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CRYSTAL STRUCTURE AND MAGNETIC PROPERTIES OF $La_{1.2}Sr_{1.8-x}Ca_xMn_2O_7$

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The effect of divalent cation substitution on the structure and magnetic properties of $La_{1.2}Sr_{1.8-x}Ca_xMn_2O_7$ (x = 0–0.900) is investigated in this paper. Partly replacing divalent cation Sr^{2+} by Ca^{2+} ions results in the weakening and then disappearance of long-range ferromagnetic ordering, and the formation of spin canting and low-temperature spin-glass. Based on structural analysis by Rietveld profile fitting, we suggest that this variation of magnetic property be related to a Jahn–Teller-type lattice distortion of MnO_6 octahedra due to the introduction of the smaller sized Ca^{2+} ions.

Keywords: structure, magnetic property, Jahn–Teller distortion
PACC: 7525, 7530, 7530E

I. INTRODUCTION

Mixed-valent manganese oxides have received much attention in recent years because of their strong coupling among lattice, spin and charge degrees of freedom, leading to colossal magnetoresistance (CMR).[1–6] While the three-dimensional perovskites (e.g., $La_{1-x}Sr_xMnO_3$) have been investigated for a long time, layered materials with a formula $La_{2-2x}Sr_{1-2x}Mn_2O_7$ are of special interest and importance because of the layered structure and their inherent anisotropic exchange interactions.[5–12]

The layered perovskites exhibit some interesting electronic, magnetic and structural properties which are very different from those of the ABO_3-type perovskites, such as the two-dimensional magnetic order and low-temperature CMR effect. These properties depend crucially on the doping level as well as the nature of the doping element. In the present understanding, the correlation between magnetism and conductivity in mixed valence manganese perovskites was originally explained by the double-exchange (DE) mechanism.[13] Recent theoretical and experimental work indicated the need to consider a strong electron-lattice coupling, due to dynamic Jahn–Teller distortions of the lattice, in order to account for the CMR effect that these materials exhibit.[14–17] It is found that when the doping level of bivalent ions at the A-site is kept constant, the main effect of the A-site substitutions is to change the structural parameters such as the Mn–O–Mn bond angle and Mn–O bond length in these perovskites (ABO_3). However, little attention has been paid to the relation of the Jahn–Teller-type lattice distortion of the MnO_6 octahedra and the magnetic properties in the layered perovskites. In particular, the Mn–O–Mn bond angle in the $(La,A)_3Mn_2O_7$ system is about 180° and it does not change significantly with internal and external pressure, in contrast to the (La, A)MnO_3 system where the bond angle is in the range of 155°–170°, which plays a crucial role in these perovskite compounds. Moreover, the bond length variation with external and internal pressure in $(La,A)_3Mn_2O_7$ and $(La,A)MnO_3$ is different.[18–21] Therefore the study of lattice effects on the transport and magnetic properties in the $(R,A)_3Mn_2O_7$ system might provide another idea for the fundamental understanding of the CMR properties. Chang *et al.*[19] found that T_C and T^* decrease with the increase of Ca content in $La_{1.4}(Sr_{1-x}Ca_x)_{1.6}Mn_2O_7$ ($x \leq 0.3$), due to the increase of the Mn–O(3) bond length.[19]

In this paper, we investigate the structure and magnetic properties of $La_{1.2}Sr_{1.8-x}Ca_xMn_2O_7$($x$=0–0.900), focusing on the special lattice distortion effects on the exchange interaction.

II. EXPERIMENTAL DETAILS

Bulk samples of $La_{1.2}Sr_{1.8-x}Ca_xMn_2O_7$ (x=0–0.900) were synthesized by the standard ceramic process. Stoichiometric amounts of La_2O_3, $CaCO_3$,

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$SrCO_3$ and $MnCO_3$ were mixed, ground, and calcined at 900°C for 24h in air with an intermediate grinding. The powder obtained was ground, pelletized, and sintered at 1350°C for 48h with an intermediate grinding. The samples were characterized by X-ray diffraction (XRD), and the crystal structures of all samples were refined with step-scanning XRD data using the Rietveld method. The magnetic measurements were performed on a SQUID magnetometer.

Ⅲ. RESULTS AND DISCUSSION

A. Structure

The XRD study indicates that all samples are of single phase with a $Sr_3Ti_2O_7$-type tetragonal structure ($I4/mmm$). The structural parameters are refined by the Rietveld technique. Figure 1 shows the experimental and calculated XRD patterns for the x=0.450 sample.

The structural parameters are shown in Fig.2. It is found that the lattice volume, cell parameters (a, c) and the ratio of c/a decrease with the increase of Ca^{2+} content x, which means that the cell parameter c contracts more quickly than a when the content x of the smaller Ca^{2+} ion increases.

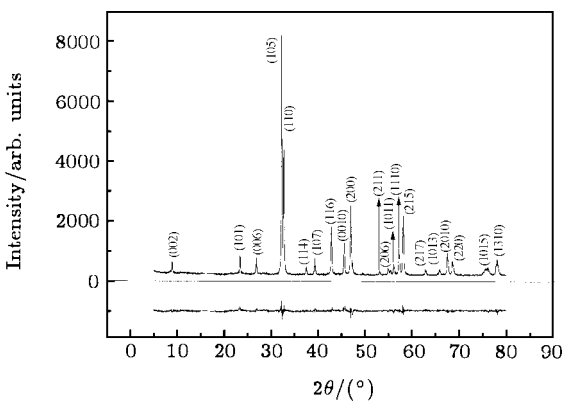


Fig.1. XRD pattern of $La_{1.2}Sr_{1.35}Ca_{0.45}Mn_2O_7$: crosses indicate the experimental data and the calculated profile is the continuous line overlying these. The lowest curve shows the difference between experimental and calculated patterns.

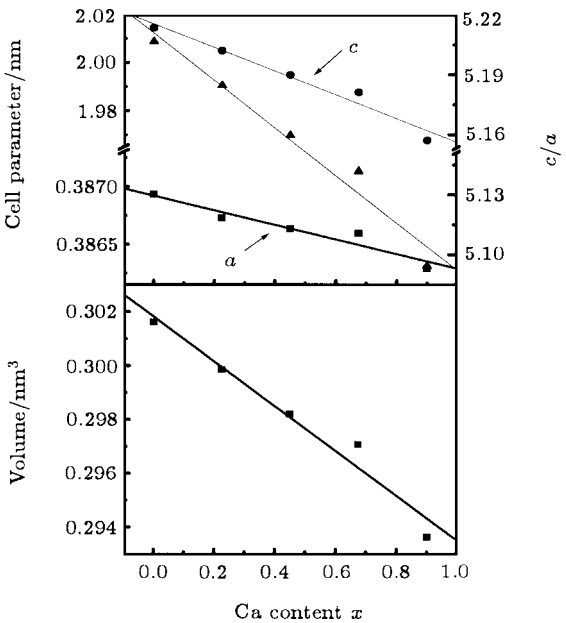


Fig.2. The variation of lattice parameters (a, c) and cell volume with Ca content x.

Table 1. The results of crystal structure refinement for all samples. R.WP and R.P denote weighted pattern R-factor and pattern R-factor, respectively.

Ca content x	0	0.225	0.450	0.675	0.900
a/nm	0.386932(23)	0.386728(21)	0.386635(14)	0.386594(11)	0.386290(17)
c/nm	2.01454(15)	2.00495(14)	1.99487(8.5)	1.98775(6.7)	1.96789(11)
Mn	(0, 0, 0.1011(29))	(0, 0, 0.1004(36))	(0, 0, 0.0997(14))	(0, 0, 0.0995(9.9))	(0, 0, 0.0989(13))
O(1)	(0, 0, 0)	(0, 0, 0)	(0, 0, 0)	(0, 0, 0)	(0, 0, 0)
O(2)	(0, 0, 0.2009(85))	(0, 0, 0.2010(92))	(0, 0, 0.2010 (40))	(0, 0, 0.2019(29))	(0, 0, 0.2026(36))
O(3)	(0,0.5, 0.0987(64))	(0,0.5, 0.0981(80))	(0,0.5, 0.0979(30))	(0,0.5, 0.0970(23))	(0, 0.5, 0.0975(28))
$d_{Mn-O(1)}$/nm	0.2037(5)	0.2014(7)	0.1988(2)	0.1976(2)	0.1947(2)
$d_{Mn-O(2)}$/nm	0.2010(18)	0.2017(15)	0.2023(8)	0.2037(15)	0.2041(7)
$d_{Mn-O(3)}$/nm	0.1935(0)	0.1934(0)	0.1933(0)	0.1934(0)	0.1932(0)
$\theta_{Mn-O(3)-Mn}$/(°)	175.184	177.93	177.92	177.09	178.34
Occu of La (P)	0.508	0.507	0.506	0.521	0.542
Occu of Sr/Ca (P)	0.492	0.493	0.494	0.479	0.458
Occu of La(P)	0.346	0.346	0.347	0.340	0.329
Occu of Sr/Ca(R)	0.654	0.654	0.654	0.660	0.671
R.WP	15.86	12.26	8.50	7.88	8.32
R.P	11.24	9.01	6.40	6.10	6.44

The results of crystal structure refinement are shown in Table 1 for all samples. There are three sites for O atoms, so three types of Mn–O bonds in the layered perovskite structure, i.e. the apical Mn–O(1) and Mn–O(2) bonds, and the equator Mn–O(3) bond. From Fig.3 we find that with increasing content x of the Ca^{2+} ion, the Mn–O(2) bond length increases while the Mn–O(1) and Mn–O(3) bond lengths decrease. Meanwhile the Mn–O–Mn bond angles remain almost unchanged. This special lattice distortion is different from that in ABO_3-type perovskites. It is obvious that this Jahn–Teller-type lattice distortion of the MnO_6 octahedra will affect the interlayer exchange interaction and lead to the change of the magnetic property.

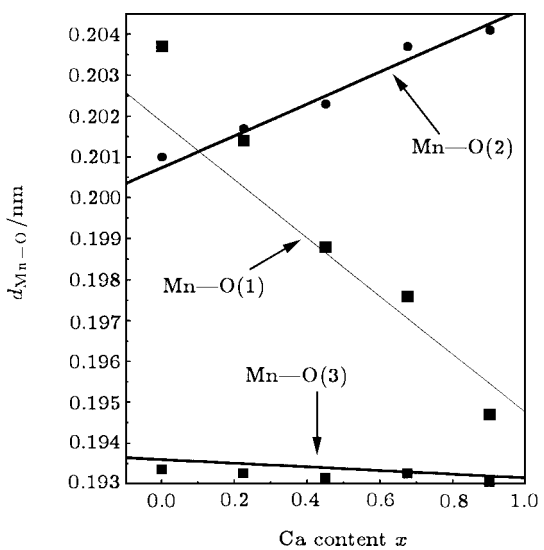


Fig.3. The variation of Mn–O bond lengths in $La_{1.2}Sr_{1.8-x}Ca_xMn_2O_7$ with Ca content x at room temperature.

B. Magnetic property

The temperature dependence of magnetization for $La_{1.2}Sr_{1.8-x}Ca_xMn_2O_7$ is shown in Fig.4. The undoped sample $La_{1.2}Sr_{1.8}Mn_2O_7$ shows two magnetic transitions at T_C ≈125K and T^* ≈250K, resulting from the three-dimensional ferromagnetic (FM) order and the two-dimensional FM order, respectively. When Ca^{2+} content increases, both T_C and T^* shift towards a lower temperature, and the spin-glass behaviour with a spin frozen temperature of 40K can be observed when $x \geq 0.450$, which is characterized by the discrepancy between field-cooled (FC) and zero-field-cooled (ZFC) magnetization at low temperature. It indicates the weakening of the FM order. At x=0.900 the long-range FM order disappears but the two-dimensional FM order still exists.

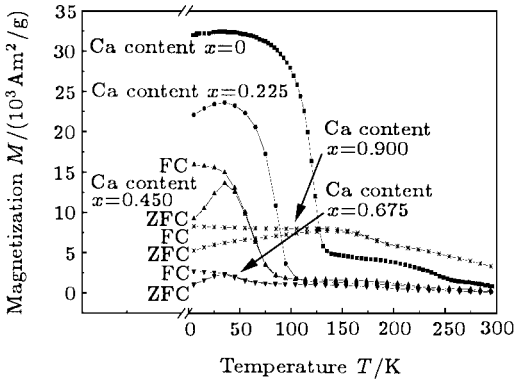


Fig.4. The temperature dependence of magnetization for $La_{1.2}Sr_{1.8-x}Ca_xMn_2O_7$, where the measuring field is 0.05T.

The field dependence of magnetization at 5K for $La_{1.2}Sr_{1.8-x}Ca_xMn_2O_7$ is plotted in Fig.5. A strong FM order is observed for x=0–0.225, but the spontaneous magnetization drops for x >0.225, showing that the long-range FM order is frustrated or destroyed, and spin canting occurs.

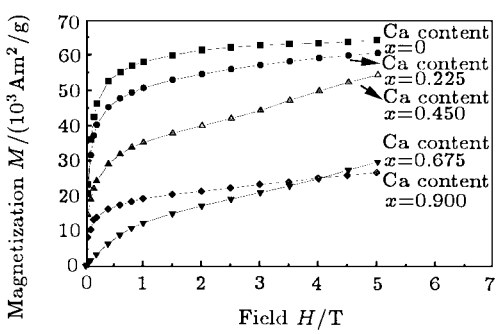


Fig.5. The field dependence of magnetization at 5K for $La_{1.2}Sr_{1.8-x}Ca_xMn_2O_7$.

The variation of magnetic properties in Ca-doped $La_{1.2}Sr_{1.8-x}Ca_xMn_2O_7$ can be understood as follows. The structure refinement results described above show that the substitution of Sr by the smaller Ca results in the changes of the Mn–O bond length, and the lengthening of the Mn–O(2) bond length reduces the exchange interaction between bilayers, which lowers the three-dimensional spin ordering temperature T_C and further strengthens the anisotropy of the exchange interaction. The exchange interaction between interlayer Mn ions is reduced by the total effects of the weakening of the interlayer exchange interaction contributed by the changes of Mn–O(2), Mn–O(1) and Mn–O(3) bonds, which results in the drop of two-dimensional spin ordering temperature T^* and the

appearance of the canted ferromagnetic ordering and clusters of spin-glass arrangement along with the increase of Ca^{2+} content x.

IV. CONCLUSIONS

The substitution of Ca for Sr in $La_{1.2}Sr_{1.8}Mn_2O_7$ results in the weakening and then disappearance of long-range FM ordering, the formation of FM clusters and spin canting or fluctuation. These variations of magnetic property are related to the Jahn–Teller-type lattice distortion of MnO_6 octahedra due to the introduction of the smaller Ca^{2+} ion.

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