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Colossal magnetoresistance behavior and ESR studies of $La_{1-x}Te_xMnO_3$ $(0.04 \leqslant x \leqslant 0.2)$

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In this paper, we report the magnetic and electrical properties of the Te-doped lanthanum manganite perovskite compound $La_{1-x}Te_xMnO_3$ and the related electron spin resonance (ESR) study. This is a material with rhombohedral structure and it shows good colossal magnetoresistance behavior. The magnetoresistance ratio $MR=[\rho(0)-\rho(H)]/\rho(0)$ is about 63% for $x=0.04$ in an applied magnetic field of 40 kOe. The resistivity of the compounds is affected by temperature and the amount of Te doping. The temperature dependence of the resistivity showed that the conductivity above the Curie temperature was dominated by the hopping of the small polarons, and the resistance was attributed to the electron-phonon and magnon scattering mechanism below the metal-insulator transition temperature. The ESR investigation indicated that the compound was in the paramagnetic phase above 230 K, and in the single ferromagnetic state below 170 K. In the temperature range of 230 to 170 K, the compound showed phase separation phenomena.

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Doped perovskite manganites $La_{1-x}D_xMnO_3$ (where D represents Ca, Sr, Ba, Ce, or Zr) have attracted much attention due to their "colossal magnetoresistance" (CMR) behavior and related physics phenomena. In this kind of compound, a metal-insulator (*MI*) transition, which always accompanied with a paramagnetic-ferromagnetic transition, occurs at a particular temperature. These phenomena were traditionally explained by the double-exchange (DE) model and Jahn-Teller effects.[1–4] In the DE model, Mn ions are considered to be in a mixed-valence state. Many researchers have investigated the doping effect. Their results show that the physical and chemical properties of the compounds depend on the doped element D and doped level x. When a divalent element, such as Ca, Sr, Ba, etc., is substituted for a part of La, the compound displays hole conductivity and has a mixed-valence of Mn^{3+}-Mn^{4+}. Recently, Das and Mandal[5,6] reported the CMR behavior in the $La_{1-x}Ce_xMnO_3$ system where the Ce^{4+} ion was used to replace La^{3+}. They suggested that the CMR behavior probably occurred in a system of a mixed-valence state of Mn^{2+}-Mn^{3+}. Meantime, Philip and Kutty pointed out that the transport properties of the La-Ce-Mn-O system had the characteristic of the adiabatic small polaron conduction in the high-temperature region.[7] Ce is a rare-earth element with tetravalence and the compounds show electronic conductivity. Therefore, it is of great interest to investigate whether the CMR effect exists in compounds in which La^{3+} is partially replaced by another tetravalence element rather than a rare-earth element. In this paper, we report the investigation of CMR properties that was caused by the substitution of tellurium ion for La ions. In addition, its electric and magnetic behaviors were investigated in the temperature range of 5 to 300 K. The phase separation phenomenon was studied by electron spin resonance (ESR) as well.

The samples of $La_{1-x}Te_xMnO_3$ $(0.04 \leqslant x \leqslant 0.2)$ were synthesized by conventional ceramic techniques. The stoichiometric mixture of high purity La_2O_3, TeO_2, and Mn_2O_3 powder was ground, pelletized and presintered at 700 and 900 °C in the flowing argon atmosphere with intermediate grindings for three times. Then the samples were sintered at 930 °C for 24 h in the flowing oxygen gas, followed by furnace cooling to room temperature. X-ray diffraction (XRD) structure analysis of the compounds was performed with a DMAX2400 diffractometer at room temperature. The powder diffraction data were Rietveld refined by DBW9411 program. The fit between the experimental spectrum and calculated value is very good.[8] It showed that the space symmetric group of the compound is $R\bar{3}CH$ and the structure parameters are listed in Table I. Thus, the samples are single phase and have trigonal symmetry. As $x>0.3$, the second phase was observed under our prepared condition, it is probably due to the difference of ionic radius between La and Te. The x-ray photoemission spectroscopy analysis of $La_{1-x}Te_xMnO_3$ revealed that the tellurium ions are in the tetravalence state, the Mn ions could be in a mixed valence state of Mn^{2+}-Mn^{3+} in the sample. The magnetic measurement was carried out with a superconducting quantum interference device magnetometer (MPMS-7) in the temperature range of 5–300 K. The electrical resistivity and the magnetoresistance were measured using the standard four-probe method. The electron spin resonance (ESR) spectroscopy measurement was performed at 9.50 GHz with a BRUKER-200D spectrometer.

Figure 1(a) shows the magnetization versus temperature curves of $La_{1-x}Te_xMnO_3$ in an applied field of 10 kOe, where $x=0.04$, 0.1, 0.15, and 0.2. At low temperature, the magnetization decreases drastically with x increasing at first, and then gradually approaches a saturation value as x increases to 0.2. The Curie temperatures T_C are about 201, 240, 255, and 255 K for $x=0.04$, 0.1, 0.15, and 0.2, respectively. T_C increases with x and gradually approaches a definite value. The above phenomenon is probably a common character of electronic doping compounds, which has been reported previously.[9,10] It suggested that the above phenomenon might come from the contribution of the competition between the DE and the core spin interaction, and the competition leaded to the canting of the core spins as the doped level increases.

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TABLE I. Refined structural parameters of $La_{1-x}Te_xMnO_3$ at room temperature. The space group is $R\overline{3}CH$.

X	a (Å)	c (Å)	$d_{\text{Mn-O}}$ (Å)	$\theta_{\text{Mn-O-Mn}}$ (^{0})	R_p(%)	R_{WP}(%)	χ^2
0.04	5.525	13.346	1.963	164.16	9.6	14.37	1.69
0.1	5.520	13.348	1.959	165.37	8.27	12.04	1.49
0.15	5.513	13.351	1.957	165.70	9.94	15.66	1.92
0.2	5.512	13.351	1.955	166.28	8.57	12.49	1.54

The temperature dependence of the resistivity under an applied field of 40 kOe for the compound $La_{1-x}Te_xMnO_3$ ($x = 0.04$–0.2) is shown in Fig. 1(b). All the compounds exhibit a metal-insulator (*MI*) transition behavior. The transition temperature T_{MI} shifts to higher temperature with the increase of Te content. The T_{MI} are about 177, 220, 237, and 240 K for $x = 0.04$, 0.1, 0.15, and 0.2, respectively. The resistivity of the compounds decreases with increasing x as the result of carrier increasing. The magnetoresistance (MR) ratio is defined as $\Delta\rho/\rho(0) = [\rho(0) - \rho(H)]/\rho(0)$, where $\rho(0)$ and $\rho(H)$ is the resistivities in zero field and applied field H, respectively. The maximum MR ratios of the compounds are about 63.5, 50.7, 46.9, and 44.95% at 40 kOe. The corresponding peak temperatures T_P are about 155, 200, 220, and 220 K for $x = 0.04$, 0.1, 0.15, and 0.2, respectively.

It is known that the electric transport behavior of a perovskite manganite compound at different temperature range is governed by different conducting mechanism. Although many factors affect the conductance of a CMR material, we are only interested in the dominant interaction between ions in the compound in this study. In paramagnetic state, the temperature dependence of resistivity could be best fitted by the expression $T \exp(E_0/K_BT)$, where K_B is the Boltzmann constant and E_0 is the activation energy. The expression is based on the conduction model of small polaron hopping. Because the lattice of manganite compounds becomes distorted around the electrons in the conduction band at high temperature, the coupled between electron and phonon yielded small polaron. As the temperature above T_C, the thermally activated hopping of the small polarons plays an important role in conductivity, which is similar to that observed in the hole doping perovskite manganite compounds. The fitting results (Table II) of the experimental curves [Fig. 1(b)] reveal that the activation energy E_0 decreases with increasing x, and the applied magnetic field reduces the activation energy of the compounds significantly.

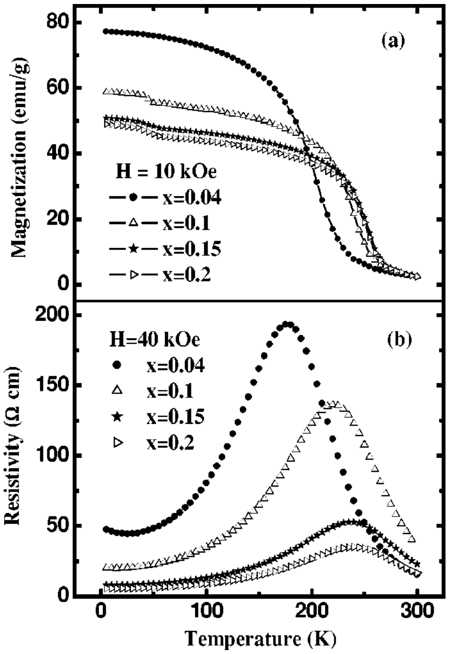

FIG. 1. Temperature curve of magnetization and resistivity for $La_{1-x}Te_xMnO_3$ ($0.04 \leqslant x \leqslant 0.2$). (a) The magnetization at magnetic field 10 kOe. (b) The resistivity in the temperature range between 5 and 300 K.

On the other hand, in the ferromagnetic state, the resistance could be considered as the sum of the contribution of the electron scattering and magnon scattering. It is well known that the electron scattering can be expressed as the T^2 dependence according to the Fermi liquid model[11] and the magnon scattering can be described as $T^{4.5}$ based on the model of the double exchange interaction, in which the phonon scattering probably has been considered.[12] Thus the curves of resistivity vs temperature can be fitted by the formula $\rho(T) = R_0 + R_E T^2 + R_M T^{4.5}$, where R_0 is the resistivity at absolute zero degree; coefficient R_E is related to electron-electron scattering and R_M related to magnon scattering. The fitting parameters are listed in Table III. Whether the sample is in an applied magnetic field or not, they decrease with increasing x. Which is probably due to both of the carrier density and the angle of Mn-O-Mn bond increases with increasing x. The Rietveld refinement of the XRD data showed that the Mn-O-Mn bond angle increased from 164.16° to 166.28° as x changed from 0.04 to 0.20. When an external magnetic field was applied to the sample, the R_0 and R_M that related to magnetic scattering decrease with increasing magnetic field. It indicates that the field drives the local momentum of Mn ions to orient in the direction of the applied magnetic field, and reduces the magnon scattering of carriers. The influence of the applied magnetic field on the coefficient R_E is weak relatively, which means that the magnetic field could not dramatically affect the electron-electron scattering. Especially, if x is more than 0.1, the electronic scattering could not be influenced by the external magnetic field at all.

TABLE II. x dependence of the activation energy E_0 (meV) of $La_{1-x}Te_xMnO_3$.

Doped level x		0.04	0.10	0.15	0.20
E_0 meV	$H = 0$ Oe	196	188	181	180
	$H = 40$ kOe	158	155	144	137

It is well known that the phase separation phenomenon, often taken place at low temperature, has been observed in hole-doped manganese oxide.[13–16] For an electron doped perovskite manganite compound, however, whether phase separation phenomenon exists was not known. In order to investigate phase separation in the temperature range between T_C and T_{MI}, the electron spin resonance (ESR) spectra versus

TABLE III. Fitting parameters of resistivity-temperature curve below Curie temperature.

Doped level x		0.04	0.10	0.15	0.20
$H=0$ Oe	R_0	84.7599	32.7476	12.50173	8.1735
	R_E	0.00381	0.00153	0.00050	0.00034
	R_M	4.8586×10^{-8}	7.5473×10^{-9}	1.8273×10^{-9}	1.0623×10^{-9}
$H=40$ kOe	R_0	38.9392	18.6206	7.14243	5.0622
	R_E	0.00342	0.00150	0.00054	0.00035
	R_M	7.773×10^{-9}	2.0323×10^{-9}	4.7558×10^{-10}	2.9733×10^{-10}

temperature were measured in the temperature range of 280 to 130 K for $La_{0.96}Te_{0.04}MnO_3$ powder sample, because its T_C is about 201 K and T_{MI} about 177 K. The absorption spectra are shown in Fig. 2(a), which reveals that the ESR spectrum is a single symmetric line at high temperature, and then it broadens and shows asymmetric as temperature below 230 K. The spectrum could be fitted by two Lorentzian curves, which is similar to the behavior of a layered manganites.[17] When $T<T_C$, a three-peaked structure [Fig. 2(b)], where the related components are labeled PM, FM1, and FM2, was observed. This structure develops and shifts to low field with decreasing temperature. As the temperature is lower than T_{MI}, the spectrum transforms into a single line, which means that the compound could be in a single ferromagnetic state. All spectra have been fitted by Lorentzian functions and the fitted parameters are showed in Fig. 3. Above 230 K, the compound is in the paramagnetic state and the ESR absorption spectrum is a single symmetric line, and the resonance field could be viewed as a linear function of temperature. However, the resonance field shows a nonlinear dependence of temperature as the temperature decreases continuously [Fig. 3(a)]. The linewidth is also the function of the temperature. Its temperature dependence above 230 K is similar to that in previous reports, and shows a linear dependence, which was interpreted by the spin-lattice relaxation mechanism.[18] As the temperature of the sample was lowered towards T_C, the sample was in two-phase coexisted state, and the linewidth of the paramagnetic component went through a minimum at $T_{\min}$, and then increased with decreas-

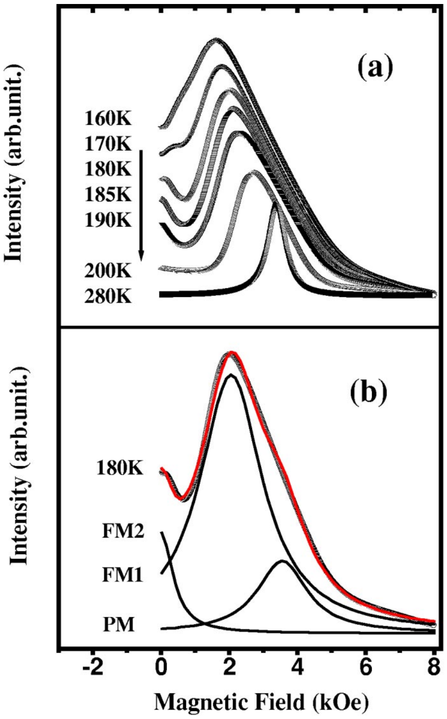

FIG. 2. (a) ESR absorption spectra of $La_{0.96}Te_{0.04}MnO_3$. The spectrum of at 280 K shows single Lorenzian line, the intensity was divided by 10. (b) ESR absorption spectra of $La_{0.96}Te_{0.04}MnO_3$ at 180 K. It was fitted by three lines, which were labeled with PM, FM1, and FM2 for paramagnetic and two ferromagnetic phases, respectively

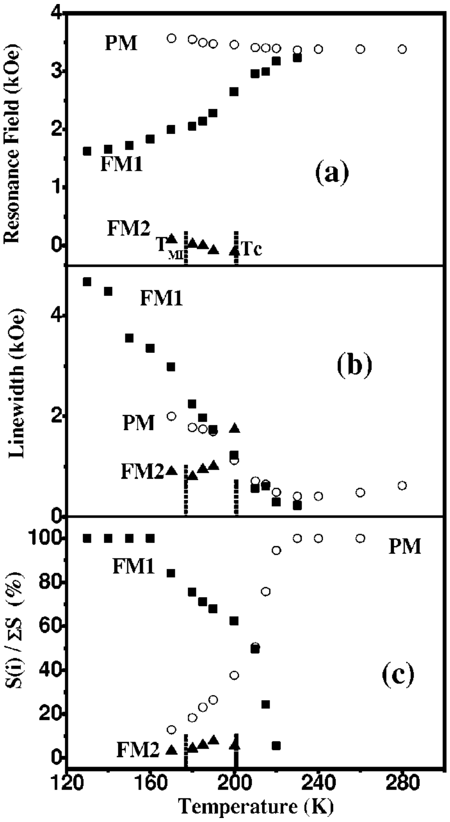

FIG. 3. Fitting parameters of ESR absorption spectra in the temperature range between 280 and 130 K. (a) Temperature curves of resonance field for paramagnetic phase PM and two ferromagnetic phases FM1, FM2. (b) Temperature curves of linewidth. (c) Integrated intensity ratio of PM, FM1, and FM2 phase. The intensity was normalized to the total integrated intensity of the spectrum.

ing temperature. $T_{\rm min}$ was about 230 K for $x=0.04$ sample. At the vicinity of T_C, the linewidths in both the PM and FM1 phase increased rapidly with temperature decreases. The temperature dependence of the linewidth of the PM component may originate from the hopping motion of small polarons[19,20] or the influence of the molecule field that results from the second phase (FM1). As mentioned above, the ESR spectrum could be fitted by two Lorentzian functions in the temperature range of 230 and 210 K. Which means that the compound is in a two phases (PM and FM1) coexisted state. For the second phase, as temperature approaches T_C, the ratio of the integrated intensity to the total integrated intensity of the spectrum rapidly increases with decreasing temperature [Fig. 3(c)]. It indicates that the volume of the second phase rapidly increases, which is probably due to the growing up of the dimension of the clusters. However, the resonance field and linewidth were not very sensitive to temperature and their values were close to that of the paramagnetic phase. Thus, the second phase can be considered as a superparamagnetic phase that consists of some small atomic clusters of ferromagnetic phase embryo in this temperature range, which eventually grows into ferromagnetic phase at T_C. The ESR absorption spectrum in the temperature interval of 200 and 170 K, as shown in Fig. 2(b), indicates that the sample is in a three-phase coexistence state. It reveals that the paramagnetic phase (PM) still exists below T_C, but its intensity reduces rapidly with decreasing temperature, and disappears at about 170 K. As temperature lower than Curie temperature, the ferromagnetic phase FM1 is the main component of the ESR spectrum. Its intensity increases and the resonance magnetic field shifts to low field side as temperature decrease. The FM2 could be either the second ferromagnetic phase or an antiferromagnetic phase because its resonance field localized at the vicinity of zero fields and the signal was too weak to elucidate component. However, the variation of its intensity and resonance field was observed. The intensity reduces and the resonance field of the FM2 component shifts to higher field with the lowering of temperature, and FM2 eventually merged into FM1 phase at about 170 K. The phenomenon of the three-phase coexistence and two-ferromagnetic-phase below T_C have been observed using muon spin relaxation, Mössbauer spectroscopy and NMR in hole doped manganites,[15,16,21] which pointed out that the volume of the ferromagnetic component of smaller hyperfine field decreased with decreasing temperature. However, our experiment results clearly revealed that the intensity (or volume) of the high internal field component (FM2) decreased with temperature and merged to the low internal field ferromagnetic phase (FM1) at the end. At $T=170$ K, residual PM1 and FM2 phase still were observed; the existence of these residual phases below T_{MI} may be due to the thermal hysteresis effect of phase transition. This kind of phase separation phenomenon in perovskite manganites probably results from the following reasons. First, it may be associated with some magnetic inhomogeneity of the samples arising from local variations of chemical composition or oxygen stoichiometry. Secondly, the carrier segregation induced the inhomogeneity of electronic distribution, which led to the carrier-rich FM regions and carrier-poor AFM zones.[22] Thirdly, above T_{MI}, the carriers were localized and formed polarons, which originated from the strong electron-phonon coupling mediated through the Jahn-Teller effect. According to the double exchange theory, a polaron is surrounded by ferromagnetic cloud to form a ferromagnetic elastic polaron. As the temperature lowering, the clouds extend spatially and eventually interact.[23] In the discussion, we ignored the effects of randomly oriented distribution of powder and demagnetization factor on the ESR line because such effects should not dominate the temperature dependence of the ESR line. Moreover, we only focused on the temperature range of 130 and 200 K, which covered both T_C and T_{MI}.

In summary, $La_{1-x}Te_xMnO_3$ is an electron-doped CMR material, which has exhibited excellent physical and chemical properties. The magnetoresistance ratio is about 63.5% at 40 kOe. The compound showed different electric transport mechanism in different temperature ranges. Above Curie temperature it was governed by the hopping of small polarons. Below the metal-insulator transition temperature, the resistance resulted from the electron and magnetic scattering. The study of ESR revealed that $La_{0.96}Te_{0.04}MnO_3$ was in paramagnetic phase above 230 K. As the temperature was lowed, it went through a paramagnetic and superparamagnetic phase and developed into a three-phase coexistence regime at T_C. This compound eventually transformed into a single ferromagnetic phase below 170 K. Based on the double exchange theory, the phase separation phenomenon was probably due to the inhomogeneity or ferromagnetic cloud surrounding the small polarons and extended with decreasing temperature.

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