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Sound Velocity Anomaly Associated with Polaron Ordering in $La_{1-X}Sr_XMnO_3$

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The sound velocity $v_s(T)$ and the electrical resistivity $\rho(T)$ of $La_{1-X}Sr_XMnO_3$ ($0.11 \leq X \leq 0.17$) have been measured and anomalies in $v_s(T)$, which are related to the polaron-ordered phase centered at $X = 1/8$, have been observed. The phase diagram between the polaron-ordering temperature T_P and X has been determined from the v_s anomalies.

KEYWORDS: sound velocity, electrical resistivity, $La_{1-X}Sr_XMnO_3$, ferromagnetic order, polaron order, structural phase transition

Since the discovery of "colossal" magnetoresistance (CMR)[1,2] in distorted perovskite manganese oxides, $La_{1-X}Sr_XMnO_3$ and related compounds have attracted the renewed interest of physicists and engineers. The main origin of CMR in this system may be the double exchange (DE) interaction, but Millis *et al.*[3] pointed out that only the simple DE mechanism can not explain CMR. In this system, interplay and competition between spins, doped charge carriers (holes), the degree of freedom of orbitals and lattice structures are considered to stage a variety of dramatic physical phenomena.[4,5] It is expected that electron-phonon and/or spin-phonon interaction may be markedly enhanced, possibly, through the Jahn-Teller coupling and may play an important role in provoking the novel physical properties of this system. Recently, Yamada *et al.*[6] observed a polaron-ordered phase in $La_{0.9}Sr_{0.1}MnO_3$ and $La_{0.85}Sr_{0.15}MnO_3$ by a neutron scattering study, which suggests the existence of anomalously strong hole-lattice interaction in these compounds. In this letter we report sound velocity anomalies which seem to be directly related to the onset the polaron ordering in $La_{1-X}Sr_XMnO_3$.

$La_{1-X}Sr_XMnO_3$ ($X = 0.11 \sim 0.17$) samples were prepared from stoichiometric mixtures of La_2O_3, $SrCO_3$ 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 measured densities of each sample are higher than 80% of that of the ideal one. All the samples were confirmed in a single phase with X-ray diffraction at room temperature. The sound velocity $v_s(T)$ was measured using the pulse-superposition method from 90 K (or 4.2 K) to 300 K. 7 MHz longitudinal waves used for the v_s measurement were generated by Z-cut $LiNbO_3$ transducers. The electrical resistivity $\rho(T)$ was measured by the standard four-probe method.

Figures 1(a)–1(e) show the temperature dependence of the sound velocity $v_s(T)$ and the electrical resistivity $\rho(T)$ for five $La_{1-X}Sr_XMnO_3$ samples. We notice two or three anomalies in both the $v_s(T)$ and $\rho(T)$ curves of each sample. For Sr concentration $X = 0.170$ in Fig. 1(a), we notice three local minimums in $v_s(T)$, i.e., at approximately 265 K, 180 K and 70 K in the order of decreasing temperature. The minimum at about 180 K shows clear hysteresis against increasing and decreasing temperature scans. With decreasing temperature, $\rho(T)$ notably decreases at about 265 K, suggesting that the ferromagnetic order of Mn spins at this temperature (T_C), then shows hysteretic behavior at approximately 180 K and begins to increase at approximately 70 K. From the hysteresis at approximately 180 K, we attribute the anomalies at this temperature (T_S) to the well-known rhombohedral to orthorhombic structural transformation.[7] As for the v_s minimum at approximately 70 K (T_P), it is noteworthy that $\rho(T)$ also increases in the vicinity of T_P.

In Figs. 1(b) and 1(c) we observe two $v_s(T)$ minimums for $X = 0.145$ and $X = 0.155$. The minimums at a high temperature T'_C are associated with a sharp decrease of $\rho(T)$, indicating the close interrelation of temperature with the ferromagnetic order. The minimums at a low temperature T_P are associated with the increase of $\rho(T)$, though the $\rho(T)$ increase seems to occur at a somewhat higher temperature than the $v_s(T)$ minimum at T_P. The electrical resistivity should increase if the doped holes enter into an ordered state and Yamada *et al.*[6] actually observed the polaron-ordered phase below the temperature where the $\rho(T)$ increase begins. Therefore, it may be reasonable to regard T_P as the polaron-ordering temperature. Comparing Figs. 1(b) and 1(c), we notice that anomalies at T_P and T'_C are similarly very conspicuous for $X = 0.155$, while for $X = 0.145$, the v_s anomaly at T_P is more profound than that at T'_C. For $X = 0.135$ in Fig. 1(d), only one minimum can be seen at approximately 180 K. It seems likely that this large minimum is actually made up of two minimums at T_P and T'_C, the dominant T_P anomaly masking out the minor T'_C anomaly. For $X = 0.110$ in Fig. 1(e), we also notice one large $v_s(T)$ minimum at $T \approx 180$ K, suggesting the masking out of the T'_C anomaly by the T_P anomaly. Comparing Fig. 1(d) and Fig. 1(e), we notice that anomalies in both $v_s(T)$ curves are qualitatively very similar. The similarity may be explained if the polaron-ordered phase in each figure has a center at $X = 1/8$ as Yamada *et*

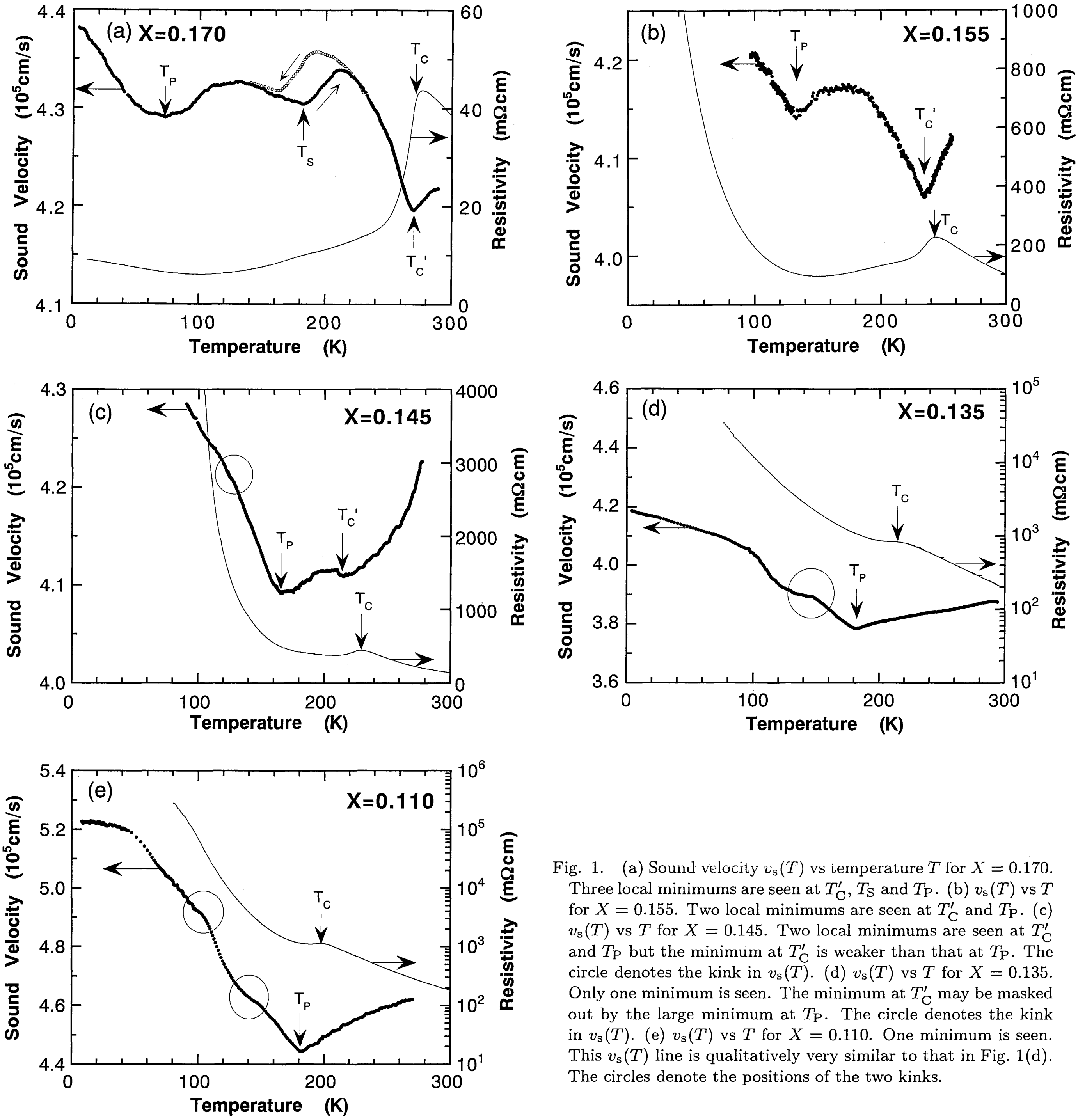

Fig. 1. (a) Sound velocity $v_S(T)$ vs temperature T for $X = 0.170$. Three local minimums are seen at T'_C, T_S and T_P. (b) $v_S(T)$ vs T for $X = 0.155$. Two local minimums are seen at T'_C and T_P. (c) $v_S(T)$ vs T for $X = 0.145$. Two local minimums are seen at T'_C and T_P but the minimum at T'_C is weaker than that at T_P. The circle denotes the kink in $v_S(T)$. (d) $v_S(T)$ vs T for $X = 0.135$. Only one minimum is seen. The minimum at T'_C may be masked out by the large minimum at T_P. The circle denotes the kink in $v_S(T)$. (e) $v_S(T)$ vs T for $X = 0.110$. One minimum is seen. This $v_S(T)$ line is qualitatively very similar to that in Fig. 1(d). The circles denote the positions of the two kinks.

al.[6)] proposed, because $X = 0.110$ and $X = 0.135$ deviate from the center by roughly the same distance.

In Fig. 2, we show the phase diagram of the polaron-ordered phase determined from the $v_S(T)$ anomalies. The T_P vs X curve seems to reach a maximum at approximately $X = 0.125$, which is consistent with the polaron-order model centered at $X = 1/8$.[6)] Thus, the anomalies of the sound velocity observed in this study have clearly supported the occurrence of the polaron-ordered phase which was originally proposed in the neutron diffraction study.[6)] In Fig. 2 we also present the ferromagnetic transition temperature T_C vs X curve for reference. In this plot, T_C is defined by the temperature at which the resistivity $\rho(T)$ starts to decrease with decreasing temperature.

In summary, for $La_{1-X}Sr_XMnO_3$ we observed sound velocity anomalies associated with several types of phase transitions. Most of the anomalies manifested themselves as local minimums of v_S. Generally, we expect the v_S minimum to occur as a combined result of lattice softening above the phase transition temperature T^* and lattice hardening below T^*. In order to clearly understand the relevant physical mechanisms, however, theoretical studies based on proper models are necessary for each individual phase transition. Important experimental results obtained in this study are summarized as

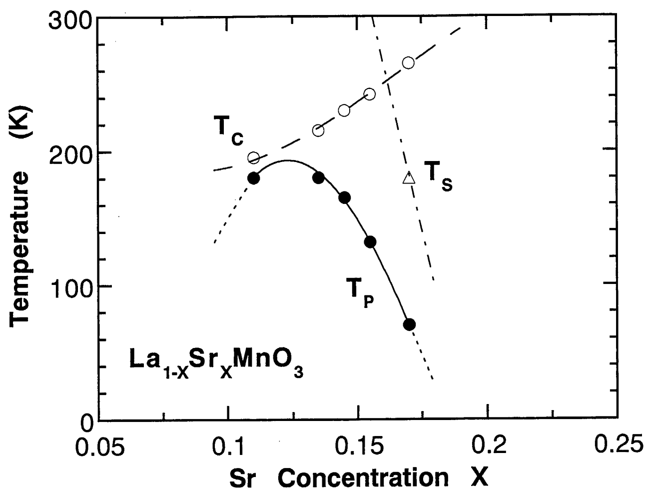

Fig. 2. Phase diagram of the $La_{1-X}Sr_XMnO_3$ system. T_P (●) shows the polaron-ordering temperature which is determined from the $v_s(T)$ minimums. Curie temperature T_C (○) and the structural transition temperature T_S (△) are determined from the $\rho(T)$ anomalies.

follows.

(i) We found the v_s anomaly associated with the polaron-ordered phase centered at $X = 1/8$. This anomaly seems to be enhanced as X approaches 1/8. The phase diagram between the polaron-ordering temperature T_P and the Sr concentration X was determined for the region $X \geq 0.11$. These anomalies at T_P suggest an improved enhancement of the electron-phonon interaction in this system. (ii) We observed a large lattice softening around the ferromagnetic transition temperature T_C for $X = 0.170$ and $X = 0.155$. The magnitude of the velocity variation Δv_s at T_C ($\Delta v_s/v_s \geq 2\%$) is very large compared to that of conventional Mn compounds, such as $RbMnF_3$.[8] A similar or even larger Δv_s was reported for the related compound $La_{1-X}Ca_XMnO_3$ at the antiferromagnetic transition T_N.[9] This large Δv_s value also suggests the anomalously strong electron-phonon or spin-phonon interaction. (iii) We observed for $X = 0.170$ the v_s anomaly associated with the rhombohedral to orthorhombic structural transition, which accompanied notable hysteretic behavior. (iv) In $v_s(T)$ curves, we observed two kinks for $X = 0.110$ and one kink for $X = 0.135$ and $X = 0.145$ besides the minimum at T_P. Local maximums in ultrasonic attenuation were also observed at the temperatures of these kinks. There is the possibility that these kinks are related to structural transitions or magnetic transitions which are not addressed in this present paper. The existence of such transitions was recently reported in the neutron diffraction study by Kawano *et al.*[10] A detailed study, for $X \leq 0.11$ in particular, is in progress.

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1) K. Chahara, T. Ohno, M. Kasai and Y. Kozono: Appl. Phys. Lett. **63** (1993) 1990.
2) R. von Helmolt, J. Wecker, B. Holzapfel, M. Schultz and K. Samwer: Phys. Rev. Lett. **71** (1993) 2331.
3) A. J. Millis, P. B. Littlewood and B. I. Shaiman: Phys. Rev. Lett. **74** (1995) 5144.
4) A. Urushibara, Y. Morimoto, T. Arima, A. Asamitsu, G. Kido and Y. Tokura: Phys. Rev. B **51** (1995) 14103.
5) R. Mahendiran, S. K. Tiwary, A. K. Raychaudhuri and T. V. Ramakrishnan: Phys. Rev. B **53** (1996) 3348.
6) Y. Yamada, O. Hino, S. Nohdo, R. Kanao, T. Inami and S. Katano: Phys. Rev. Lett. **77** (1996) 904.
7) A. Asamitsu, Y. Morimoto, R. Kumai, Y. Tomioka and Y. Tokura: Phys. Rev. B **54** (1996) 1716.
8) B. Golding: Phys. Rev. Lett. **20** (1968) 5.
9) A. P. Ramirez, P. Schiffer, S-W. Cheong, C. H. Chen, W. Bao, T. T. M. Palstra, P. L. Gammel, D. J. Bishop and B. Zegarski: Phys. Rev. Lett. **76** (1996) 3188.
10) H. Kawano, R. Kajimoto, M. Kubota and H. Yoshizawa: Phys. Rev. B **53** (1996) R14709.