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Journal of the Physical Society of Japan
Vol. 70, No. 3, March, 2001, pp. 628–631

Anomalous Lattice Softening at $X = 0.19$ and 0.82 in $La_{1-X}Ca_XMnO_3$

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(Received December 13, 2000)

The longitudinal sound velocity $v_s(T)$ has been measured for $La_{1-X}Ca_XMnO_3$ crystals, and anomalous softenings of $v_s(T)$ have been observed at the peculiar Ca concentrations of $X = 0.19$ and $X = 0.82$. For the $X = 0.19$ sample, in which the ferromagnetic (FM) metallic phase competes with the FM insulating phase with a polaron ordering, the anomalous $v_s(T)$ softening occurs immediately below the FM transition temperature T_c. For the $X = 0.82$ sample, in which the charge-ordered (CO) phase competes with the canted antiferromagnetic (CAF) phase, the deep local minimum of $v_s(T)$ occurs around the CO transition temperature T_{CO}. These anomalous $v_s(T)$ softenings result from the giant lattice fluctuations which originate from phase competitions and suggest strong charge-lattice and spin-lattice coupling in this system.

KEYWORDS: $La_{1-X}Ca_XMnO_3$, sound velocity, electron-phonon coupling, lattice distortion, ferromagnetism, charge ordering, canted antiferromagnetism

Carrier-doped perovskite manganese oxides, $(RE_{1-X}AE_X)MnO_3$ (RE: rare-earth ion, AE: alkaline earth ion), undergo a variety of dramatic phenomena such as colossal magnetoresistance (CMR), metal-insulator (M-I) transition and charge ordering.[1,2] The CMR effect is believed to involve strong electron-phonon interaction in addition to a double-exchange mechanism.[3] The most important origin for the strong electron-phonon coupling is likely to be the Jahn-Teller effect due to Mn^{3+} spins. The local distortions of the MnO_6 octahedra play an important role in determining the transport properties of the doped carriers, as suggested by neutron and X-ray diffraction studies.[4,5]

Important information on the lattice dynamics can also be obtained from the sound velocity $v_s(T)$ measurement. For $La_{1-X}Sr_XMnO_3$[6,7] and $La_{1-X}Ca_XMnO_3$,[8] we reported the sound velocity anomalies associated with charge ordering. For low hole concentrations, the distribution of the temperature T^* at which v_s anomaly occurs was centered at $X = 1/8$, which was consistent with the polaron-ordered phase reported by Yamada *et al.*[9]

In this paper, we report the very salient slowing down of $v_s(T)$ in $La_{1-X}Ca_XMnO_3$ (LCMO) observed at the peculiar Ca concentrations of $X = 0.19$ and $X = 0.82$. We discuss the origin of the softenings on the basis of the phase diagram in this system.

The $La_{1-X}Ca_XMnO_3$ ($X = 0.15 \sim 0.95$) samples were prepared from stoichiometric mixtures of La_2O_3, $CaCO_3$ and Mn_3O_4 powders. The mixtures were calcined at 1000°C for 24 h in air, pressed into pellets and then sintered at 1500°C for 8 h in air. The density of each sample was determined by measuring the volume and the weight, which were confirmed to be more than 85% of the ideal values. X-ray diffraction analyses at room temperature confirmed that all the samples showed a pure orthorhombic structure. The sound velocity $v_s(T)$ was measured using a pulse-superposition method from 4.2 K (or 90 K) to 300 K (or 400 K). Seven megahertz longitudinal waves used for the v_s measurement were generated by Z-cut $LiNbO_3$ transducers. The electrical resistivity $\rho(T)$ was measured by a standard four-probe method. The thermal dilatation $dL(T)/L$ was measured between 20 K and 300 K using a strain-gauge method. The magnetization $M(T)$ was measured from 10 to 300 K by a superconducting quantum interference device (SQUID) magnetometer.

Figure 1 shows the temperature dependence of the sound velocity $v_s(T)$ for the $0.15 \leq X \leq 0.22$ samples. For the $X = 0.15$ sample, an abrupt upturn in $v_s(T)$ is observed below the characteristic temperature $T^* \approx 140$ K. However, the $v_s(T)$ anomaly is hardly discernible at the ferromagnetic Curie temperature, $T_c = 175$ K. The temperature T^* decreases to 120 K for the $X = 0.18$ sample. As reported in the previous paper,[8] the X dependence of T^* is centered at the Ca concentration $X = 1/8$, and the $v_s(T)$ upturns at T^* correspond to the polaron ordering. The anomaly at T^* suggests the strong electron-phonon interaction in this system. In contrast, the T^* anomaly disappears for the $X = 0.19$ sample and the anomalous softening in $v_s(T)$ occurs immediately below $T_c = 180$ K. Then, $v_s(T)$ takes a deep local minimum at $T' = 160$ K and sharply increases with further decrease in temperature. For the $X = 0.22$ sample, only the $v_s(T)$ upturn was observed immediately below T_c, which suggests the strong coupling of the lattice to the spins.

Figure 2 presents the thermal dilatation $dL(T)/L$ for the same samples. As is evident, dL/L for $X \leq 0.18$ shows no anomaly at T_c, while dL/L for $X \geq 0.19$ shows a clear contraction at T_c with decreasing temperature. The data of dL/L clearly demonstrate that there should be a phase boundary between $X = 0.18$ and $X = 0.19$.

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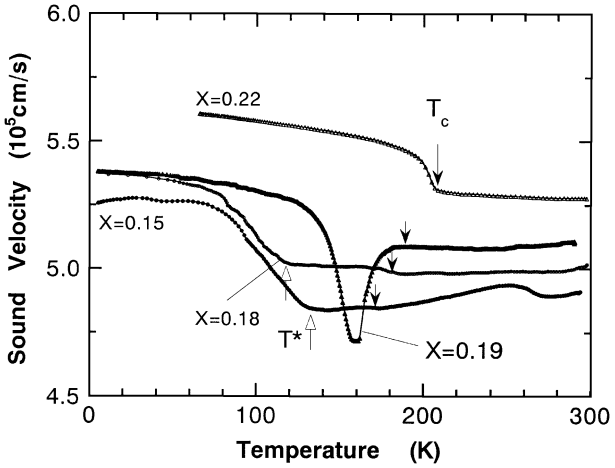

Fig. 1. Temperature dependence of the sound velocity $v_s(T)$ of the $La_{1-X}Ca_XMnO_3$ samples for $0.15 \leq X \leq 0.22$. Closed arrows indicate the FM transition temperature T_c determined from the magnetization $M(T)$ measurement. Open arrows for $X = 0.15$ and 0.18 show the characteristic temperature T^* at which the $v_s(T)$ upturn occurs.

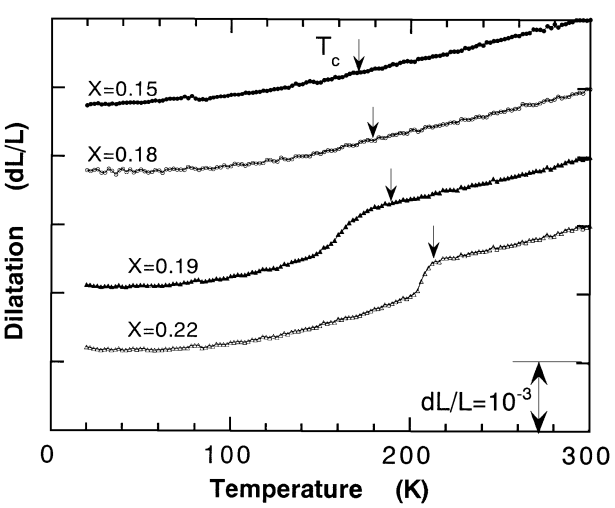

Fig. 2. Temperature dependence of the thermal dilatation $dL(T)/L$ for the same samples shown in Fig. 1. The arrows indicate T_c determined from the $M(T)$ measurement. The data demonstrate that there should be a phase boundary between $X = 0.18$ and $X = 0.19$.

The results in Fig. 2 suggest that the lattice contraction occurs accompanied by the transition from the paramagnetic insulator to the FM metal in this X range.

Figure 3 presents $v_s(T)$ for $X = 0.75$, 0.82, 0.82 and 0.95. All the samples in this figure, except $X = 0.95$, show pretty large lattice softening around the charge-ordering temperature T_{CO} ($X = 0.75$, 0.82) or the canted antiferromagnetic (CAF) transition temperature T_{CAF} ($X = 0.90$)[10] but the softening is the most drastic for $X = 0.82$. It is worthwhile to note that the v_s anomaly is small for $X = 0.95$. This finding supports the idea that the intrinsic origin of the eminent v_s anomaly is the Jahn-Teller distortion around the Mn^{3+} ions; the number density of the Mn^{3+} ions becomes very small at this Ca^{2+} ion concentration.

Figure 4 presents $dL(T)/L$ for the same samples as

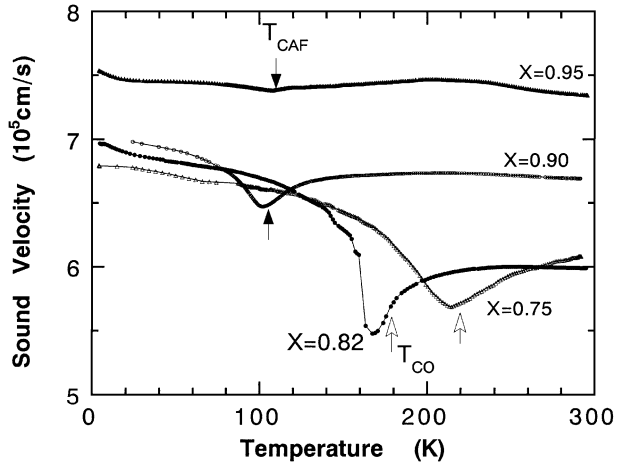

Fig. 3. Sound velocity $v_s(T)$ of the $La_{1-X}Ca_XMnO_3$ samples for for $X = 0.75$, 0.82, 0.90 and 0.95. Open and closed arrows indicate the charge-ordered (CO) transition temperature T_{CO} and the canted antiferromagnetic (CAF) temperature T_{CAF} determined from the $M(T)$ measurements.

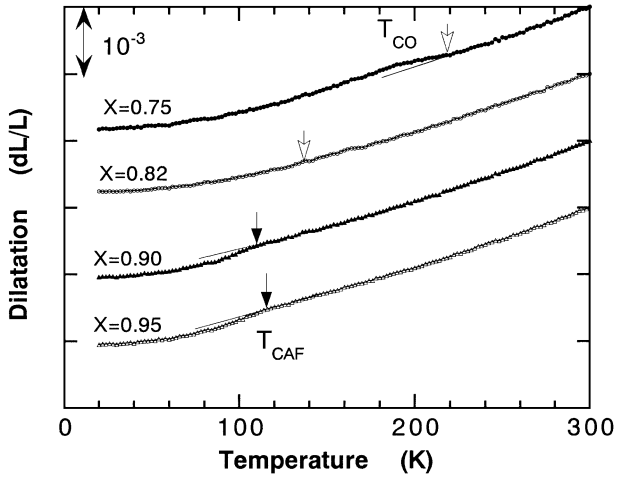

Fig. 4. Temperature dependence of the thermal dilatation $dL(T)/L$ for the same samples shown in Fig. 3. The data are consistent with the existence of the phase boundary at $X \approx 0.82$.

in Fig. 3. With decreasing temperature, dL/L of the $X = 0.75$ shows expansion at T_{CO}, while dL/L of the $X = 0.90$ sample shows a contraction at T_{CAF} and the anomaly is not discernible for $X = 0.82$. These data again demonstrate that the phase boundary exists in the vicinity of $X = 0.82$. It is also to be noted that the lattice contracts at T_{CAF}. Although the $X = 0.90$ sample does not show metallic conduction below T_{CAF}, its resistivity is far smaller[10] than that of charge-ordered LCMO samples. There seems to be a general tendency for dL/L to show contraction at the transitions into conductive phases.

As we have seen, considerable lattice softening occurs at the critical concentration near the phase boundaries in $La_{1-X}Ca_XMnO_3$. Figure 5 presents the phase diagram of the LCMO system determined by the present authors on the basis of the magnetization $M(T)$ and the sound velocity $v_s(T)$.[8,10] In $La_{1-X}Ca_XMnO_3$ at around

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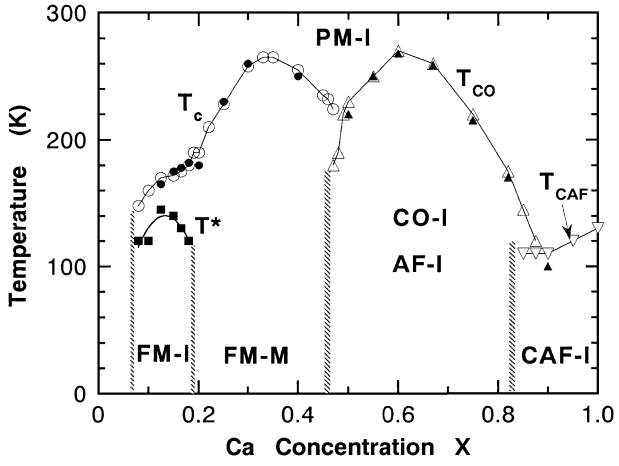

Fig. 5. The phase diagram of the $La_{1-X}Ca_XMnO_3$ system determined by the present authors. T_c is the Curie temperature which is determined from the $M(T)$ [○] and $v_s(T)$ [●]. T^* is the CO temperature which is determined from the $v_s(T)$ anomaly [■]. T_{CO} is the CO temperature which is determined from the $M(T)$ [△] and $v_s(T)$ [▲]. T_{CAF} is the CAF temperature determined from the $M(T)$ [▽].[8,10]

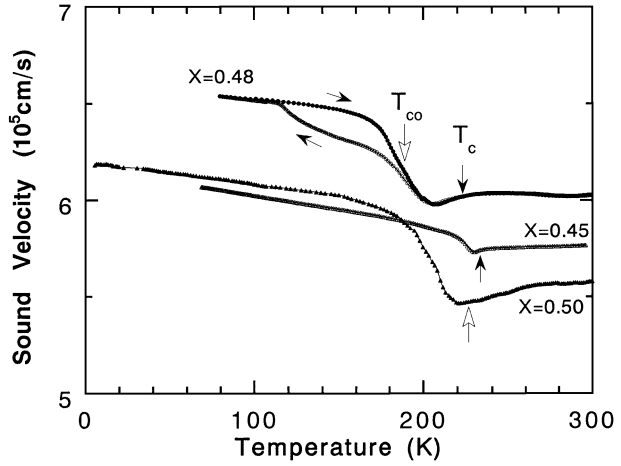

Fig. 6. Temperature dependence of the sound velocity $v_s(T)$ of the $La_{1-X}Ca_XMnO_3$ samples for $X = 0.45$, 0.48 and 0.50. Closed and open arrows indicate T_c and T_{CO}, respectively, determined from the $M(T)$ measurements. Hysteretic behavior is observable for $X = 0.48$.

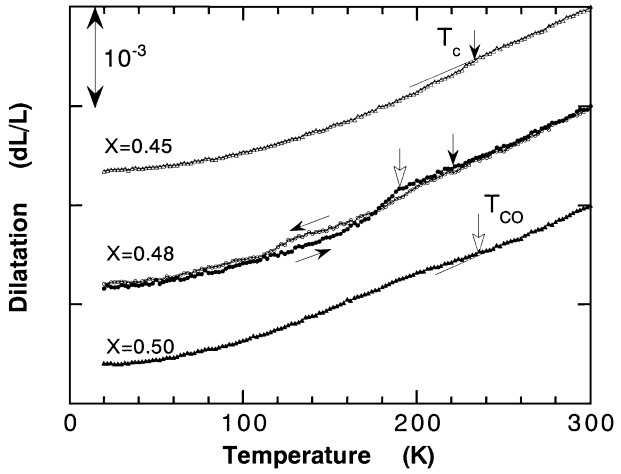

Fig. 7. Thermal dilatation $dL(T)/L$ for the same samples shown in Fig. 6. Hysteretic behavior is discernible for $X = 0.48$.

$X = 0.48$, there is another important phase boundary between the ferromagnetic metal and the charge-ordered insulator.[11–13] Figure 6 presents $v_s(T)$ for $X = 0.45$, 0.48 and 0.50 and Fig. 7 presents $dL(T)/L$ for the same samples. Figure 8 shows the magnetization $M(T)$ under the applied field of 0.5 T. As shown in Fig. 8, the $X = 0.45$ sample is ferromagnetic and $X = 0.50$ belongs to the CO phase. The $X = 0.48$ sample shows a two-step transition; the ferromagnetic phase below $T_c = 230$ K is replaced by the charge-ordered phase at lower temperatures.[14] The CO transition shows marked hysteresis between the increasing and decreasing temperature scans. The hysteresis is also clearly observable for $v_s(T)$ and $dL(T)/L$ in Figs. 6 and 7. Again, dL/L of ferromagnetic $La_{0.55}Ca_{0.45}MnO_3$ shows a contraction at T_c and charge-ordered $La_{0.50}Ca_{0.50}MnO_3$ shows expansion at T_{CO} with decreasing temperature. In Fig. 6, we note that the lattice softening is very small at these concentrations X near the FM-CO phase boundary. In order to obtain a clearer quantitative view of the v_s softening, we plot in Fig. 9 the reduced sound velocity v_s/v_{min} vs the reduced temperature t ($= T/T_c$ or T/T_{CO}) for $X = 0.19$, 0.48 and 0.82.

Now let us discuss the origin of the sound velocity softening in the LCMO system. The longitudinal sound velocity is given by the following equation;

$$v_s = \sqrt{\frac{3(1-\sigma)}{\rho(1+\sigma)K_T}}, \tag{1}$$

where K_T is the compressibility, σ the Poisson ratio and ρ the mass density. The compressibility K_T is related to the correlation of the local volume fluctuation $[V(r)-\langle V(r)\rangle]$,[15]

$$K_T = \frac{1}{k_B}\int dr' \langle [V(r) - \langle V(r)\rangle] \times [V(r') - \langle V(r')\rangle]\rangle, \tag{2}$$

where k_B is the Boltzmann constant and the angular bracket indicates the statistical average. Equations (1) and (2) suggest that the occurrence of very large local fluctuations is responsible for the observed giant lattice softening for $La_{0.81}Ca_{0.19}MnO_3$ and $La_{0.18}Ca_{0.82}MnO_3$. The main origin of the large volume fluctuations is considered to be the two-phase competition, i.e., the competition between the insulating and metallic phases at $X = 0.19$ and that between the CO and CAF phases at $X = 0.82$. If the free energy difference with regard to the Ca concentration X is smooth and of second-order-like across these phase boundaries, large-scale fluctuations of the order parameters may occur in the vicinity of T_c and T_{CO}, because additional freedom of the order parameter fluctuations corresponding to the competing third phase is permitted. As the data for the thermal dilatation $dL(T)/L$ suggest, the fluctuations of the order parameter accompany the strong lattice fluctuations in this $La_{1-X}Ca_XMnO_3$ system, resulting in the marked sound velocity softening.

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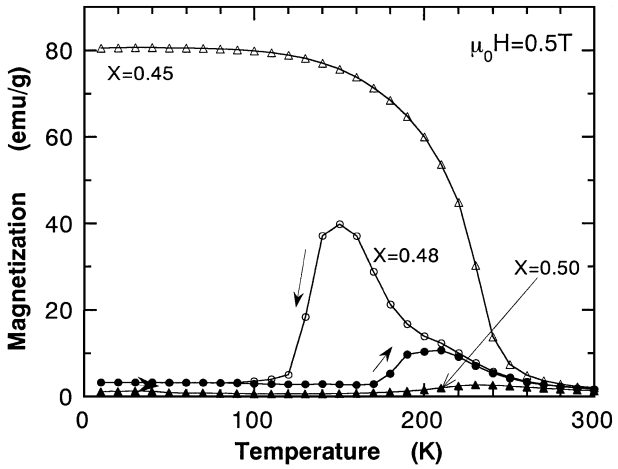

Fig. 8. Magnetization $M(T)$ of the $La_{1-X}Ca_XMnO_3$ samples for $X = 0.45$, 0.48 and 0.50 under the applied field of 0.5 T. $M(T)$ for $X = 0.48$ shows marked hysteresis.

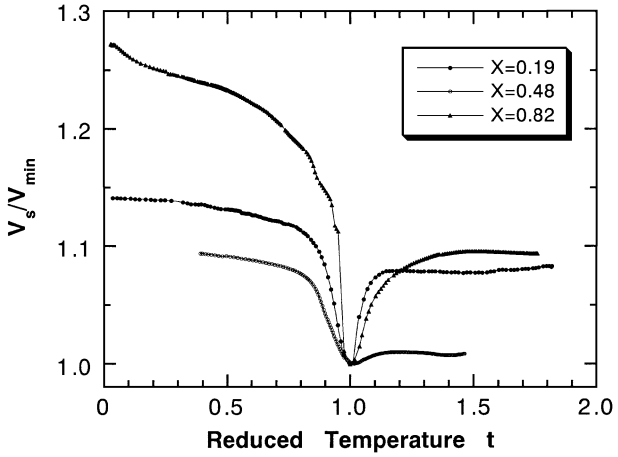

Fig. 9. Normalized sound velocity v_s/v_{min} vs the reduced temperature t ($= T/T_c$ or T/T_{CO}) for the $X = 0.19$, 0.48 and 0.82 samples.

In contrast, $v_s(T)$ of $La_{0.52}Ca_{0.48}MnO_3$ does not show any significant softening around T_c, in spite of the competing FM-I and CO phases. As all the hysteresis behaviors of $v_s(T)$, $dL(T)/L$ and $M(T)$ clearly demonstrate, the phase transition between the FM-M and the CO phases are typically of the first order. Thus the phase boundary between them is not smooth in terms of the free energy, which may preclude the occurrence of the correlated local volume fluctuations around the phase transition temperatures.

In summary, conspicuous slowing down of the longitudinal sound velocity $v_s(T)$ in $La_{1-X}Ca_XMnO_3$ has been observed for $X = 0.19$ and $X = 0.82$. Around $X = 0.19$, the insulating ferromagnetic (FMI) phase competes with the metallic FMM phase, while around $X = 0.82$, the charge-ordered phase competes with the CAF phase. The anomalous lattice softenings result from the correlated large local lattice volume fluctuations around phase transition temperatures. The large lattice fluctuation may be possible if the free energy difference with regard to the Ca concentration X is small and smooth (second-order-like) between the competing two phases of this strongly carrier-lattice- and spin-lattice-coupled system. We suggest that the free energy differences are small and smooth across the FMI-FMM phase boundary at $X \sim 0.19$ and across the CO and CAF phase boundary at $X \sim 0.82$. In contrast, $v_s(T)$ softening was not observed for the FMM-CO phase boundary at $X \sim 0.48$. With decreasing temperature, $La_{0.52}Ca_{0.48}MnO_3$ shows a typical first-order transition from FMM to CO phase with very large hysteresis. The free energy difference is not smooth across this phase boundary at $X \sim 0.48$. The phase diagram of $La_{1-X}Ca_XMnO_3$ over the entire X range was proposed on the basis of the electrical resistivity $\rho(T)$, magnetization $M(T)$, thermal dilatation $dL(T)/L$ and $v_s(T)$ measurements.

Sound velocity measurement was performed under the interuniversity cooperative research program of the Institute for Materials Research, Tohoku University. This work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture (No. 09640414).

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