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Possible Role of Disorder on Magnetostructural Transition in $La_{1-x}Ba_xMnO_3$

N. G. Kim and J. H. Jung*

Department of Physics, Inha University, Incheon 402-751, Korea

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Magnetic field induced structural transition has been systematically investigated for $La_{1-x}Ba_xMnO_3$ with the fine control of carrier doping ($0.15 \le x \le 0.20$). Application of a magnetic field results in the suppression of the rhombohedral-orthorhombic transition temperature (T_S) and the increase of insulator-metal transition temperature (T_{MI}). Near $x = 0.17$, where T_S is similar to T_{MI} at zero magnetic field, we found that the T_S smoothly decreased with magnetic field even though it intersected the T_{MI} near 3 T. Also, the magnetostructural phase diagram obtained from the temperature sweep and from the magnetic field sweep is not significantly modified. By comparing the magnetostructural transition in $La_{1-x}Sr_xMnO_3$, we have suggested that the large disorder originated from ionic size differences between La and Ba may weaken the sensitivity of the kinetic energy of e_g electrons on the degree of lattice distortion in $La_{1-x}Ba_xMnO_3$.

Keywords : magnetostructural transition, $La_{1-x}Ba_xMnO_3$, disorder

1. Introduction

During the last decade, doped manganites with perovskite structure, i.e., $R_{1-x}A_xMnO_3$ (R=trivalent rare-earth ions and A=divalent ions) have been widely investigated due to their unique physical properties and possible applications [1]. The interest in these materials stems from colossal magnetoresistance, however, they also exhibits many other interesting phenomena such as charge ordering, phase separation, and so on [2]. The basic mechanism has been explained by the double-exchange model for the coexistence of ferromagnetism and metallicity [3]. However, extensive studies have suggested the importance of cooperative interplays among the charge, spin, lattice, and orbital degrees of freedom [4-6].

One of the intriguing physical properties in doped manganites is a structural phase transition due to external stimuli, such as magnetic field and pressure. Magnetostriction has been reported to be orders of magnitude larger than other materials and it does to be closely related with metallicity. Especially, Asamitsu *et al.* have reported the magnetic field induced structural transition, named magnetostructural transition, from the rhombohedral to orthorhombic structures in $La_{1-x}Sr_xMnO_3$ [7]. According to their works, such transition pronounces for the narrow doping level, e.g., x=0.170, where magnetic field induced magnetization differs in both phases whose free energies are nearly degenerate at zero magnetic field. Due to such limitation, the reports on other manganites are quite rare [8-10] which prevents the further understanding on this intriguing phenomenon.

In this paper, we have systematically investigated the magnetostructural transition in $La_{1-x}Ba_xMnO_3$ ($0.15 \le x \le 0.20$) by using resistivity and magnetization measurements. We have observed the smooth change of structure from rhombohedral to orthorhombic phases with magnetic field for all doping levels, including $x = 0.2$ [8, 9]. By comparing the reports on $La_{1-x}Sr_xMnO_3$, we have suggested the possible role of disorder on the magnetostructural phenomenon in $La_{1-x}Ba_xMnO_3$.

2. Experiments

We have prepared $La_{1-x}Ba_xMnO_3$ single crystals by the floating-zone method. Polycrystalline rods, typically 60 mm × 5 mmφ, were prepared with the prescribed ratios of high-purity La_2O_3, $BaCO_3$, and Mn_3O_4 powders at 1370 °C. Using a halogen lamp image furnace, the crystals were successfully grown in air with feeding speed of 5-10 mm/h [11]. X-ray powder diffraction measurements showed that all the crystals were in single phases. By using an electron-probe microanalysis, we have confirmed that their chemical compositions were close to stoichi-

*Corresponding author: Tel: +82-32-860-7659,
Fax: +82-32-872-7562, e-mail: jhjung@inha.ac.kr

ometric values. For the resistivity measurement, the crystal was cut into a rectangular shape and the electrical contact was done by the silver paint with heat treatment at 550 °C. We have measured the temperature and magnetic field dependent resistivity and magnetization by using the four probe method and by the superconducting quantum interference device magnetometer, respectively.

3. Results and Discussion

Fig. 1 shows the temperature dependent resistivity for $La_{1-x}Ba_xMnO_3$ at selected magnetic fields, i.e., temperature sweep. At zero magnetic field, the samples show the typical insulator-metal transition T_{MI} with paramagnetic-ferromagnetic transition T_C near 200~250 K, as marked with solid triangles. And then, they finally show the insulating behaviors at low temperature as similar to lightly doped manganites [12]. In addition to the insulator-metal transition, one may notice a jump in resistivity for all compositions with hysteresis, as marked with open triangles. The temperature significantly moves to the lower temperature with doping level x as well as with magnetic field.

The resistivity jump has been known to be originated from the structure transition T_S, i.e., from the rhombohedral structure at high temperature to the orthorhombic one at low temperature [7, 8]. The decrease of T_S with magnetic field and the low (high) resistivity values during the cooling (warming) run, therefore, implies the preference of rhombohedral phase for the hopping of e_g electrons. This result is consistent with the fact that a tolerance factor in rhombohedral phase is larger than that in orthorhombic phase [7]. Note here that, the T_S intersects the T_{MI} in x = 0.17 near 3 T. However, the T_S does not intersect the T_{MI} in other compositions up to 7 T.

In accompanying the structure transition, the magnetization also changes with hysteresis during cooling (solid circles) and warming runs (open circles) [see, inset of Fig. 1(c)]. In the hysteresis region, the value of magnetization during the cooling run is larger than that during the warming run. It implies that the low resistivity state, i.e., rhombohedral phase, prefers high magnetization while the high resistivity state, i.e., orthorhombic phase, does low magnetization.

Fig. 2(a) shows the magnetic field dependent structural transition temperatures for x = 0.15, 0.17, and 0.20 in $La_{1-x}Ba_xMnO_3$, obtained from resistivity measurement during the cooling run T_{SC} (solid symbols) and warming run T_{SW} (open symbols). The rhombohedral (R) structure at high temperature changed into orthorhombic (O) one at low temperature with the hysteresis region. As the

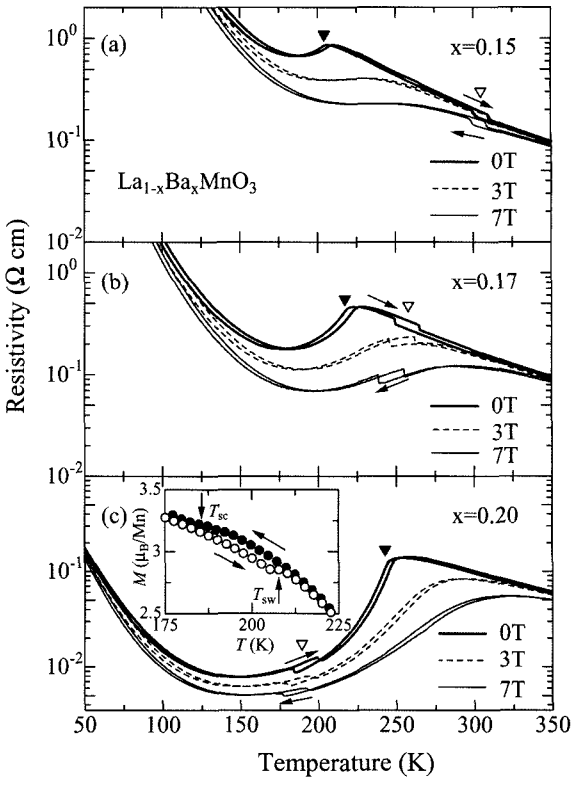

Fig. 1. Temperature dependent resistivity for $La_{1-x}Ba_xMnO_3$ single crystals with (a) x = 0.15, (b) 0.17, and (c) 0.20 at selected magnetic fields. The open and filled triangles represent the structural phase transition and the Curie temperatures, respectively. In the inset of (c), the temperature dependent magnetization is also shown under cooling (solid circles) and warming runs (open circles).

magnetic field increases, both T_{SC} and T_{SW} tend to be lowered with slight changes in hysteresis regions. The amount of the T_{SC} (T_{SW}) changes at 7 T are strongly depend on the doping levels, i.e., 3 (3 K), 17 (13 K), and 7 (8 K) for x = 0.15, 0.17, and 0.20, respectively.

To investigate the behaviors of T_S with magnetic field in detail, we show normalized values of T_{SC} at each magnetic field with respect to that in zero field, i.e., $T_{SC}(H)/T_{SC}(0)$ [Fig. 2(b)]. The values of $T_{SC}(H)/T_{SC}(0)$ range from 0.99 to 0.94 depending on x, however, they are apparently linearly decreased with magnetic field as denoted by dashed lines. [The same behavior was confirmed for $T_{SW}(H)/T_{SW}(0)$.] The values of $T_{SC}(H)/T_{SC}(0)$ are not systematically changed with doping x, but maximized near x = 0.17 and 0.18, and minimized near x = 0.15 and 0.16. From the systematic analysis of T_S and T_C with x at zero magnetic field (not shown), we have found that the former and the latter systematically decreases and increases with doping, respectively. And, the T_S and T_C meets near x = 0.17 and 0.18 [see, Fig. 1].

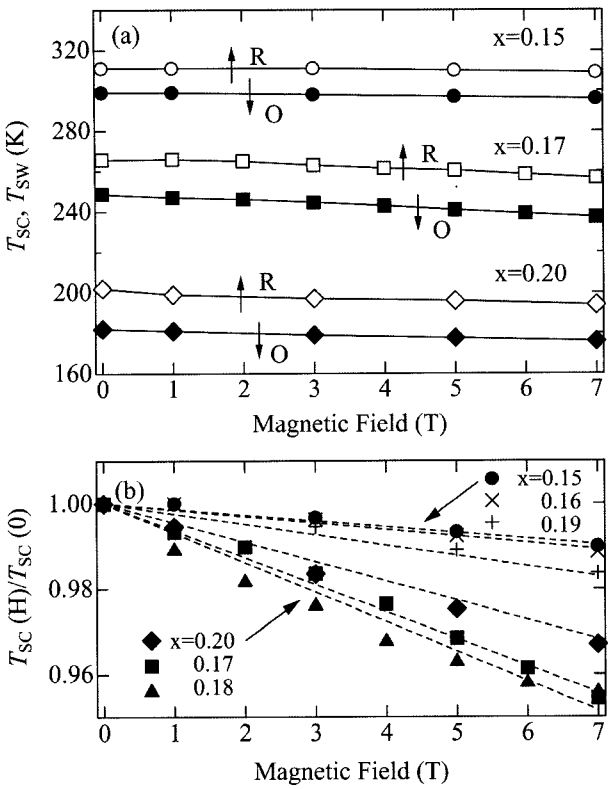

Fig. 2. (a) Magnetic field dependent rhombohedral (*R*)-orthorhombic (*O*) transition temperatures for x = 0.15, 0.17, and 0.20 in $La_{1-x}Ba_xMnO_3$. The solid and open symbols represent the T_S obtained from cooling (T_{SC}) and warming runs (T_{SW}), respectively. (b) Normalized values of magnetic field dependent T_{SC} with respect to zero field, i.e., $T_{SC}(H)/T_{SC}(0)$. In (b), dashed lines are merely guides for an eye.

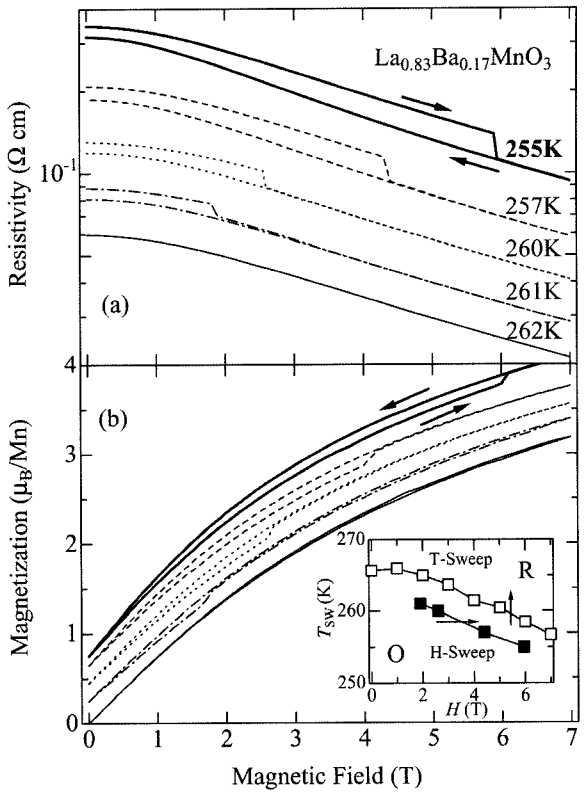

Fig. 3. Magnetic field dependent (a) resistivity and (b) magnetization for $La_{1-x}Ba_xMnO_3$ (x = 0.17) at selected temperatures. For clarity, we shifted the values of resistivity and magnetization. In the inset of (b), the structural transition temperature under warming runs (T_{SW}) for temperature (*T*) sweep (open squares) and for magnetic field (*H*) sweep (solid squares) is shown for comparison.

Therefore, one may infer that the T_S significantly changes with magnetic field when T_S is similar to T_C, i.e., T_S-T_C ~ 34 (–33 K) for x = 0.17 (0.18), and T_S-T_C ~ 97 (60 K) for x = 0.15 (0.16).

Figs. 3(a) and 3(b) show the magnetic field dependent resistivity and magnetization, respectively, for x = 0.17 at selected temperatures, i.e., magnetic field sweep. [For clarity, we shift the values of resistivity and magnetization for each temperature.] Note that the T_S of x = 0.17 is similar to the T_C at zero magnetic field and the former intersects the latter near 3 T [see, Fig. 1(b)]. Before applying magnetic field, the sample was cooled down to 200 K in zero field, and then it was heated up to selected temperatures. Therefore, the sample was initially in orthorhombic phase.

One may notice that the value of resistivity shows sharp jump at specific magnetic field, and it does not return back to the initial value even without magnetic field. For example, the value of resistivity at 255 K at zero magnetic field is estimated to be 0.347 Ω cm. With increasing magnetic field, the value smoothly decreases initially and then sharply decreases near 6 T. When we decrease the magnetic field down to 0 T again, the value of resistivity estimated to be 0.317 Ω cm, which is different from the initial value. With increasing temperature, the specific magnetic field decreases, and the irreversible behavior disappeared above 262 K. The similar behaviors can be noticed in magnetic field dependent magnetization at the same temperatures [see, Fig. 3(b)]. Based on the results in Fig. 1, we can infer that the orthorhombic structure at zero field changes into rhombohedral one at high magnetic field, and the rhombohedral structure continue even without applied magnetic field.

In the inset of Fig. 3(b), we plotted the values of magnetic field at which the structure transition occur during the magnetic field (*H*) sweep (solid squares) and compared with the temperature (*T*) sweep (open squares). The T_{SW} obtained from magnetic field sweep linearly decreases as similar to temperature one. However, the values of T_{SW} obtained from magnetic field sweep are lower than those

from temperature one by about 5 K, which suggests the expansion of rhombohedral phase. Also, the phase diagram clearly shows that the structural phases are path dependent. For example, it is rhombohedral phase for magnetic field sweep while orthorhombic phase for temperature sweep at 4 T and 260 K.

Asamitsu *et al.* [7] and Moritomo *et al.* [13] have investigated the structural transition in $La_{1-x}Sr_xMnO_3$ with magnetic field and pressure, respectively. Near x = 0.170, they have observed that the T_S is sharply decreased at the specific magnetic field and pressure, at which the T_S coincides with the T_C (T_{MI}). Also the structural phase diagram obtained from magnetic field sweep was sharply modified from that obtained from temperature sweep, especially near 1.5 T at which $T_S \sim T_C$. [Note that the T_S of x = 0.175 was reported to be linearly decreased with pressure, since the T_S did not coincide with the T_C for any pressures]. They have explained the behaviors of x = 0.170 based on the free energy argument. Since the free energy of rhombohedral structure is lower than orthorhombic one at high magnetization and the transfer integral of the former is larger than the latter, sharp structural changes occur even at the cost of elastic energy when the T_S intersects the T_C at high magnetic field and pressure. Also the sharp modification of structural phase diagram has been explained by a thermal fluctuation in temperature sweep, while not in magnetic field sweep.

Later, Arkhipov *et al.* [8] and Laukhin *et al.* [9] have investigated the structural transition in $La_{1-x}Ba_xMnO_3$ (x = 0.2) with magnetic field and pressure, respectively. For both cases, they have observed the linear decrease of T_S and have explained based on the similar free energy argument. Note, however, that the T_S of x = 0.2 is already lower than T_C, hence, the T_S does not intersect the T_C for any magnetic fields [see, Fig. 1(c)] and pressures. On the other hand, our experimental results clearly show that the T_S do not sharply decrease with magnetic field in $La_{0.83}Ba_{0.17}MnO_3$, although the T_S intersects T_C near 3 T, which is sharply contrast to $La_{0.83}Sr_{0.17}MnO_3$ case.

We believe that one of the possible reasons for the smooth decrease of T_S in $La_{0.83}Ba_{0.17}MnO_3$ with magnetic field is the effect of disorder on the hopping of e_g electron. Rodriguez-Martinez and Attfield [14] have reported the effect of disorder on T_C of $R_{0.7}A_{0.3}MnO_3$. Through the systematic investigation, they have suggested that the cation disorder due to the size difference between R and A ions causes the random displacement of oxygen and acts as preformed Jahn-Teller distortion which favors both carrier localization and orthorhombic structure. In fact, the T_C of $La_{0.83}Ba_{0.17}MnO_3$ is around 220 K while that of $La_{0.83}Sr_{0.17}MnO_3$ is around 265 K [7], which suggests the larger disorder in the former. [According to Ref. 14, we can infer that the value of disorder for $La_{0.83}Ba_{0.17}$ is nine times larger than for $La_{0.83}Sr_{0.17}$ [15].]

Large disorder would result in small kinetic energy and magnetization differences between rhombohedral and orthorhombic phases in $La_{0.83}Ba_{0.17}MnO_3$. As consistent with this scenario, Arkhipov *et al.* [8] have reported the coexistence of rhombohedral and orthorhombic structures near T_S in $La_{0.8}Ba_{0.2}MnO_3$, which might result in smooth magnetostructural transition. Since the magnetostructural transition occurs through the mutual coupling among kinetic energy of the e_g electrons, local spin moments of the t_{2g} electrons, and lattice degree of freedom, the disorder should play some role in this intriguing phenomenon. Therefore we may conclude that the disorder is one of the important ingredients for the free energy consideration for magnetostructural transition in doped manganites.

4. Conclusion

We have systematically investigated the magnetostructural transition in $La_{1-x}Ba_xMnO_3$ with changing doping levels. In contrast to $La_{1-x}Sr_xMnO_3$, we have found that the rhombohedral-orthorhombic transition temperature was smoothly decreased for any magnetic fields and any doping levels. We have suggested that the disorder originated from size difference between La and Ba may affect the kinetic energy of the e_g electrons, hence does the degree of lattice distortion in $La_{1-x}Ba_xMnO_3$.

Acknowledgments

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[15] The disorder can be quantitatively obtained by the variance, i.e., $\sigma^2=\Sigma y_i R_i^2-\langle R_A\rangle^2$ where y_i, R_i, and R_A represent the fractional occupancies, ionic radii (La^{3+}=1.22 Å, Sr^{2+}=1.31 Å, Ba^{2+}=1.47 Å), and mean radius of R and A ions, respectively.