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Low-temperature structural phase transition and electronic anomalies in $La_{1.775}R_{0.10}Sr_{0.125}CuO_4$ (R=Nd,Sm,Gd,Tb)

T. Suzuki and M. Sera
Institute for Materials Research, Tohoku University, Sendai 980, Japan
T. Hanaguri
Department of Pure and Applied Science, University of Tokyo, Komada, Tokyo 153, Japan
T. Fukase
Institute for Materials Research, Tohoku University, Sendai 980, Japan
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Sound velocity and powder x-ray diffraction in $La_{1.9-x}R_{0.1}Sr_xCuO_4$ (R=Nd,Sm,Gd,Tb) reveal that the transition temperature to the tetragonal low-temperature (TLT) phase increases with decreasing the ionic radius of R up to 150 K (R=Tb around $x \sim 0.125$). Prominent change of the resistivity ρ and the thermoelectric power S is observed in the narrow region of x around 0.125 and at almost the same temperature near 80 K in the Tb-, Gd-, and Sm-substituted samples whose crystal structure is the TLT phase. In the Nd-substituted sample, less prominent but significant change of S is also observed below ~50 K where the crystal structure is the orthorhombic midtemperature phase. These results suggest that the change of the transport properties is responsible for the change of the electronic state itself rather than for the structural phase transition and this modification of the electronic state is more pronounced in the TLT phase.

$La_{2-x}Ba_xCuO_4$ undergoes a structural phase transition from the tetragonal high-temperature (THT) phase to the orthorhombic midtemperature (OMT) phase at T_{d1}. It is widely accepted that the second phase transition to the tetragonal low-temperature (TLT) phase takes place at $T_{d2} \sim 60$ K in a narrow region around $x = 0.125$.[1] In this concentration region around $x \sim \frac{1}{8}$, it was reported that the superconducting temperature T_c is extremely suppressed[2] and the transport properties show anomalous behavior below T_{d2}.[3,4] The doping effects have been extensively studied and indicate the importance of the carrier concentration corresponding to $x \sim \frac{1}{8}$ for the suppression of T_c.[5–7] From these results, in the early stages, it seemed that the OMT-to-TLT transition causes the modification of the electronic state. However, we pointed out from the results of the ultrasonic measurements that the OMT-to-TLT transition existed in rather a wide range of x between 0.09 and greater than 0.16.[8] This is consistent with the recent results from synchrotron x-ray diffraction.[9] As for the lattice instability, there is no difference between $x = 0.125$ and 0.15 although in the former T_c is drastically suppressed but in the latter the bulk superconductivity is observed. In $La_{1.6-x}Nd_{0.4}Sr_xCuO_4$, although the TLT (or $Pccn$) phase exists in a wide range of x, the bulk superconductivity exists for a wide range of x except in a narrow region around $x \sim 0.12$.[10,11] In $La_{1.875-y}Nd_yBa_{0.125}CuO_4$, while T_{d2} increases with increasing y, which is as high as ~180 K for $y = 0.4$, the anomalies of the transport properties are observed, not at T_{d2}, but at ~70 K.[12] In $La_{2-x}Sr_xCu_{0.99}Zn_{0.01}O_4$ (Ref. 13) and $La_{2-x}Sr_xCuO_4$,[14] a large reduction of T_c is observed in a narrow region around $x \sim 0.115$ although the crystal structure is orthorhombic down to 10 K. It is noted that the value of the Hall coefficient of $La_{1.875}Ba_{0.125}CuO_4$ at 300 K is close to that of $La_{1.885}Sr_{0.115}CuO_4$.[15] Our purpose is to study the origin of the suppression of T_c and to investigate if the anomalies of the transport properties are really caused by the structural phase transition. $La_{2-x-y}Nd_yBa_xCuO_4$ is not the most suitable system to investigate this question. This is because in $La_{1.875-y}Nd_yBa_{0.125}CuO_4$, the transition from the TLT to another low-temperature orthorhombic phase is observed at ~50 K by x-ray diffraction,[16] which is close to the temperature where the transport properties show the anomalies. There is also a problem with $La_{2-x-y}Nd_ySr_xCuO_4$ since at $x \sim 0.12$ and $y \sim 0.4$, the structural phase transition temperature from the OMT phase to the $Pccn$ phase is ~65 K, which is also close to the temperature where the anomalies of the transport properties are observed.[17] An influence on the transport properties resulting from the structural phase transition is inevitable in the above two systems. In contrast, we have found that in the $La_{2-x-y}R_ySr_xCuO_4$ (R=Nd,Sm,Gd,Tb) system, the structural phase transition temperature to the TLT phase increases greatly with decreasing the ionic radius of the rare-earth metals and another phase was not observed below this transition temperature. In this system the crystal structure at low temperatures changes from the OMT to the TLT with increasing y around $x \sim 0.12$. Therefore, $La_{2-x-y}R_ySr_xCuO_4$ is a good system to study the variation with composition of T_c, the structural phase transition temperature to the TLT phase and the anomalies in the transport properties, and also to investigate the relation between the crystal structure and the modification of the electronic state. In this paper, we report results of the ultrasonic velocity, the powder x-ray diffraction, the electrical resistivity, and the thermoelectric power in $La_{1.775}R_{0.10}Sr_{0.125}CuO_4$, and discuss the relation between the transport properties and the crystal structure.

The sintered samples used in this study were prepared

by the usual solid-state reaction of a mixture of predried La, Sr, Cu, and R oxides. All the samples were confirmed to be single phase by x-ray diffraction. The sound velocity V_s was measured using the pulse-superposition method with 7 MHz longitudinal waves generated by Z-cut $LiNbO_3$ transducers. The low-temperature powder x-ray diffraction was measured using a conventional diffractometer (Rigaku Co., RAD-C) with a curved graphite monochromator in the scattering beam path, using Cu $K\alpha$ radiation. Electrical resistivity ρ was measured by the usual four-probe method. The thermoelectric power S was measured by the usual dc method.

Figure 1 shows the temperature dependence of the sound velocity V_s of $La_{1.775}R_{0.10}Sr_{0.125}CuO_4$. As reported before, the sound velocity V_s in $La_{1.875}Sr_{0.125}CuO_4$ exhibits a large decrease with decreasing temperature below room temperature down to T^u_{d1}, the temperature where the THT-to-OMT structural phase transition takes place. Here, the superscript u in T^u_{d1} denotes that it is evaluated from the ultrasonic measurements. An upturn of V_s is observed below 10 K which may correspond to the precursor of the OMT-to-TLT structural phase transition. While in the Nd-substituted sample, V_s shows a similar temperature dependence to that in $La_{1.875}Sr_{0.125}CuO_4$, in the case of the samples whose La sites are substituted by other rare-earth metals, a large enhancement of V_s is observed at $T^u_{d\alpha}$ with decreasing temperature as in $La_{1.875}Ba_{0.125}CuO_4$ and $T^u_{d\alpha}$ increases very rapidly with decreasing the ionic radius of the rare-earth metals. An s-shaped variation of the V_s-T curve is observed around $T^u_{d\beta}$ below the $T^u_{d\alpha}$ in the samples substituted by Sm, Gd, and Tb. The definitions of $T^u_{d\alpha}$ and $T^u_{d\beta}$ are shown in Fig. 1. This suggests the existence of the successive structural phase transitions as reported in $La_{2-x-y}Nd_ySr_xCuO_4$.[10] Figure 2 shows the $(110)_t$ peak at different temperatures [subscript t means the tetragonal notation for (110) diffraction pattern in the THT phase] in $La_{1.775}Gd_{0.10}Sr_{0.125}CuO_4$. The splitting of the $(110)_t$ peak indicates that the crystal structure is orthorhombic down to ~135 K. The orthorhombic and tetragonal phases coexist in a temperature range between 120 and 100 K, and the splitting of the $(110)_t$ peak disappears below 100 K. Figure 3 shows the temperature dependence of the splitting width of the $(110)_t$ peak and V_s in $La_{1.775}Gd_{0.10}Sr_{0.125}CuO_4$. The temperatures where the change of the splitting width is seen correspond to the temperature where the upturn and the s-shaped variation in V_s are observed. This indicates that the sample exhibits the successive structural phase transitions of OMT→the orthorhombic low-temperature phase, which is another type of orthorhombic phase (perhaps $Pccn$) →TLT as in $La_{2-x-y}Nd_ySr_xCuO_4$.[11] Judging from the similarity in the temperature dependences of V_s, the Sm-, Gd-, and Tb-substituted samples may also exhibit the same set of the successive structural phase transitions. From these results, the phase diagram shown in Fig. 4 is obtained.

Figure 5 shows a temperature dependence of the electrical resistivity ρ. Although the resistivity of the sample substituted by Nd shows a similar temperature dependence to that in $La_{1.875}Sr_{0.125}CuO_4$ and superconductivity below 32 K, the samples substituted by Sm, Gd, and Tb show an increase of ρ below ~80 K and T_c is extremely suppressed. However, no anomaly is observed at the structural phase transition temperatures in all the samples. Figure 6 shows a temperature dependence of S normalized to the value at 300 K, which is about 30 μV/K in all the samples. While the sample substituted by Nd shows similar behavior to $La_{1.875}Sr_{0.125}CuO_4$, the samples substituted by Sm, Gd, and Tb show the anoma-

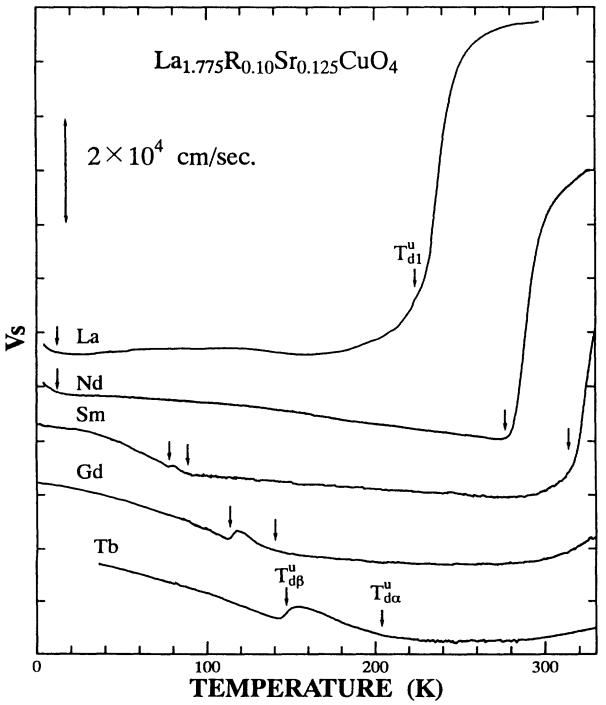

FIG. 1. Temperature dependence of the 7 MHz longitudinal sound velocity in $La_{1.775}R_{0.10}Sr_{0.125}CuO_4$.

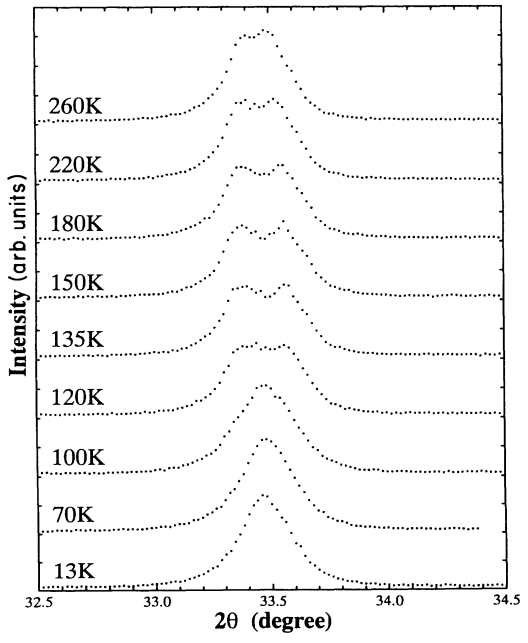

FIG. 2. Powder x-ray-diffraction data for $La_{1.775}Gd_{0.10}Sr_{0.125}CuO_4$ at different temperatures. The peaks correspond to the $(110)_t$ Brag reflection.

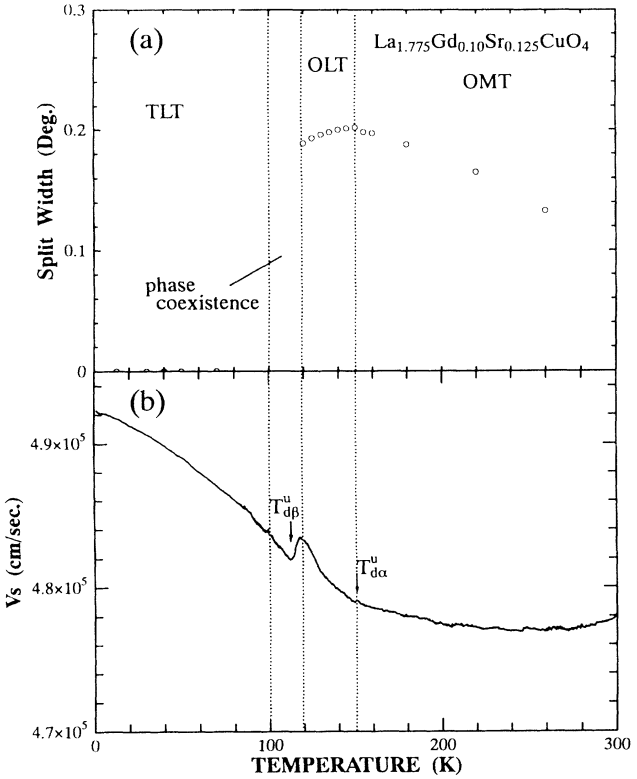

FIG. 3. (a) Temperature dependence of the splitting width of the $(110)_t$ peak. (b) Temperature dependence of the sound velocity in $La_{1.775}Gd_{0.10}Sr_{0.125}CuO_4$.

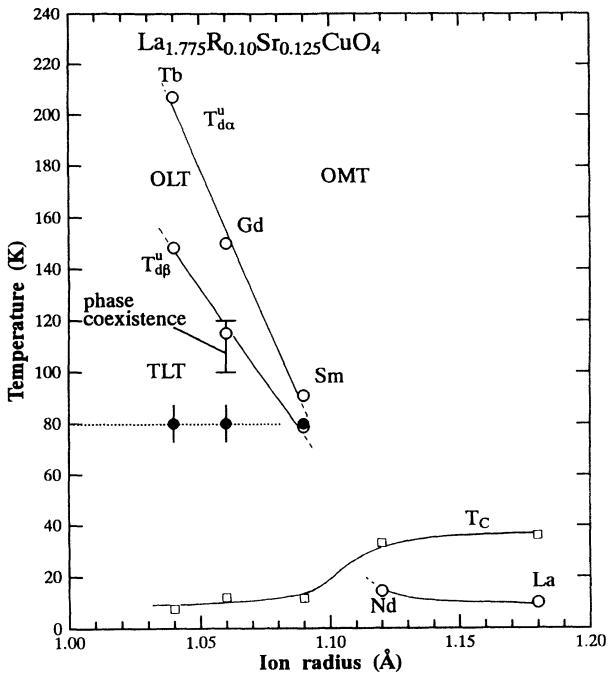

FIG. 4. Phase diagram of $La_{1.775}R_{0.10}Sr_{0.125}CuO_4$. The axis of abscissa indicates the ion radius of the substituted R metals. Open circles: the structural phase transition temperature evaluated from the ultrasonic measurements; closed circles: the temperature that the thermoelectric power shows the anomalous decrease with decreasing temperature; open squares: T_c determined by the resistivity change. The lines are guides to the eye.

lous decrease below ~80 K and the sign reversal of S at ~50 K as observed in $La_{1.875}Ba_{0.125}CuO_4$.[3] No anomaly is observed at the structural phase transition temperatures in the samples substituted by Gd and Tb. In the Sm-substituted sample, however, a small discontinuity of S is observed around the structural phase transition to the TLT phase. This may be due to the accidental condition that the structural phase transition temperature is close to the temperature where the transport property shows the anomaly. From measurements of S in $La_{1.9-x}Gd_{0.1}Sr_xCuO_4$, we confirmed that the anomalous decrease is observed only in a narrow region around $x \sim 0.125$. These results indicate that the conduction electrons do not significantly couple with the structural phase transitions that occurred at $T^u_{d\alpha}$ or $T^u_{d\beta}$. The creation of two nonequivalent sites of the in-plane oxygen atoms by the tilting of the CuO_6 octahedra[18,19] and the reduction of the density of states at the Fermi level[20] due to the band splitting in the TLT phase[21] was discussed as the origin of the suppression of T_c around $x \sim 0.12$. However, these possibilities may be ruled out because the transport properties do not show any anomaly at the structural phase transition temperature to the TLT phase in the Gd- and Tb-substituted samples. In samples substituted by Sm, Gd, and Tb, it is clear that the electronic state is largely modified below ~80 K and its modification may be the origin of the suppression of T_c. It should be noted that the anomalous decrease is observed in S when the structural phase transition temperature to the TLT phase is higher than ~80 K. While in $La_{1.875}Sr_{0.125}CuO_4$, the sudden decrease of S is ob-

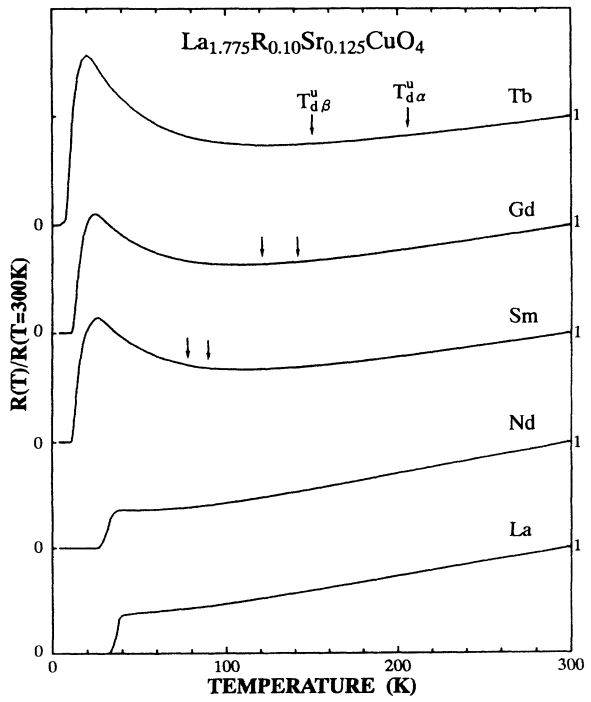

FIG. 5. Temperature dependence of the resistivity ρ normalized to the value at 300 K.

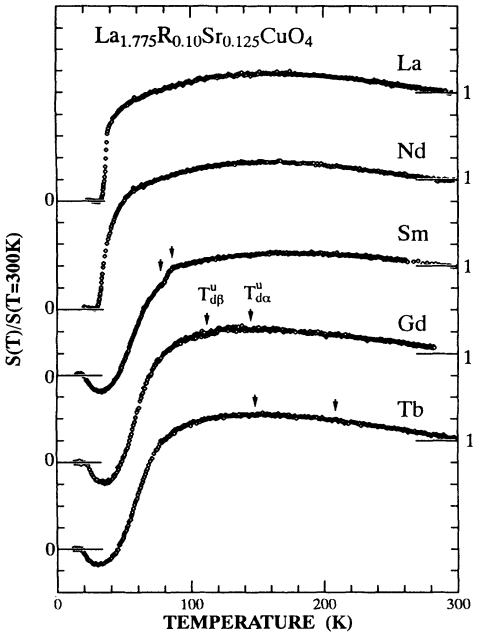

FIG. 6. Temperature dependence of the thermoelectric power S normalized to the value at 300 K in $La_{1.775}R_{0.10}Sr_{0.125}CuO_4$.

served at T_c with decreasing temperature, in the Nd-substituted sample, the gradual decease of S is observed below ~50 K (Fig. 6) which is much higher than T_c. In the Nd-substituted sample, while the crystal structure is orthorhombic down to very low temperature, the modification of the electronic state seems to exist below ~50 K, although it is small. Furthermore, as mentioned above, also in $La_{2-x}Sr_xCuO_4$, the small anomaly of the T_c-x curve exists around $x \sim 0.115$. From these results, it can be considered that the modification of the electronic state in $La_{2-x}Sr_xCuO_4$ with $x \sim 0.12$, which is very small and perhaps takes place below ~40 K, is largely enhanced when the structural phase transition temperature to the TLT phase becomes higher than the temperature where the anomalies are observed in the transport properties. That is, in $La_{2-x}M_xCuO_4$ (M=Ba,Sr) at $x \sim 0.12$, the electronic state itself has an instability causing the suppression of T_c and this instability is enhanced by the existence of the TLT phase. In conclusion, we have investigated the relation between the structural phase transition and the transport properties in $La_{1.9-x}R_{0.1}Sr_xCuO_4$. The structural phase transition temperature to the TLT phase increases with decreasing the ionic radius of R, reaching 150 K for the smallest R=Tb with $x = 0.125$. The anomalous decrease of the thermoelectric power S with decreasing temperature is observed below ~80 K only in a narrow region around $x \sim 0.125$. In $La_{1.775}R_{0.10}Sr_{0.125}CuO_4$, this rapid decrease of S begins at ~80 K in the samples substituted by Sm, Gd, and Tb whose structural phase transition temperature for the TLT phase is higher than ~80 K. In the Nd-substituted sample, whose crystal structure is the OMT phase at least down to ~15 K, the gradual decrease of S is also observed below ~50 K. These results suggest that the anomalous change of the transport properties is responsible for an instability of the electronic state itself, and is not directly responsible for the structural phase transition. The modification of the electronic state in $La_{1.875-y}R_ySr_{0.125}CuO_4$ is greatly enhanced in the TLT phase compared to the OMT phase.

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