Charge order and spin order of $\text{La}_{0.3}\text{Ca}_{0.7}\text{Mn}_{1-x}\text{W}_x\text{O}_3$ system

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Abstract The influences of W doping at Mn site on the charge order and spin order were studied by measuring $M$-$T$ curves, $M$-$H$ curves and ESR spectra of $\text{La}_{0.3}\text{Ca}_{0.7}\text{Mn}_{1-x}\text{W}_x\text{O}_3$ ($x = 0.00$, 0.04, 0.08, 0.12, 0.15) system. The results showed that: When $0.00 \leq x \leq 0.08$, the system exhibits charge ordering (CO) phase, and its spin order experiences the change of paramagnetism (PM)-charge ordering (CO)-antiferromagnetism (AFM) with decreasing temperature; when $x \geq 0.12$, the charge ordering (CO) phase melts, part of charge ordering (CO) phase remains in the paramagnetism (PM) background, the spin order of the system is mainly paramagnetism (PM), and ferromagnetic (FM) clusters appear at low temperature.

Keywords: charge order, spin order, melting, remains.

The colossal magnetoresistance (CMR) effect and charge ordering (CO) phenomenon in perovskite manganites have become very important research objects in the field of materials science. The charge ordering (CO) is that, in some materials with specific proportion of Mn ions and when the temperature is below a certain value (charge ordering temperature $T_{\text{CO}}$), there form the periodic arrangements of $\text{Mn}^{3+}$ and $\text{Mn}^{4+}$ in the real space in the system, and the carriers are strongly localized. Although this kind of manganese material is researched widely and profoundly, some fundamental problems of physical mechanism (such as the microscopic formation mechanism of CMR effect and charge ordering state) are still not very clear. In $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ system, when the doping amount of $\text{Ca}^{2+}$ ions is $0.5 \leq x \leq 0.875$, the system will exhibit charge, spin and orbit ordering states at low temperature. Many experiments showed that, with the occurrence of charge ordering transition, there occur abnormal changes in both the magnetic and electric properties of the system and the lattices. For example, with temperature decreasing to $T_{\text{CO}}$, resistivity increases sharply; specific heat capacity changes suddenly, and lattice constant changes drastically.

Doping ion with magnetism (such as Cr, Co, Ni, or Ru) at Mn site is an effective method to melt CO phase. The $\text{La}_{0.3}\text{Ca}_{0.7}\text{MnO}_3$ has charge, spin and orbit ordering according to Mori et al. As the radius of $\text{W}^{6+}$ is similar to that of $\text{Mn}^{3+}/\text{Mn}^{4+}$, we choose the substitution of W for Mn in $\text{La}_{0.3}\text{Ca}_{0.7}\text{MnO}_3$ ($0.00 \leq x < 0.15$) in the study of the process of the charge order melting and the spin order change with W increasing concentration. The results showed that: when $0.00 \leq x \leq 0.08$, the system exhibits charge ordering (CO) phase, and its spin order experiences the change of paramagnetism (PM)-charge ordering (CO)-antiferromagnetism (AFM) with decreasing temperature; when $x \geq 0.12$, the charge ordering (CO) phase melts, part of charge ordering (CO) phase remains in the paramagnetism (PM) background, the spin order of the system is mainly paramagnetism (PM), and ferromagnetic (FM) clusters appear at low temperature.

1 Experiments

Polycrystalline samples $\text{La}_{0.3}\text{Ca}_{0.7}\text{Mn}_{1-x}\text{W}_x\text{O}_3$ ($0.00 \leq x \leq 0.15$) were prepared by the solid–state reaction method. The preparing process is as follows: $\text{La}_2\text{O}_3$ with high purity was dewatered at 600℃ for 6 h (because $\text{La}_2\text{O}_3$ is prone to absorb moisture), then it was matched with the chemical reagents CaCO$_3$, MnO$_2$, WO$_3$ with high purity in nominal composition. They were sufficiently mixed and ground, and then prefired at 900℃ for 12 h. After being cooled naturally, the sample was taken out and carefully ground, and sintered respectively at 1050, 1150, 1300℃ for 12 h to obtain good crystallinity. The sample was pressed into pellets with a diameter of 13 mm and a thickness of about 1 mm. Then the samples with $x=0.00$, 0.04 were sintered at 1340℃ for 24 h; the samples with $x=0.08$, 0.12, 0.15 were sintered at 1400℃ for 24 h, and finally were all cut into samples of long-strip chunks.

Powder X-ray diffraction of the sample was carried...
out using a Japanese 18 kW diffractometer (MXP18-AHF) with Cu-Kα radiation (λ=0.1542 nm). Magnetization-temperature (M-T) curves were measured by an M-9300 vibrating sample magnetometer (VSM), which was made by Lake Shore Co. The samples were cooled to 5 K in zero field and measured in a magnetic field of 0.5 T under warming condition. Magnetization-magnetic field (M-H) curves were also measured by the VSM. Electron spin resonance (ESR) spectra were measured by a BRUKER ER-200D resonance spectrometer; powder samples were used; the microwave frequency was 9.61 GHz; the measured spectrum was differential absorption spectrum; and the measuring temperature range was 100–350 K.

2 Results and discussion

XRD measuring results of the samples showed that when $x \leq 0.15$ all the samples of La$_{0.3}$Ca$_{0.7}$Mn$_{1-x}$W$_x$O$_3$ ($0.00 \leq x \leq 0.15$) were in good single phase, and the substitution of W for Mn did not induce apparent structure change.

2.1 Charge order

Fig. 1 shows zero field cooling M-T curves of all the samples.

As shown in Fig. 1(a), for the undoped or low doped samples ($0.00 \leq x \leq 0.08$), the magnetism of the system strengthens when $x$ changes from 0.00 to 0.04, and the magnetism of the system weakens when $x$ changes from 0.04 to 0.08. Meanwhile, there is an apparent peak in M-T curve which is the apparent sign for the appearance of CO phase. The charge ordering transition temperature $T_{CO}$ corresponding to peak for the three samples are 262, 269 and 276 K respectively, and the M-T curves of the three samples all experience PM-CO-AFM transition with decreasing temperature. As shown in Fig. 1(b), when $x \geq 0.12$, the samples exhibit the magnetic behaviors which differ completely from those of low doped samples: the CO phase does not appear, the M-T curves do not exhibit PM-FM transition point either, the spin order of the system is always in PM state, FM clusters appear at low temperature range, and the peak site of the M-T curves is corresponding to the freezing of ferromagnetic clusters in arbitrary directions which leads to a decrease in the magnetization. These phenomena indicate that, accompanied by exquisite change of spin order, CO phase melts when $x \geq 0.12$.

As we know, for the undoped sample whose amount of Mn$^{4+}$ ions is in the range of 0.50 – 0.875, the system exhibits charge ordering arrangements of Mn$^{3+}$, Mn$^{4+}$ below $T_{CO}$. With decreasing temperature, the system exhibits AFM as well as CO phase. For the samples with $x = 0.04$, 0.08, the value of $T_{CO}$ increases gradually with an increase in W doping, indicating that CO phase is more stable. The reasons is that, when $x = 0.00$, the proper proportion of Mn$^{3+}$ and Mn$^{4+}$ is 0.30/0.70; with $x$ increasing, Mn$^{3+}$ ions increases gradually and Mn$^{4+}$ ions decrease gradually; when $x = 0.08$, Mn$^{3+}$/Mn$^{4+} = 0.46/0.46$, which is the best proportion of CO phase.

However, with the continuous increase in W doping, the amount of Mn$^{4+}$ ions decreases while the amount of Mn$^{3+}$ ions increases. When Mn$^{4+}$ ions are less than Mn$^{3+}$ ions, the ordering arrangement of Mn$^{4+}$/Mn$^{3+}$ is destroyed, which leads to the melting and disappearance of CO phase when $x \geq 0.12$. At the same time, as
the CO phase melts, the cruising property of $e_g$ electron becomes better. The cruising $e_g$ electron brings about the ferromagnetic interaction between Mn$^{3+}$ and Mn$^{4+}$, and then the system exhibits ferromagnetic clusters at low temperature range.

2.2 Spin order

(i) Macromagnetism. To research the spin state change of the system at different temperatures, we measured $M$-$H$ curves at typical temperatures for samples with $x \leq 0.12$, as shown in Fig. 2.

For the undoped sample, as shown in Fig. 2(a), the $M$-$H$ curves at $T_{CO}$ and other typical temperatures are strict straight lines, but the $M$-$H$ curves near $T_{CO}$ have larger slopes, which is in accordance with the PM-CO-AFM transition exhibited on the $M$-$T$ curve with $x=0.00$. When $T < T_{CO}$, the spin order of CO phase transforms from PM order into AFM order, only the minor PM left by AFM transition has contribution to measurement, and AFM phase cannot appear in actual measurement. So the slopes of the $M$-$H$ curves below $T_{CO}$ are much smaller than those of the $M$-$H$ curves above $T_{CO}$. For the sample with $x=0.04$, the $M$-$T$ curve exhibits FM composition at low temperature range, and so do the $M$-$H$ curves at 5, 50, 100 K. As shown in the inset of Fig. 2(b), the $M$-$H$ curves at 269 and 280 K are straight lines, which indicates that the system is in PM at and above $T_{CO}$. For the sample with $x=0.08$, as shown in Fig. 2(c), the $M$-$H$ curves at typical temperatures are similar to those of $x=0.00$, which indicates that the $M$-$T$ curve of the system also experiences PM-CO-AFM transition. For the sample with $x=0.12$, as shown in Fig. 2(d), the beginning parts of $M$-$H$ curves at 5 and 30 K exhibit FM characteristics, and the inset of Fig. 2(d) shows the PM characteristics of the $M$-$H$ curves above 75 K, which also indicates that a few ferromagnetic clusters exist in the paramagnetic background at low temperature.

The spin order change of the system is closely related to the proportion change and the occupation of

![Fig. 2. $M$-$H$ curves of samples La$_{0.7}$Ca$_{0.3}$Mn$_{1-x}$W$_x$O$_3$ ($0.00 \leq x \leq 0.12$). (a) $x=0.00$; (b) $x=0.04$; (c) $x=0.08$; (d) $x=0.12$.](image-url)
Mn$^{3+}$/Mn$^{4+}$ induced by doping. In 1955, Wollan and Koehler\cite{11} studied La$_{1-x}$Ca$_x$MnO$_3$ samples by neutron diffraction. They systematically analyzed several possible magnetic structures and the occupation of Mn$^{3+}$/Mn$^{4+}$, and gave the schematic diagrams of all the possible spin orders. According to the conclusions of Wollan and Koehler, we calculated the change conditions of Mn$^{3+}$, Mn$^{4+}$ with $x$ in the La$_{0.7}$Ca$_{0.3}$Mn$_{1-x}$W$_x$O$_3$ ($0.00 \leq x \leq 0.15$) system. For the sample with $x=0.00$, the proportion of Mn$^{3+}$/Mn$^{4+}$ is 0.30/0.70, and the sample contains 78% C-type AFM. Mn$^{3+}$/Mn$^{4+}$ in its cells is orderly arranged (the arrangement and spin conditions of Mn$^{3+}$, Mn$^{4+}$ in C-type AFM are shown in Fig. 3). In the rest 22% cells, the substitution of Mn$^{3+}$ for Mn$^{4+}$ will destroy the ordered arrangement and leads to spin disorder in the cells, so the $M$-$H$ curves in Fig. 2(a) exhibit PM state. For the sample with $x=0.04$, the proportion of Mn$^{3+}$/Mn$^{4+}$ is 0.38/0.58, the sample contains 51% C-type AFM and 49% random substitution of Mn$^{3+}$ for Mn$^{4+}$, and larger proportion of random substitution leads to the double-exchange interaction between Mn$^{3+}$ and Mn$^{4+}$ which forms FM property, so the $M$-$H$ curves at 5, 50 and 100 K exhibit FM property, strict PM relations are only exhibited at 269, 280 K higher than $T_{CO}$, and the comparatively high $M$ value of the sample with $x=0.04$ as shown in Fig. 1(a) also proves this. For the sample with $x=0.08$, the proportion of Mn$^{3+}$/Mn$^{4+}$ is 0.46/0.46, the sample is in complete CO phase, but this CO phase is the charge ordering in the clusters divided by W and belongs to short-range behavior. Although the system remains C-type AFM at low temperature, there is still a part of PM composition, so the $M$ value of $x=0.08$ in Fig. 1(a) is smaller than that with $x=0.04$. In addition, the $M$-$H$ curves of the sample with $x=0.08$ have very good linearity in the whole temperature range, and the slope near $T_{CO}$ is much larger than that at 5, 50, and 100 K, indicating that PM state decreases gradually and forms AFM at low temperature range, and AFM is so strong that it cannot be destroyed even at 6 T. The proportion of Mn$^{3+}$/Mn$^{4+}$ in the sample with $x=0.12$ is 0.54/0.34 and that in the sample with $x=0.15$ is 0.60/0.25, their CO phase disappears, and the system is divided into smaller clusters by W, but the double-exchange interaction between Mn$^{3+}$ and Mn$^{4+}$ in the clusters causes the spin state of the system at low temperature to exhibit a certain ferromagnetic property.

(ii) Micromagnetism. As we know, $M$-$T$ curves and $M$-$H$ curves are the macroscopic which reflects the microscopic statistical average. And to obtain more information of spin state we should carry out microscopic measurement. Therefore, we measured electron spin resonance (ESR) spectra of the system from 100 to 350 K, as shown in Figs. 4—7.

For the undoped sample, as shown in Fig. 4(a), the ESR spectra in the temperature range above 200 K are PM resonance lines with $g=2$, the intensity of PM resonance signal strengthens gradually when the temperature decreases from 300 to 280 K and weakens gradually when the temperature decreases from 270 ($T_{CO}$) to 100 K, which is in good accordance with the $M$-$T$ curve in Fig. 1(a). Obviously, the intensity weakening of PM resonance lines below $T_{CO}$ implies that the AFM appears and grows gradually because only the rest part of PM makes contribution to ESR. The ESR results also clearly indicate that when $T>T_{CO}$, the system is naturally in disordered state, in which the distribution at lattice points and the spins of Mn$^{3+}$, Mn$^{4+}$ both are random; when $T<T_{CO}$, Mn$^{3+}$/Mn$^{4+}$ are in orderly periodic arrangement, and their spins transform from disordered arrangement into AFM arrangement with decreasing temperature. The enlarged figure in Fig. 4(b) also shows that the resonance lines apparently shift to low field when $T<180$ K, which indicates that FM signal appears at low temperature range.

For the sample with $x=0.04$, as shown in Fig. 5, the main signal of ESR is very similar to that with $x=0.00$. But it is interesting that when $T$ is higher than 210 K the ESR lines are apparently composed of PM lines (denoted by straight lines) and FM lines (denoted by “↑” lines). When $T$ is lower than 200 K, the PM lines are submerged in ESR main lines, but the main lines are all located in low field with $g>2$. All this indicates that FM phase separates from PM phase both before and after the formation of CO phase. It is worth pointing out that in ESR spectra there is still FM phase separated from PM phase at 270 and 280 K above $T_{CO}$. This explains the fact that even when $T>T_{CO}$, Mn$^{3+}$/Mn$^{4+}$ are
Fig. 4. (a) ESR spectra of the sample ($x=0.00$); (b) enlarged figure at 100–180 K.

Fig. 5. (a) ESR spectra of the sample ($x=0.04$); (b) enlarged figure at 120–200 K.

in random arrangement, so spins of Mn$^{3+}$ and Mn$^{4+}$ are in disordered state and the system is in PM state, that is, FM fluctuation. Because PM lines are so strong as to cause a little FM to be submerged in the macroscopic measurement, the $M$-$H$ curves at high temperature range in Fig. 2(b) are only for PM. While below 200 K, not only does the intensity of PM lines weaken, and FM phase emerges gradually in the ESR spectra, but also FM phase can be measured and the slope of PM phase decreases greatly on $M$-$H$ curves.

For the sample with $x=0.08$, as shown in Fig. 6, the ESR spectra are very similar to those of the undoped sample in Fig.4, and they are PM resonance lines with $g$~2 in the whole measuring temperature range. But
with decreasing temperature, the intensity of resonance signal weakens gradually and faint FM resonance lines appear only below 160 K, but they are very difficult to be recognized even in enlarged Fig. 6(b), also indicating that the CO phase in clusters is more stable from the aspect of micromagnetism. In addition, the $M$-$H$ curves at all temperatures in Fig. 2(c) exhibit good straight lines, indicating that $M$ on the $M$-$T$ curve in Fig. 1(a) is completely caused by the PM, and AFM order at low temperature range is transformed from PM state.

For the sample with $x=0.12$, as shown in Fig. 7(a), the ESR curves are all PM lines in the measuring temperature range, because FM clusters appear below 100 K, while the minimum temperature of ESR measurement is 100 K. But the intensity of resonance signal strengthens gradually with the temperature decreasing from 300 to 230 K and weakens gradually with the temperature decreasing from 230 to 100 K, indicating that there is partial CO phase left in the PM background.

For the sample with $x=0.15$, as shown in Fig. 7(b), the ESR curves are all normalized PM lines in measuring temperature range, and the intensity of resonance signal strengthens gradually with decreasing temperature, indicating that not only does CO phase completely melt, but also the spin state of the system exhibits a certain FM with decreasing temperature. In fact, when $x=0.12$ ($0.15$), $\text{Mn}^{3+}/\text{Mn}^{4+}=0.54/0.34 (0.60/0.25)$, the formation of FM is advantageous.

### 2.3 Melting of charge order

The results of macroscopic and microscopic experiments above show that, with an increase in W doping, W not only divides Mn$^{3+}$, Mn$^{4+}$ of C-type AFM ordering arrangements into short-range categories, but also changes the proportion of Mn$^{3+}$/Mn$^{4+}$. When $x=0.00$, 0.04, 0.08, 0.12, 0.15, the proportion of Mn$^{3+}$/Mn$^{4+}$ changes gradually from 0.30/0.70, 0.38/0.58, 0.46/0.46 (which are of CO semiconductor) to 0.54/0.34, 0.60/0.25 (which are of FM metal). It is worth noticing that the FM property of the system strengthens in addition to the existence of CO phase when $x$ increases from 0.00 to 0.04. But the system is in complete CO phase when $x=0.08$. The FM metallic region of La$_{0.3}$Ca$_{0.7}$Mn$_{1-x}$WO$_3$ system is also different from that of the parent body La$_{1-y}$Ca$_y$MnO$_3$ (0.20 $\leqslant y \leqslant 0.50$). For example, $x=0.12$ in La$_{0.3}$Ca$_{0.7}$Mn$_{1-x}$WO$_3$ system is corresponding to $y=0.39$ in La$_{1-y}$Ca$_y$MnO$_3$ system. Under this condition, Mn$^{3+}$, Mn$^{4+}$ in La$_{1-y}$Ca$_y$MnO$_3$ system are arranged randomly, while the ESR results of La$_{0.3}$Ca$_{0.7}$Mn$_{1-x}$WO$_3$ system indicate the remains of CO phase. This shows that when $x \geq 0.12$ the CO phase in La$_{0.3}$Ca$_{0.7}$Mn$_{1-x}$WO$_3$ system disappears gradually. This is a melting process.

### 3 Conclusions

1. When $0.00 \leq x \leq 0.08$, the system has CO phase,
and the spin order of the system undergoes PM-CO-AFM change with decreasing temperature.

(2) When $x \geq 0.12$, the CO phase melts and partial CO phase remains in the PM background, the spin order of the system is mainly PM, and FM clusters appear only when temperature decreases.

(3) When $x = 0.04$, the short-range ferromagnetic order is separated from paramagnetic background.

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References

4. Ibarra, M. R., de Teresa, J. M., Blasco, J. et al., Lattice effects, stability under a high magnetic field, and magnetoresistive properties of the charge-ordered mixed-valence La$_{0.5}$Ca$_{0.5}$MnO$_3$ perovskite, J. Phys. Rev., 1997, 56B: 8252—8256.

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