols have been described in [4]. Note only that the second harmonic of the longitudinal magnetization M_2 was measured in parallel *dc* and *ac* harmonic magnetic fields $H(t) = H + h\sin\omega t$ ($h \leq 35$ Oe, $f = \omega/2\pi$ = 15.7 MHz). The $\mathrm{Re}M_2(H)$ and $\mathrm{Im}M_2(H)$ parts of the M_2 were simultaneously recorded as functions of a *dc* magnetic field H for various sample temperatures (T = 85–315 K). This field was scanned symmetrically relative to the point $H = 0$ for detecting a field hysteresis of the signal. The amplitude of the H-scan was 300 Oe. The diffraction experiments were performed using a PNPI 48-counter powder neutron diffractometer (Ge monochromator, λ = 1.383 Å) in a cryostat at 4.2–300 K. The neutron diffraction data were analyzed using the program FullProf was emploed for the structure refinement.

3. Experimental results and discussion

The measured diffraction profiles for 4–300 K are found to be well fitted using a rhombohedral space group (*R3c*). Fig. 1 shows temperature dependences of the structural parameters that mainly reflect the lattice compressing under cooling. A sharp decrease of the unit cell volume, lattice constants (a) and Mn–O bond length (b), characterizing a rhombohedron, at $T_{IM} \approx 253$ K is due to the I-M transition determined from the transport measurements (see Fig. 2). The spontaneous magnetization increases monotonously on cooling below $T_C \approx 244$ K, as usually occurs at P-F phase second order transition, reaching the value 3.45 μ_B/Mn at 4 K that is close to 3.5 μ_B/Mn corresponding to ion composition (Mn^{3+}–Mn^{4+}) for x = 2.95 (not presented). Fig. 2 displays the transport properties [5]. The T dependence of resistivity reveals the I-M transition at $T_{IM} \approx 253$ K $> T_C$. The magnetoresistivity exhibits a minimum slightly below T_{IM}.

Fig. 3 presents the T dependences of the linear ac susceptibility (a) and amplitude of the third magnetization harmonic $|M_3|$(b). It is seen that $\chi''/\chi' < 0.04$, and therefore $\chi' \approx \chi_0$, where χ_0 is the static susceptibility. To analyze $\chi_0(\tau)$ dependence ($\tau = (T-T)/T_C$), T_C, is to be determined. Its value can be

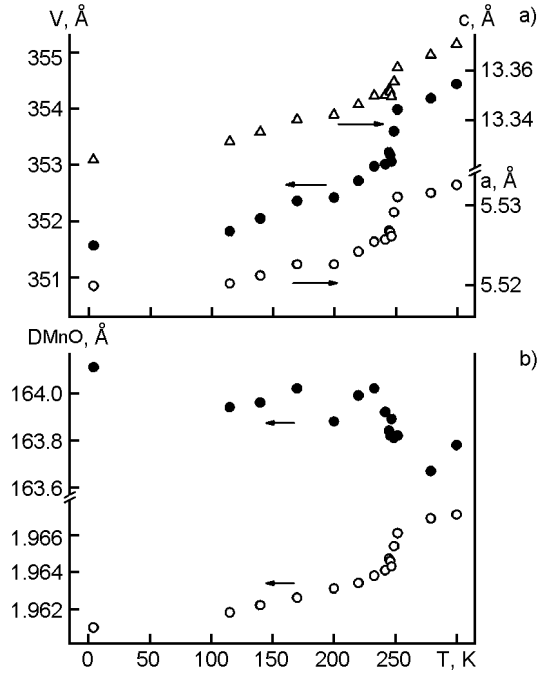

Fig. 1. Temperature dependences of structural parameters obtained from neutron diffraction data (the *R3c* symmetry): (a) T dependences of the structural constants and the unit-cell volume; (b) Mn–O bond length and Mn–O–Mn angle vs T.

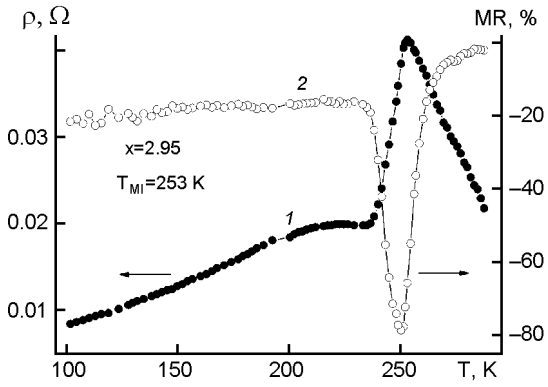

Fig. 2. Plots of the resistivity ρ (*1*)) and magnetoresistivity $MR(T) = \{[R(H)-R(0)]/R(0)\}\cdot 100$ % at $H = 9$ kOe (*2*) vs T.

found from the $|M_3(T)|$ data (Fig. 3b) havund a maximum at $T_C \approx 244$ K. The inset in Fig. 3a displays the critical behavior of $\chi'(\tau) \propto \tau^{-\gamma}$. The fitting in the $(5\cdot 10^{-3} < \tau < 0.13)$ range gives a value of $\gamma = 1.21(7)$ that is close to that for a 3D isotropic ferromagnet ($\gamma \approx 4/3$). The T dependence of $1/4\pi\chi'(T)$ (inset in Fig. 3b) does not indicate the presence of the F clusters above T_C. The F clusters cause a deviation of the data down from the high temperature inverse Cure-Weiss line, while we observe here the usual opposite critical deviation. Thus, the traditional *ac* χ measurements are insufficient to reveal their appearance.

To clarify the critical behavior above T_C, the second harmonic of magnetization, $M_2(H,T)$, was investigated under condition $M_2 \propto h^2$ when the longitudinal response is described by the second order dynamic susceptibility $\chi_{\|}^{(2)}(\omega, H, T)$. The properties of this function were considered in [2]. Fig. 4 displays the $\mathrm{Re}M_2(H)$ and $\mathrm{Im}M_2(H)$ depend-

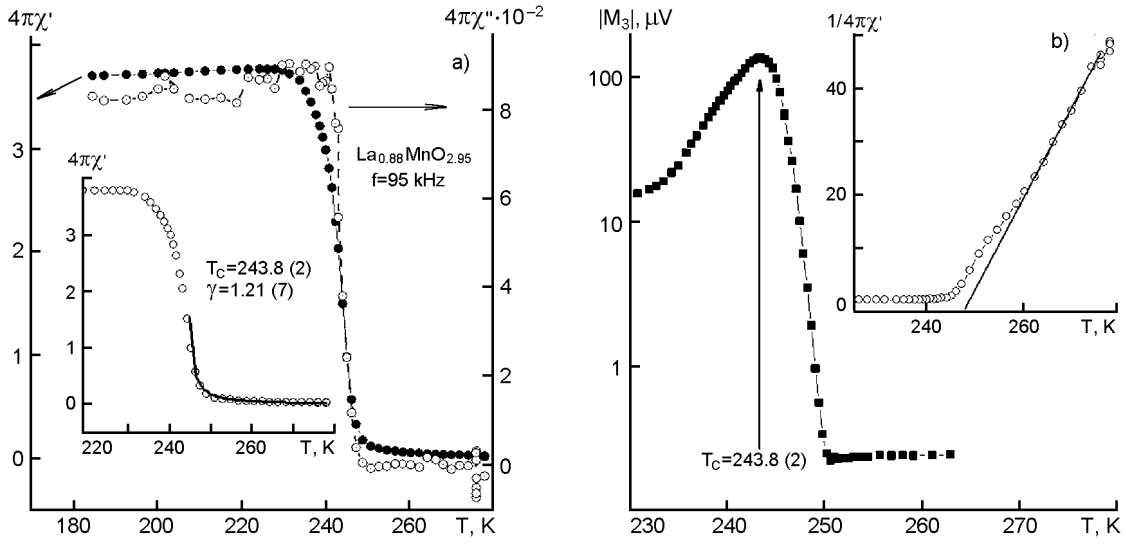

Fig. 3. Temperature dependences of the linear *ac* susceptibility (a) and amplitude of the third harmonic of magnetization (b). Inset in (a): the fit of $4\pi\chi'$ by the power law (solid line). Inset in (b): $1/4\chi'$ vs temperature where solid line displays the inverse Cure-Weiss law.

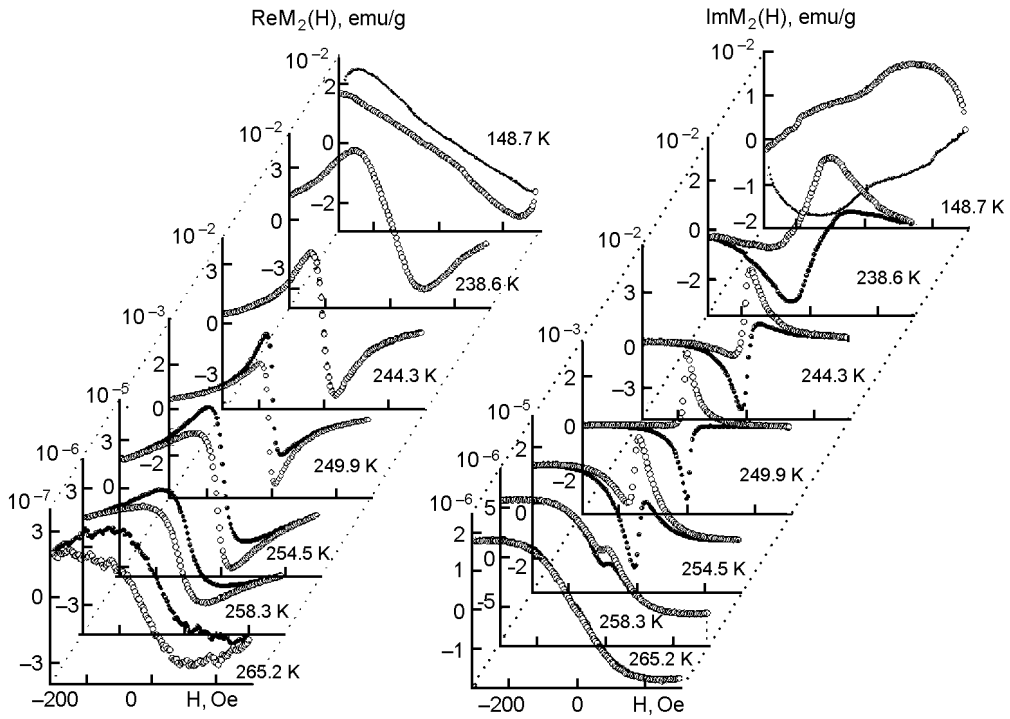

Fig. 4. Two phase components of the second magnetization harmonic M_2 vs the *dc* magnetic field H at some characteristic temperatures. Full and open symbols present the direct and reverse H-scans, respectively.

ences for some characteristic temperatures that are related to the three ("impurity", normal and clustered (anomalous)) T ranges with the different $M_2(H,T)$ dependences. Similar ranges were found in the NdBa and $La_{0.88}MnO_{2.91}$ insulator systems [2–4]. In the "impurity" range (315–289 K) (not shown), a practically T-independent signal is observed. It exhibits a weak H-hysteresis with a small M_2 value at $H = 0$ that provides a clear evidence of spontaneous magnetization in this phase. Indeed, M_2 is a pseudovector and even function of h. Therefore, $M_2(H)$ is odd in H with $M_2(0) = 0$ in the paramagnetic phase. Accordingly, the response with $M_2(0) \neq 0$ in the "impurity" range is associated with a small amount of a magnetically ordered impurity phase. In the normal range (289–258 K $\approx T^*$), the signal begins to increase with lowering temperature, and we observe the typical response that can be attributed to a 3D isotropic ferromagnet in a weak field ($g\mu H << |T_C\tau^{5/3}$). In this regime, $\mathrm{Re}M_2(H) \propto H$ and $\mathrm{Im}M_2(H)$ show nearly linear dependence on H [2–4].

An example of this behavior is the data at 265.2 K (Fig. 4). It is seen that $\mathrm{Im}M_2(H)$ agrees with the prediction whereas $\mathrm{Re}M_2(H)$ reveals H-hysteresis. Compared to the response of $La_{0.88}MnO_{2.91}$ [4], the critical linear contribution of the P phase is modified by the "impurity" phase that has a high concentration at $x = 2.95$. The clustered region ($T^* = 258$ K to $T_C = 244$ K) is characterized by the origination of an additional F signal. This is clearly seen in the $\mathrm{Im}M_2(H)$ dependence as a hysteresis loop for $H < 100$ Oe with an extreme in a very weak field $H \sim 10$ Oe (Fig. 4b, $T =$ 258.3 K). The new signal increases sharply at cooling (Fig. 4b and Fig. 5b, $\mathrm{Im}M_{2min}$), whereas the field position of its extreme remains weakly T-dependent down to T_C (Fig. 5a). This behavior can be attributed to a volume increase of the new clustered phase.

In the $\mathrm{Re}M_2(H)$ dependence, the clustered signal also accounts for formation of the extreme at low fields and the field hysteresis below T^* (Fig. 4a). The hysteresis signal of this component is definitely related to the appearance of the new F phase, because $\mathrm{Re}M_2(0)$ at T^* is about ten times large than the "impurity" signal, and $\mathrm{ReM}_2(0)$ begins to increas at cooling below T^*. The field position of the minimum at $H > 0$ (H_{min}) decreases and extremal value of

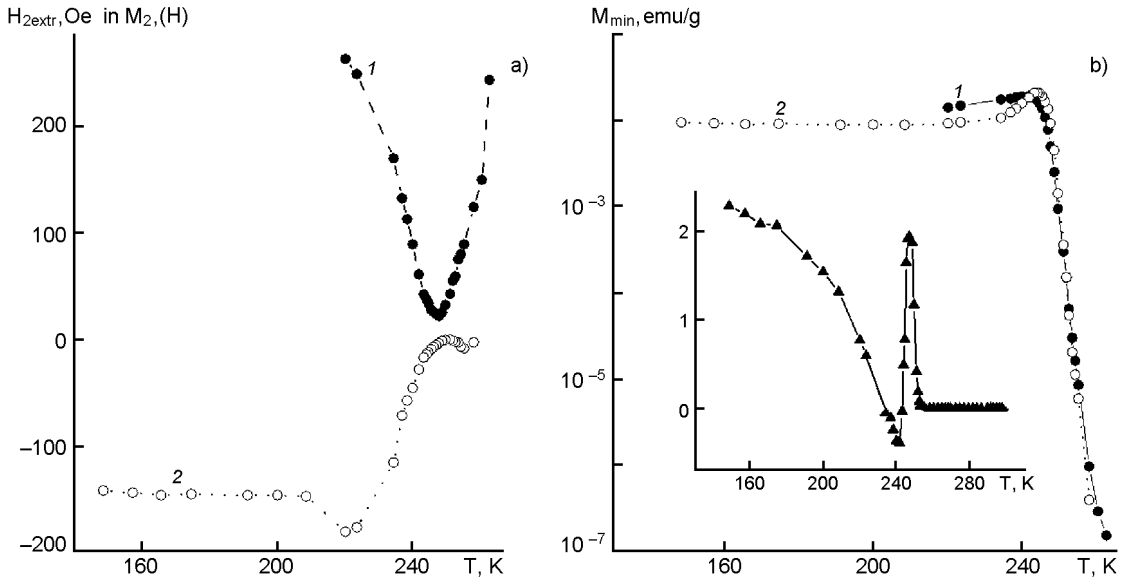

Fig. 5. Temperature dependences of $\mathrm{Re}M_2(H)$ and $\mathrm{Im}M_2(H)$ parameters: (a) T-behavior of the H positions of the minima in $\mathrm{Re}M_2(H)$ and $\mathrm{Im}M_2(H)$; (b) T-evolution of $-\mathrm{Re}M_2(H)$ and $-\mathrm{Im}M_2(H)$ at their minima. Inset in (b): $\mathrm{Re}M_2(T)$ at $H = 0$.

the $\mathrm{Re}M_2(H)$ ($-\mathrm{Re}M_{2min}$) increases with lowering temperature from T^* down to T_C (Fig. 5). For this component, H_{min} changes with temperature, since $\mathrm{Re}M_2$ is the sum of the comparable signals from the F clusters and the critical P phase. The temperature dependences of the $\mathrm{Im}M_{2\mathrm{min}}$, $\mathrm{Re}M_{2min}$, and H_{min} in ($\mathrm{Re}M_2$) show the extremes approximately at T_C (Fig. 5). The inset in Fig. 5b displays T-dependence of $\mathrm{Re}M_2(H = 0)$. A nonzero value of this signal above T_C results from the spontaneous magnetization of the sample that is due to the F regions. This signal increases at cooling, reflecting the growing volume of the clustered phase, and reaches a maximum at T_C. A narrow negative peak slightly below T_C is due to development of a F ordering in the paramagnetic matrix.

It is remarkable that all the main peculiarities of the T-evolution of the arising new clustered phase, which are indicated above, coincide with those for $Nd_{0.75}Ba_{0.25}MnO_3$ and $La_{0.88}MnO_{2.91}$ compounds [3, 4]. Note, for example, the specific $\mathrm{Re}M_2(T)$ dependence at $H = 0$ (inset in Fig. 5b). An essential quantitative difference is the magnitude of the F cluster signal which is noticeable large in this manganite due to increasing concentration of the clustered phase. $\mathrm{Re}M_2(T,0)$ in the maximum (inset in Fig. 5b), for instance, is ten times greater than the same value for insulating $La_{0.88}MnO_{2.91}$.

Thus, the $M_2(H,T)$ response of the F clusters is insensitive to the I-M transition, and behaves like that of the insulating manganites with the isolated F clusters, in spite of the fact that those form a percolative conductive pathway at T_{IM}. It is the main unexpected result. Indeed, formation of the percolative conducting pathway provides the percolative ferromagnetic double exchange network that should result in development of the F ordering in the system of the F clusters near $T_{IM} > T_C$. However, the measurements do not give any clear evidences of this transition. Note that even the isolated F clusters show the M_2 signal at $H = 0$ which evidences the presence a remanence magnetization of the sample. This means that the F clusters are in a blocking regime when temperature is below the blocking temperature determined by a magnetic anisotropy and the cluster volume [4, 6]. The remanence magnetization in this regime may, generally speaking, mask the appearance of their cooperative ordering at T_{IM}. A trivial possibility is that the signal of the F percolative network including a considerable part of the clustered phase is much less than that of the remaining isolated F clusters. This variant can be ruled out because a strong signal reduction would be observed below T_{IM}.

Thus, the FM percolative network and the isolated FM clusters reveal similar responses. This results in a certain restriction

on the FM percolative network structure, since it is rather difficult to coordinate its FM character with a strong favor for uniform magnetization below T_{IM} and its magnetic behavior above T_{IM} when the connected FM network is broken into the separated randomly oriented FM clusters. For instance, the FM percolative network cannot include long FM filaments magnetized along the filament because its response is incompatible with that of the isolated filament fragments (the small randomly oriented pieces). The FM percolative cluster is an extremely complicated object. We indicated here only a naive appropriate variant, namely, it may contain many domain elements, every domain resembling in its size and shape the initial FM clusters. Additional studies are needed to clarify this important nontrivial matter directly related to the peculiarities of the CMR.

Note further that below T_{IM}, the $M(H)$ dependence for our sample shows a peculiarity near $H \sim 800$ Oe [5] which contradicts to usual critical behavior of a ferromagnet above T_C. The FM infinite network certainly accounts therefor, since this specific feature was not observed in the insulating $La_{0.88}MnO_{2.91}$. The same peculiarity was also found in traditionally doped $Nd_{0.7}Sr_{0.3}MnO_3$ single crystal below $T_{IM} \approx 212$ K $> T_C \approx 204$ K at a close H value [7]. This peculiarity was not explained in these works. It is interesting to analyze quantitatively the $M(H)$ dependence for this mixed state. As we see, the critical behavior of this system has a complicated character due to origination of the infinite FM cluster and its interaction with the PI matrix.

4. Conclusion

To conclude, we have investigated the crystal structure and the magnetic properties of polycrystalline $La_{0.88}MnO_{2.95}$. It has been found that the crystal structure is described by the rhombohedral space group ($R3c$). This compound exhibits the P-F ($T_C \approx 244$ K) and I-M ($T_{IM} \approx 253$ K) phase transitions, and reveals a colossal magnetoresistance near T_{IM}. According to the $M_2(H,T)$ data, below $T^* \approx 258$ K, the FM clusters appear in the PI matrix undergoing the second-order phase transition. Their concentration increases at cooling so that it exceeds the percolative threshold value below T_{IM}, and the sample exhibits a metallic behavior. This is the percolative scenario of metallization. The clustered state develops in the rhombohedral symmetry, and its appearance is not reduced to the JT distorted phases as it might be concluded basing on the results for the traditionally doped manganites [8, 9]. The $M_2(H,T)$ response is insensitive to the I-M transition exhibiting a singularity at T_C only, and behaves like that of the insulating manganites with the isolated FM clusters. This restricts to a certain extent the possible structure of the infinite FM network. The complicated critical behavior of this compound is a consequence of the mixed magnetic state where the FM regions forming the infinite FM clusters below T_{IM} interact strongly with the PI matrix. The additional studies, especially concerning the H-effect on the transitions, are needed to clarify completely the properties of this remarkable system with the self-organized clustered structure.

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Фазові переходи парамагнетик-феромагнетик та ізолятор-метал у $La_{0.88}MnO_{2.95}$

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Представлено результати структурних нейтронно-дифракційних досліджень та дані про транспортні й магнітні властивості (лінійної й нелінійних (другого та третього порядку) сприйнятливостей) для полікристалічного металічного $La_{0.88}MnO_{2.95}$. Ця сполука зазнає фазових переходів парамагнетик-феромагнетик (П-Ф) ($T_C \approx 244$ K) та ізолятор-метал ($T_{IM} \approx 253$ K $> T_C$) та виявляє колосальний магнітоопір поблизу T_{IM}. Аналіз дифракційних даних виконано з використанням ромбоедричної просторової групи ($R3c$) у температурній області 4–300 K. За даними $M_2(H,T)$, нижче $T^* \approx 258$ K ФМ кластери з'являються у ПІ матриці, яка зазнає переходу другого роду. На відміну від традиційно допованих аналогів, ця сполука виявляє кластерний стан у високо симетричній ромбоедричній фазі. Концентрація ФМ кластерів зростає при охолодженні, так що при температурі нижче T_{IM} вона вища від порогу протікання, і зразок виявляє металічну поведінку. T-еволюція цього кластерного стану несподівано виявляється дуже близькою до еволюції цього стану в ізоляторному $La_{0.88}MnO_{2.91}$ з Ф основним станом. Показано, що це призводить до певних обмежень на структуру ФМ перколяційної мережі, яка формується при T_{IM}. Критична поведінка цієї системи має складний характер в основному внаслідок виникнення нескінченного ФМ кластера нижче T_{IM} та його взаємодії з ПІ матрицею.