Structure—Properties Relationships for Manganese Perovskites

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Structure--Properties Relationships For Manganese Perovskites

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ABSTRACT
By combining the results of dc magnetization, ac susceptibility, magnetoresistivity, magnetostriction, and x-ray and neutron powder diffraction data for stoichiometric La$_{1-x}$Sr$_x$MnO$_3$ we have constructed a phase diagram that describes the magnetic, transport, and structural properties and the relationships among them as a function of composition and temperature. Correlations among physical and structural properties have been observed that are consistent with a competition between ferromagnetism and JT distortion. A metallic state occurs below the Curie temperature when both coherent and incoherent JT distortions are suppressed.

INTRODUCTION
For several decades the La$_{1-x}$A$_x$MnO$_3$ (A = Sr, Ba, Ca) compounds have been considered a classical example of materials for which the interactions between electrons are mediated mostly by magnetic super- and double-exchange interactions.[1-3] Recently, increased interest has been generated for these compounds because of a colossal magnetoresistive effect for the ferromagnetic phase (x $\geq$ 0.1) near the Curie temperature, $T_c \sim 140 - 380$ K.[4] Renewed theoretical work has shown that the explanation of the transport and magnetic properties requires consideration of electron-phonon couplings in addition to magnetic interactions.[5-7] For LaMnO$_3$, a high-spin electronic configuration $t_{2g}^3e_g^1$ for the Mn$^{3+}$ ions with core-like $t_{2g}$ states and extended $e_g$ orbitals is susceptible to a strong electron-phonon coupling of the Jahn-Teller (JT) type that splits the $e_g$ states into filled $d_{2g}$ and empty $d_{x^2-y^2}$ orbitals, and, thus, produces large asymmetric oxygen displacements around the Mn ions. The super-exchange interaction that induces ferromagnetic coupling within the Mn-O planes between JT-
ordered orbitals of dissimilar symmetry and antiferromagnetic coupling perpendicular to the planes between orbitals of the same symmetry produces A-type, 3-dimensional antiferromagnetic structure. With substitution of divalent elements for La, electrons are removed from the d_{z^2} orbital causing weakening of both the JT-electron-phonon coupling and the superexchange interaction. Empty states in the e_g orbitals allow for the "breathing-mode" electron-phonon coupling of the charge ordered type that can produce charge localization and a double-exchange ferromagnetic interaction that favors metallic state.[3,8,9]

Competition between magnetic and electron-phonon interactions and structural transitions results in a very rich structure-property phase diagram for substituted LaMnO_3 materials.[10-12] Upon substitution of Sr, La_{1-x}Sr_xMnO_3 transforms from an antiferromagnetic insulator to a ferromagnetic insulator at x ≈ 0.1 and to a ferromagnetic metal at x ≈ 0.16. The Curie temperature increases from ~ 150 K for x = 0.1 to ~ 300 K for x = 0.2, and to ~380 K for x = 0.3. Three crystallographic phases have been identified at room temperature. For pure and lightly substituted materials, the orthorhombic Pbnm structure (O'), characterized by large coherent orbital ordering of the JT-type was found.[10,11,13-16] Above x = 0.08 - 0.12, a phase (O*) with the same orthorhombic Pbnm structure but characterized by a considerably smaller coherent JT-orbital ordering is observed.[10,11] At higher Sr substitution level, x = 0.16 - 0.18, the rhombohedral R3m structure (R), characterized by the absence of a coherent JT orbital ordering, was observed.[10]

The reported values of the compositions and temperatures for the structural, magnetic and resistive transitions vary substantially in the literature, depending on the sample processing method and synthesis conditions.[17] The discrepancies among existing phase diagrams may result from comparing behavior of compositions that are incorrectly assumed to have the same doping level.[18,19] We have recently shown that there can be large deviations from nominal stoichiometry for low and moderate substitution levels (0 ≤ x ≤ 0.3) - the perovskite structure can form a large concentration of vacancies, v, on both the La and Mn sites during synthesis under oxidizing conditions. Since the physical and structural properties are complex and are very sensitive to the hole concentration, we have established the intrinsic phase diagram
(see Fig. 4) as a function of the hole doping; i.e., as a function of the Sr substitution level for samples that contain no metal-site vacancies (v = 0). [20-22]

SAMPLE PREPARATION AND CHARACTERIZATION

Polycrystalline samples of La$_{1-x}$Sr$_x$MnO$_3$ with $0.1 \leq x \leq 0.2$ and $\Delta x = 0.005$, were synthesized using a wet-chemistry method that leads to homogenous mixing of the metal ions. The final firing temperatures and oxygen atmosphere as well as holding times and cooling rates for obtaining stoichiometric samples were determined from TGA measurements performed using slow heating (2 deg/ min.) and cooling (0.6 deg/ min.) rates. Figure 1 shows the oxygen contents from TGA data for a sample with $x = 0.185$. The materials obtained after slow cooling in 100 and 20 % O$_2$ have the effective oxygen contents substantially above 3. Using the measured oxygen contents shown on Fig. 1, the vacancy concentrations of these samples can be estimated (assuming equal amounts on both metal sites) as $v = d/(d+3)$. The weights of the samples approached stable levels, indicating a stoichiometric oxygen content of 3.002±0.002 for temperatures around 1360 C. Stoichiometric La$_{1-x}$Sr$_x$MnO$_3$ samples were prepared in air by quenching from high temperatures, 1450 C for $x = 0.10$, and gradually lower temperatures for samples with larger $x$, to 1350 C for $x = 0.20$. Powder x-ray diffraction at room temperature confirmed single-phase material in each case and was used to determine structural phase boundaries. The $x = 0.10$ sample is orthorhombic-O' and a transition from the orthorhombic O' to the O* structure occurs around $x = 0.11$. The $x = 0.115$ composition is mixed phase, mostly O*. Compositions from $x = 0.12$ to 0.165 are pure orthorhombic O*. A transition from the orthorhombic O* phase to rhombohedral phase occurs for the $x = 0.17$ composition. Above $x = 0.17$, samples are rhombohedral.

PROPERTIES OF La$_{0.835}$Sr$_{0.165}$MnO$_3$

We have constructed the structure-properties phase diagram by combining the results of physical property and structural measurements. The magnetic and structural phase transitions were found to exhibit distinctive signatures in each kind of measurement. In Fig. 2 is shown magnetization and resistivity data for an $x = 0.165$ sample for which the ferromagnetic transition appears in the orthorhombic O* structure. Two features are seen in the magnetic data (Fig. 2a): The clearly visible ferromagnetic
transition at $T_c = 256$ K and the less apparent decreased-magnetization anomaly at $T_s = 125$ K. Both transitions can be precisely defined for small magnetic fields ($\sim 20$ Oe) from the largest slope of the $M(T)$ curves. These magnetic transitions are clearly correlated with the resistive transitions (Fig. 2b), the sharp drop of resistivity at $T_c$, and the metal-insulator transition at $T_s$. In addition, the resistivity and ac susceptibility have shown anomalies at $T_r = 310$ K that correspond to the rhombohedral-orthorhombic (R-O*) structural transition. Magnetization and resistivity data obtained for other La$_{1-x}$Sr$_x$MnO$_3$ samples showed similar transitions at consistently changing temperatures allowing the correlated transport, magnetic, and structural phenomena to be characterized for each kind of phase transition that occurs in this system.

The neutron diffraction technique was used to accurately determine bond lengths, bond angles, and incoherent oxygen displacements. The pattern of the coherent displacements and the symmetry of the incoherent displacements have been used to obtain information about polaronic electron-phonon interactions in both the paramagnetic and ferromagnetic phases. Figure 3 shows the Mn-O bond lengths and the anisotropic Debye-Waller parameters for La$_{0.635}$Sr$_{0.165}$MnO$_3$. The sample is rhombohedral at high temperature, 340 K, and all Mn-O bonds are of equal length; i.e., there is (by symmetry) no coherent JT distortion for this phase. The Debye-Waller parameter is isotropic with magnitude that indicates the presence of incoherently distorted Mn-O$_6$ octahedra. On cooling below 340 K, the rhombohedral structure changes to orthorhombic O* with a small coherent JT distortion, $\sim 0.01$ Å. The average bond length increases significantly. These structural changes are consistent with increased resistivity at $T \sim 312$ K in the paramagnetic phase upon the transition from the rhombohedral to O* phase. On further cooling, an abrupt decrease of the lattice parameters appears at the ferromagnetic transition temperature $T_c \sim 256$ K. The individual Mn–O bond lengths do not show clear drops below $T_c$ and the coherent Jahn-Teller distortion remains practically unchanged. However, below $T_c$, the average Mn-O bond length shows a slight decrease, $\sim 0.003$ Å. Simultaneously, the average bond angle displays a slight increase, $\sim 0.4$ degrees. The incoherent JT distortion along the Mn-O bond shows a slight decrease. The sharp drops of resistivity at the ferromagnetic transition can be explained, thus, as resulting from removal of charge localization below $T_c$ by a strong electron-phonon JT-coupling and a narrowing of the band-width in
addition to removal of the spin scattering by double-exchange. On cooling below ~ 160 K, an additional structural change takes place in the ferromagnetic phase. The temperature range of this structural change correlates very well with the resistive and magnetic anomalies which can be clearly identified with the vestiges of the structural O* to O' change. The equatorial bonds show an abrupt change that indicates an increase of the coherent JT distortion from ~ 0.01 to ~ 0.03 Å. All these changes are consistent with the O* to O' transition that is suppressed in the ferromagnetic state. The average bond-length shows a slight increase and the average bond angle displays a slight decrease on cooling. These changes are, again, consistent with the more insulating bonds in the O' phase as seen by the metal-insulator resistive transition.

The magnetic structure and its correlation with the coherent JT distortion have been studied as a function of temperature using neutron powder diffraction, magnetoresistance, and magnetostriction. A correlation between the ferromagnetic spin orientation and the coherent JT distortion was observed, indicating a coupling between the structural and magnetic properties. Fig.3(c) shows the refined spin angle φ with respect to the crystallographic c-axis. For the La_{0.835}Sr_{0.165}MnO_3 sample one can observe simultaneous transitions for both the spin orientation and the coherent JT distortion. Above 160 K, where the coherent JT distortion is very small, the refined spin angle, φ, is ~ 18°. The spin angle jumps to 40° at 120 K and remains at this value to the lowest temperature, while the JT distortion reaches its maximum value at ~ 120 K and remains constant to the lowest temperature. The magnetoresistance data have shown that the corresponding metal-insulator transition in the ferromagnetic phase is practically insensitive to applied magnetic field. On the other hand, the temperature of the ferromagnetic transition temperature increases from 256 K at 0 T to 290 K at 7 T. With increasing magnetic field the ferromagnetic transition begins to overlap with the resistive anomaly originating from the structural R/O* transition in the paramagnetic phase. As a result the resistive anomaly caused by the structural R/O* transition is clearly suppressed. The magnetostriction measurements are consistent with these observations. For x = 0.165, the pronounced minimum at 250 K is clearly observed only at 0 T. At a magnetic field of 5 T the minimum is reduced and broadened and at 10 T it is not observable at the highest temperatures of our measurements (300 K).
observed large change of magnetostriction indicates considerable changes of the lattice constants during the ferromagnetic transition for the La$_{0.835}$Sr$_{0.165}$MnO$_3$ sample with the O* structure as seen from neutron diffraction.[20] Similar rapid decreases of lattice constants and anisotropic Debye-Waller factors were observed for the La$_{0.75}$Ca$_{0.25}$MnO$_3$ sample with O* structure, and interpreted in terms of removal of the incoherent JT-distortions during the ferromagnetic transition.[23] The broad maximum of magnetoresistance was observed in the temperature range 120 - 135 K to be practically independent of magnetic field. Thus, it appears that when the structural O*/O' transition occurs in the ferromagnetic phase, no additional structural changes are induced by the external magnetic fields up to 10 T.

PHASE DIAGRAM

Based on similar data obtained for the whole series of samples, the following structure-properties relationships were developed for moderately substituted La$_{1-x}$Sr$_x$MnO$_3$. In the high temperature paramagnetic regime three structural phases are present: Orthorhombic Pbnm structure characterized by the large coherent orbital ordering of the JT-type and small incoherent JT-distortions, Orthorhombic Pbnm structure characterized by a small coherent JT-orbital ordering and large incoherent JT-distortions, and Rhombohedral R3m structure characterized by the absence of a coherent JT-orbital ordering and large incoherent JT-distortions. For $0.10 < x < 0.145$, during the ferromagnetic transition, the orthorhombic O' phase changes to an orthorhombic O'' phase characterized by suppressed coherent JT-orbital ordering and large incoherent JT-distortions. For $0.15 < x < 0.17$, on cooling during the ferromagnetic transition the insulating orthorhombic O* phase changes to a metallic O* phase characterized by small coherent and small incoherent JT-distortions. Below the Curie temperature, in the ferromagnetic phase, this orthorhombic O* phase changes to an orthorhombic O'' phase characterized by suppressed coherent JT-orbital ordering and large incoherent JT-distortions that is insulating. For $0.175 < x < 0.20$, on cooling during the ferromagnetic transition the semiconducting R phase changes to a metallic R phase with small incoherent JT-distortions. Below the Curie temperature, in the ferromagnetic phase, this R structure changes to an orthorhombic Pbnm structure O* characterized by small coherent JT-orbital ordering and small incoherent JT-distortions that is still
metallic. Development of ferromagnetic order, thus, suppresses the coherent JT-
distortions for the O' phase and incoherent distortions for the O* and R phases. The
arrangement of the spins varies from ferromagnetic ordered mainly along the b-axis (x =
0.11) to ferromagnetic almost along the c-axis (x = 0.185) in the Pbnm symmetry.

The data clearly show that the ferromagnetic phase has lower resistivity than the
paramagnetic phase. However, the ferromagnetic transition is accompanied by
structural changes that can also cause a decrease of resistivity. The suppression of
coherent JT-distortions lowers the resistivity but is not sufficient to produce a metallic
phase unless large incoherent JT-distortions are also removed. The electron-phonon
Jahn-Teller interactions and the magnetic super-exchange and double-exchange
interactions are of similar strength. These interactions compete for the same eg
electrons and, thus, lead to colossal spin-charge-lattice coupling.

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REFERENCES

FIGURE CAPTIONS

Fig. 1  Oxygen contents in 1, 20, and 100 % O₂ from thermogravimetric measurements for La₀.₈₃₅Sr₀.₁₆₅MnO₃₊δ sample. The data were obtained during slow cooling at 0.6 deg/min.

Fig. 2  Magnetization in a 20 Oe applied field (a) and resistivity (b) and for the La₀.₈₃₅Sr₀.₁₆₅MnO₃ sample.

Fig. 3  Refined structural and magnetic parameters from neutron powder diffraction measurements as a function of temperature for La₀.₈₃₅Sr₀.₁₆₅MnO₃ sample: (a) Mn-O bond lengths and their average value, (b) anisotropic Debye-Waller factors perpendicular and parallel to Mn-O bond, and (c) spin angle with respect to crystallographic c-axis.

Fig. 4  Phase diagram summarizing the magnetic and structural properties of La₁₋ₓSrₓMnO₃ as a function of composition, 0.10 ≤ x ≤ 0.2, and temperature, 12 ≤ T ≤ 350 K. O’, O”, O‘*, and R stand for the small coherent JT-distorted orthorhombic (σJT ~ 0.004 Å), large coherent JT-distorted orthorhombic (σJT ~ 0.05 Å), suppressed coherent JT-distorted orthorhombic (σJT ~ 0.02 Å), and the rhombohedral phases, respectively.
Fig. 1
Fig. 2
Fig. 3

(a) Mn-O bond length (Å) vs. temperature (K)

(b) Anisotropic $U(O_{eq})(Å^2)$ vs. temperature (K)

(c) Spin angle (°) vs. temperature (K)

Temperature (K): 0 50 100 150 200 250 300 350

Mn-O bond lengths: $Mn-O_{eq1}$, $Mn-O_{eq2}$, $<Mn-O>$

Anisotropic $U(O_{eq})$: $U_{par}$, $U_{perp}$

Spin angles: $La_{0.835}Sr_{0.165}MnO_3$