

Thermal conductivity and structural instability in La- and Cu-site-substituted La_2CuO_4

M. Sera, M. Maki, M. Hiroi, N. Kobayashi, T. Suzuki, and T. Fukase

Institute for Materials Research, Tohoku University, Sendai 980, Japan

(Received 25 January 1995; revised manuscript received 28 March 1995)

The thermal conductivity κ and the sound velocity in La_2CuO_4 are found to be significantly decreased by Nd, Zn, and Ni doping, reflecting the lattice instability of this compound. The rapid decrease of κ with x in $\text{La}_{2-x}\text{M}_x\text{CuO}_4$ ($M=\text{Sr},\text{Ba}$) in a small- x region that was previously reported by us is understood to be the result of an enhancement of the lattice instability induced by M doping, just as in the Nd-, Zn-, and Ni-doped insulating systems. The y dependence of the transition temperature from the LTO1 (low-temperature orthorhombic 1) to LTT (low-temperature tetragonal) phase in $\text{La}_{1.875-y}\text{R}_y\text{Sr}_{0.125}\text{CuO}_4$ ($R=\text{Nd},\text{Sm},\text{Eu},\text{Gd}$) indicates that the larger the difference of the ionic radii between La^{3+} and R^{3+} ions, the more easily the transition to the LTT phase is induced. We propose that the LTT region exists around the R^{3+} ion even in the LTO1 phase and extends with the decrease of temperature and the structural transition to the LTT phase is induced when the LTT region becomes connected in a whole area of the crystal. We also point out the importance of the local lattice distortion for the Cu-site-substitution effects on $\text{La}_{2-x}\text{M}_x\text{CuO}_4$.

It is well known that the anomalous electronic state, which suppresses the appearance of the superconductivity, is realized in the LTT (low-temperature tetragonal, space group $P4_2/n\text{cm}$) phase around $x=1/8$ of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ and the rare-earth doped $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$.¹⁻⁷ Although extensive studies have been performed on this subject, the origin of this anomalous electronic state has not yet been understood. Büchner *et al.* insisted on the importance of the magnitude of the tilt angle of the CuO_6 octahedra for the appearance of the anomalous electronic state in the LTT phase around $x=1/8$.⁸ From the studies on $\text{La}_{1.875-y}\text{R}_y\text{Sr}_{0.125}\text{CuO}_4$ ($R=\text{Nd},\text{Sm},\text{Eu},\text{Gd}$ and Tb) and $\text{La}_{2-x-y}\text{Nd}_y\text{Ba}_x\text{CuO}_4$, we showed that the anomalous behaviors of the transport properties around $x=1/8$ are observed always below ~ 70 K even if the transition temperature T_{d2} from the LTO1 (low-temperature orthorhombic 1, space group $Bmab$) to the LTT phase becomes higher than ~ 70 K by the R doping and insisted on the importance of the instability of the electronic state itself which is pronounced in the LTT phase.^{9,10} In order to understand the anomalous electronic state in the LTT phase around $x=1/8$, it is necessary to understand the lattice instability of La_2CuO_4 itself. In the La_2CuO_4 related compounds, there exists the following four phases: the HTT (high-temperature tetragonal, space group $I4/mmm$) phase, the LTO1 phase, the LTO2 (low-temperature orthorhombic 2, space group P_{ccn}) phase, and the LTT phase. These phases are specified by the tilt of the CuO_6 octahedra. When Landau theory is used for the understanding of the tilting instabilities of those compounds (Ref. 2), the above phases are specified as follows using the order parameters (Q_1, Q_2) which represent the tilts around the $[110]$ and $[\bar{1}\bar{1}0]$ axes of the HTT phase: HTT ($Q_1=Q_2=0$), LTO1 ($Q_1 \neq 0, Q_2=0$), LTO2 ($Q_1 \neq Q_2 \neq 0$), and LTT ($Q_1=Q_2 \neq 0$). Hereafter, we use T_{d2} as the transition temperature from LTO1 to LTT or LTO2 phase. It is known that in $\text{La}_{1.6}\text{Nd}_{0.4}\text{CuO}_4$, the LTO2 phase appears but in $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ and $\text{La}_{1.6-x}\text{Nd}_{0.4}\text{Sr}_x\text{CuO}_4$ ($x \geq 0.1$) the LTT phase appears below T_{d2} .^{2,5} In order to investigate the lattice instabilities related to the tilts of the CuO_6 octahedra in La_2CuO_4 , we have studied the thermal conductivity κ of the insulating systems

of $\text{La}_{2-y}\text{Nd}_y\text{CuO}_4$ and $\text{La}_2\text{Cu}_{1-z}\text{D}_z\text{O}_4$ ($D=\text{Zn},\text{Ni}$) because in these compounds it is not necessary to take the contribution from electrons which should exist in $\text{La}_{2-x}\text{M}_x\text{CuO}_4$ ($M=\text{Sr},\text{Ba}$) into account. Furthermore, to understand the mechanism of the structural transition at T_{d2} , we have studied the y dependence of T_{d2} of $\text{La}_{1.875-y}\text{R}_y\text{Sr}_{0.125}\text{CuO}_4$ ($R=\text{Nd},\text{Sm},\text{Eu},\text{Gd}$).

All the samples used in the present experiment were sintered ones made by a usual method, which is written elsewhere.¹⁰ Figure 1 shows the temperature dependence of κ of $\text{La}_{2-y}\text{Nd}_y\text{CuO}_4$. The results show that κ is largely decreased by the Nd doping. The decrease of κ with y is very rapid in a small- y region and becomes small for $y > 0.1$. By only a small Nd doping with $y=0.05$, κ becomes nearly half of that of La_2CuO_4 . As $\text{La}_{2-y}\text{Nd}_y\text{CuO}_4$ is an insulator, there is no contribution from electrons. By comparing the sound velocity with κ at around 100 K, it is found that κ is closely related to ν_s in the LTO1 phase and the main part of the decrease of κ by Nd doping in the LTO1 phase seems to be a result of the decrease of ν_s when we assume that the phonon thermal conductivity is simply expressed as $\kappa_{ph} = C_{ph}\nu_s^2\tau_{ph}/3$. Here, C_{ph} , ν_s , and τ_{ph} are the specific heat, sound velocity, and relaxation time of phonons, respectively. The large softening is observed below ~ 200 K in $\text{La}_{1.6}\text{Nd}_{0.4}\text{CuO}_4$ (Ref. 10) and it should be related to the con-

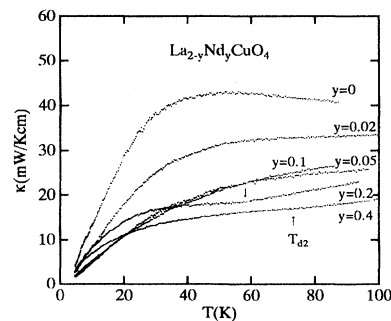


FIG. 1. Temperature dependence of the thermal conductivity of $\text{La}_{2-y}\text{Nd}_y\text{CuO}_4$. The arrow in the figure indicates the transition temperature T_{d2} from the LTO1 to LTO2 phase.

densation of the second of the doubly degenerate CuO_6 octahedra tilting phonons at X point in the HTT phase. The observed rapid decreases of κ and ν_s with y in $\text{La}_{2-y}\text{Nd}_y\text{CuO}_4$ in a small- y region indicate that the LTO1 phase in La_2CuO_4 is inherently unstable as was pointed out by Thurston *et al.*¹¹ In this way, the lattice instability in La_2CuO_4 is reflected largely in ν_s and κ . The reason why κ of the samples with $y = 0.05$ and 0.1 are smaller than those in $y = 0.2$ and 0.4 below ~ 40 K is simply because the former samples are in the LTO1 phase and the latter samples are in the LTO2 phase where the hardening of the lattice is observed.¹⁰ The small enhancement of κ is observed below T_{d2} in $\text{La}_{1.6}\text{Nd}_{0.4}\text{CuO}_4$, which is not contradictory to the observed small increase of ν_s below T_{d2} by $\sim 1\%$.¹⁰ We observed the pronounced enhancement of κ below T_{d2} in $\text{La}_{1.875-y}\text{R}_y\text{Sr}_{0.125}\text{CuO}_4$ for $y > y_c$.¹² Here, y_c is the critical concentration above which the LTT or LTO2 phase appears. The studies to understand the origin of the enhancement of κ of the Sr-doped samples below T_{d2} are now in progress.

We have also measured the temperature dependence of κ of the insulating systems of $\text{La}_2\text{Cu}_{1-z}\text{D}_z\text{O}_4$ ($D = \text{Zn}, \text{Ni}$) and the same tendency for κ vs doping concentration as in $\text{La}_{2-y}\text{Nd}_y\text{CuO}_4$ was observed. That is, κ is decreased by the D doping. Also in $\text{La}_2\text{Cu}_{0.8}\text{Zn}_{0.2}\text{O}_4$ a similar softening below ~ 200 K was observed as in $\text{La}_{1.6}\text{Nd}_{0.4}\text{CuO}_4$.¹⁰ These results indicate that the same mechanism for the decrease of κ and the softening below ~ 200 K as in $\text{La}_{2-y}\text{Nd}_y\text{CuO}_4$ is applicable to the D -doped systems. The fact that the decrease of κ is larger in the Zn-doping case than in the Ni-doping case indicates that the larger lattice instability is induced by the Zn doping. This tendency is observed also in $\text{La}_{1.875-y}\text{Nd}_y\text{Sr}_{0.125}\text{Cu}_{1-z}\text{D}_z\text{O}_4$ ($D = \text{Zn}, \text{Ni}$) below and above T_{ds} .¹²

T_{d1} of La_2NiO_4 and La_2CuO_4 is 770 K (Ref. 13) and 540 K, respectively, and T_{d2} of La_2CoO_4 and La_2NiO_4 is 135 K (Ref. 14) and 70 K (Ref. 15) below which temperature the LTT phase is realized, respectively. From the simple extrapolation by using the T_{d2} values of La_2CoO_4 and La_2NiO_4 , T_{d2} of La_2CuO_4 is estimated to be ~ 0 K. This should be related to the continuous softening of the lower branch of the TO phonon which is the uncondensed mode in the LTO1 phase with the decrease of temperature.¹¹ These results and the above-mentioned drastic enhancement of the lattice instability induced by the doping which does not depend on the substituted site, i.e., La or Cu site indicate that the LTO1 phase in La_2CuO_4 is inherently unstable against the tilts of the CuO_6 octahedra transverse to the tilt axis in the LTO1 phase. Then, it is naturally expected that also by Sr or Ba doping, the same kind of lattice instability is induced as in the above insulating systems. We have studied κ of $\text{La}_{2-x}\text{M}_x\text{CuO}_4$ ($M = \text{Sr}, \text{Ba}$) and reported the characteristic x dependence of κ of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ at constant temperature as shown in Fig. 2, i.e., κ decreases with x up to ~ 0.2 and increases rapidly and then decreases with x for $x > 0.35$.⁴ The similar x dependence of κ was observed also in $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ but its decrease with x in a small- x region is larger than in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$.⁴ We explained these behaviors as follows in our previous paper.⁴ In a small- x region, the thermal current is carried mainly by phonons and with the increase of x , the phonon contribution becomes less because

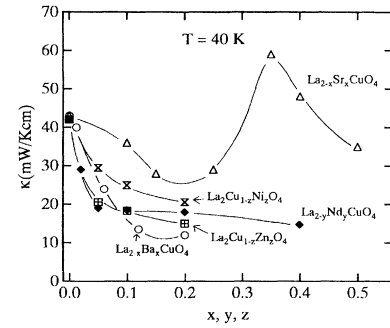


FIG. 2. Doping concentration dependence of the thermal conductivity of $\text{La}_{2-y}\text{Nd}_y\text{CuO}_4$, $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$, $\text{La}_2\text{Cu}_{1-z}\text{Zn}_z\text{O}_4$, and $\text{La}_2\text{Cu}_{1-z}\text{Ni}_z\text{O}_4$ at 40 K. The results for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ and $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ are cited from Ref. 4.

phonons are scattered by both electrons and lattice imperfections induced by the Sr doping and, instead, the electronic contribution becomes important in a larger- x region. However, the present results for Nd-, Zn-, and Ni-doped samples strongly suggest that this x dependence of κ reflects the lattice instability in $\text{La}_{2-x}\text{M}_x\text{CuO}_4$ ($M = \text{Sr}, \text{Ba}$) rather than the increase of the number of the scattering centers of phonons in a small- x region. The increase of κ for $x > 0.25$ in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ may be partly due to the increase of the carrier contribution and partly due to the increase of ν_s as a result of the entrance into the HTT phase. The observed larger decrease of κ by Ba doping than by Sr doping suggests that the larger lattice instability is induced by the former rather than by the latter, which may be related to the appearance of the LTT phase in $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$.

Figure 3 shows the y dependence of T_{d2} of $\text{La}_{1.875-y}\text{R}_y\text{Sr}_{0.125}\text{CuO}_4$ ($R = \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}$) which is obtained from the measurements of κ , ν_s , and S . Although Sm-, Eu-, and Gd-doped samples show a similar y dependence of T_{d2} , that of the Nd doped one is different from these three systems. This difference will be discussed later. The critical concentration y_c above which the LTT (or LTO2) phase exists is ~ 0.13 , 0.05 , 0.04 , and 0.03 for Nd-, Sm-, Eu-, and Gd-doped samples, respectively. This indicates that the larger the difference of the ionic radii between La^{3+} and R^{3+} ions, the wider the range of the local lattice distortion induced by the R doping and the more easily the cooperative structural transition from the LTO1 to the LTT (or LTO2) phase is induced. This suggests the importance of the local lattice distortion around the R^{3+} ion in the structural transition to the LTT phase and it is difficult to expect the homogeneous LTT phase when the y_c value is small. It is expected that the region where the same structure as in the LTT (or LTO2) phase, which we call the LTT (or LTO2) region hereafter, emerges around the R^{3+} ion and the structural transition is induced when the LTT (or LTO2) region becomes connected in a whole area of the crystal. That is, the LTT (or LTO2) region exists around R^{3+} ion even in the LTO1 phase and the LTT (or LTO2) region extends with the decrease of temperature, which was discussed by Billinge, Kwei, and Takagi.¹⁶ Here, we propose the following mechanism of the structural transition at T_{d2} . Figure 4 shows the deformation of the CuO_6 octahedra around the substituted R^{3+} ion whose ionic radius is smaller than that of La^{3+} . Figure 4(a) shows the deformation around the R^{3+} ion when the mother

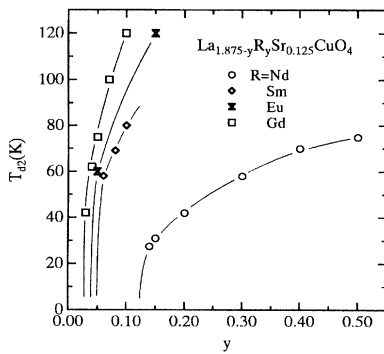


FIG. 3. y dependence of T_{d2} of $\text{La}_{1.875-y}\text{R}_y\text{Sr}_{0.125}\text{CuO}_4$ ($R=\text{Nd}, \text{Sm}, \text{Eu},$ and Gd) determined by the measurements of κ , ν_s , and S .

CuO_6 octahedra are not tilted. The apical oxygens of the nearest CuO_6 octahedra approach the R^{3+} ion and those of the second nearest neighbors move away from the R^{3+} ion and so on, as if the ripple extends from the R^{3+} ion. Figure 4(b) shows the deformation around the R^{3+} ion in the LTO1 phase where the tilt axes of the CuO_6 octahedra are taken along the $[110]$ direction. By the superposition of the tilts of the CuO_6 octahedra induced by the R^{3+} ion and the tilts of the mother CuO_6 octahedra around the $[110]$ direction in the LTO1 phase, two LTT (or LTO2) regions appear around the R^{3+} ion as shown in Fig. 4(b). The tilt axes are different by 90° between these two LTT regions. The lower apical oxygens of the CuO_6 octahedra in the upper CuO layer are expected to move as shown by the small thin arrows in Fig. 4(b) in order to get the energy gain for the Coulomb interaction between the apical oxygens. Then, the tilt axis is rotated by 90° from layer to layer. The structural transition is induced when the LTT (or LTO2) region is connected by the percolation as mentioned above. The same is true when the ionic radius of the doped ion is larger than that of La^{3+} , as in the case of the Ba^{2+} ion. The only difference is the direction along which the apical oxygens of the CuO_6 octahedra around the Ba^{2+} ion move; that is, the apical oxygens of the first and second nearest CuO_6 octahedra move away from

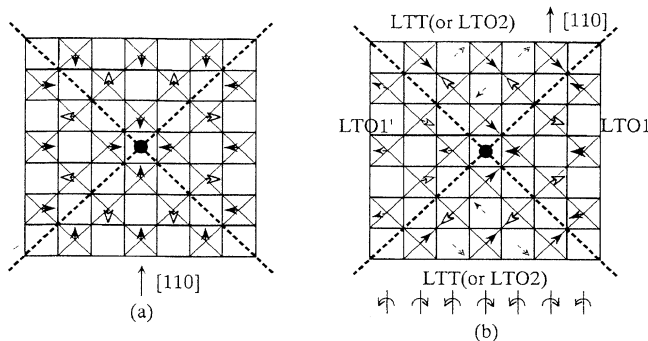


FIG. 4. Deformation of the CuO_6 octahedra around the substituted R^{3+} ion whose ionic radius is smaller than that of La^{3+} (a) when the mother CuO_6 octahedra are not tilted and (b) when R ion is doped in the LTO1 phase where the mother CuO_6 octahedra are tilted around the $[110]$ direction. The closed circle in the center means the substituted R^{3+} ion and La^{3+} ions are not drawn. The arrows indicate the motion of the apical oxygen of the CuO_6 octahedra and the small thin arrows indicate the motion of the lower apical oxygen of the CuO_6 octahedra of the upper CuO layer. While both LTO1 and LTO1' regions are orthorhombic, the tilting angle of the CuO_6 octahedra is larger in the LTO1 region than in LTO1' region.

and approach the Ba^{2+} ion, respectively. However, this difference between the R^{3+} and Ba^{2+} ions seems to be related to the different pressure dependences of T_{d2} between these two systems: dT_{d2}/dP is positive in the former and negative in the latter.^{17,18} In the present scheme, the coexistence of the LTO1 and LTT (or LTO2) phases is inevitable as shown in Fig. 4(b) and the volume fraction of the LTO1 region decreases with the decrease of temperature below T_{d2} as a result of the expansion of the LTT (or LTO2) region. These were really observed in $\text{La}_{1.875}\text{Ba}_{0.125}\text{CuO}_4$,¹⁹ where the LTT volume fraction increases with the decrease of temperature below T_{d2} and saturates to the value of $\sim 95\%$ below ~ 40 K. Although Ba^{2+} ions should be substituted at random, if we simply assume that Ba^{2+} ions are ordered as one Ba^{2+} ion for 4×4 La sites in $\text{La}_{1.875}\text{Ba}_{0.125}\text{CuO}_4$, the structural transition to the LTT phase is induced when the LTT region extends to the second nearest CuO_6 octahedra, which is consistent with the results by Billinge, Kwei, and Takagi.¹⁶ At the lowest temperature, the LTT region extends to the third or fourth neighbors and one Ba^{2+} ion forms two domains as shown in Fig. 4(b) and the domain size is ~ 10 Å. Furthermore, it is also expected that the LTT volume fraction is $\sim 30\%$ at T_{d2} and $\sim 90\%$ at the lowest temperature. The domain size of ~ 10 Å is the same order as the antiferromagnetic correlation length and the superconducting coherence length and seems to play some role in the suppression of T_c around $x \sim 1/8$, which was also pointed out by Billinge, Kwei, and Takagi.¹⁶ Of course, in a real compound, as Ba^{2+} ions are distributed at random, the domain size also should be distributed.

As Fig. 3 shows, according to the difference of the y_c values, the R dopings are classified into two groups, i.e., Nd and (Sm, Eu, Gd). In the latter systems, the y_c value is small ($0.05 \sim 0.03$) as mentioned above and the increase of T_{d2} with y above y_c is very large. On the other hand, in the case of Nd doping, the y_c value is not small and the increase of T_{d2} with y above y_c is much smaller than the latter systems. It is reported that in the case of Pr doping, the LTT or LTO2 phase does not appear even by as large an amount of doping as $y = 0.85$.²⁰ Then, the R dopings are classified into three groups of Pr, Nd, and (Sm, Eu, Gd). These classifications may be explained as follows. In the case of Pr doping, due to the small difference of the ionic radii between La^{3+} and Pr^{3+} ions, the effect of the tilts of the nearest CuO_6 octahedra does not extend even to the second nearest neighbors and therefore, the cooperative structural transition is not induced. In the case of Nd doping, the effect of the tilts of the CuO_6 octahedra around the Nd^{3+} ion extends to the second nearest neighbors at low temperatures and the structural transition to the LTT phase takes place at T_{d2} for $y > 0.13$. Because the appropriate amount of Nd^{3+} ion is already doped at y_c , the effect of Nd doping is leveled, which may be the reason why the increase of T_{d2} with y is rather small for $y > y_c$. In the case of Sm, Eu, and Gd dopings, the y_c value is small. When the effect of the tilts of the CuO_6 octahedra extends to more than fourth or fifth nearest neighbors at T_{d2} , the y_c value is expected to be small. If we estimate it as a result of the percolation of the LTT region simply by assuming that R^{3+} ions are ordered, for example, the y_c value is ~ 0.06 and ~ 0.03 when one R^{3+} ion is substituted for 6×6 and 8×8 La

sites, respectively. When the y_c value is small, there still remains a wide area of the LTO1 region at T_{d2} . Then, T_{d2} can be easily increased by further R doping into the LTO1 region. This may be the reason why the increase of T_{d2} with y above y_c is large in these systems.

It is known that in the case of $\text{La}_{2-y}\text{R}_y\text{CuO}_4$, the system is in the LTO2 phase below T_{d2} which is different from the LTT phase in $\text{La}_{1.875}\text{Ba}_{0.125}\text{CuO}_4$. Which phase of the LTT or LTO2 phase appears below T_{d2} seems to depend on whether T_{d1} is decreased or increased by the doping in La_2CuO_4 . When T_{d1} increases with y as in $\text{La}_{2-y}\text{R}_y\text{CuO}_4$, the orthorhombicity at low temperatures becomes larger than that of La_2CuO_4 by the doping. Then, because of this large anisotropy, it is difficult to induce the lattice distortion with the same amplitude Q_2 as Q_1 for the tilts of the CuO_6 octahedra in the LTO1 phase, which leads to the LTO2 phase. On the other hand, when T_{d1} decreases with x as in $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$, the orthorhombicity at low temperatures becomes smaller than that of La_2CuO_4 and it is easier to induce the distortion with $Q_1=Q_2$ leading to the LTT phase. This may be the reason why the LTO2 phase appears in $\text{La}_{2-y}\text{Nd}_y\text{CuO}_4$ and the LTT phase in $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ below T_{d2} . As for the contribution from the carrier introduced by Sr or Ba doping to the structural transition, it is considered as follows. It is known that the a axis of La_2CuO_4 is decreased by Sr or Ba doping regardless of its larger ionic radius than that of La^{3+} (Ref. 21), which indicates the important contribution from the carrier to the shrinkage of the CuO layer. As the a axis is dominated by the Cu-O distance, the decrease of the a axis means the decrease of the mismatch between the CuO and LaO layer. Then, we can say that the existence of the carrier introduced by Sr or Ba doping is favorable for the appearance of the LTT phase. T_{d2} of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ shows the maximum at ~ 70 K around $x \sim 0.14$ and decreases with x (Refs. 7 and 10) simply because T_{d1} decreases with x , i.e., the LTT phase is suppressed by the lowering of the HTT phase in a larger- x region, while T_{d2} of the Nd-doped system does not show such a behavior but shows the continuous increase with y because T_{d1} is monotonously increased by the doping.

Finally, we discuss the Cu-site-substitution effects on the physical properties of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$. It is known that the localization effect on the electrical resistivity by the Cu site substitution is large in a small- x region and small in a large- x region, the suppression of T_c by the Cu site substitution is large in a small- x region and small in a large- x region, and the suppression of T_c is larger by the Zn doping than by the Ni doping.²²⁻²⁴ While of course, the difference of the carrier concentration and the difference of the Ni^{2+} ion being magnetic and the Zn^{2+} ion being nonmagnetic should be taken into account, the above properties can be explained from the standpoint of the local distortion induced by the doping as follows. In a small- x region, due to the large orthorhombicity at low temperatures, the lattice is soft and the local distortion induced by the D doping is large as mentioned above. In a large- x region, because of the small orthorhombicity, the lattice is hard and the local distortion induced by the D doping is small. This may be related to the reason why the localization effect is larger in a small- x region than in a large- x region and the suppression of T_c by the D doping is larger in a small- x region than in a large- x region. As mentioned above, the lattice distortion induced by the D doping is larger in the Zn-doping case than in the Ni-doping case; this is possibly related to the larger suppression of T_c in the former than in the latter. In addition to the fact that Zn^{2+} is nonmagnetic and Ni^{2+} is magnetic, because the lattice distortion induced by the D doping is larger in the Zn-doping case than in the Ni-doping case, the antiferromagnetic correlation in the normal state is much more easily destroyed by the Zn doping than by the Ni doping. These may be related to the different Cu-site-substitution effects on the transport and magnetic properties in the normal state.²⁵⁻²⁷

The authors would like to thank Professor M. Arai, Professor Y. Endoh, Professor K. Asayama, Professor M. Sato, Professor T. Fujita, Professor M. Tachiki, and Professor T. Kasuya for stimulating discussions. This work is partly supported by Kasuya fund and by Grant-in-Aid for Scientific Research on Priority Areas "Science of High- T_c Superconductivity" given by Ministry of Education, Science and Culture, Japan.

¹A. R. Moudenaugh *et al.*, Phys. Rev. B **38**, 4569 (1988).

²J. D. Axe *et al.*, IBM J. Res. Dev. **33**, 382 (1989).

³M. Sera *et al.*, Solid State Commun. **69**, 851 (1989).

⁴M. Sera *et al.*, Solid State Commun. **76**, 923 (1990).

⁵M. K. Crawford *et al.*, Phys. Rev. B **44**, 7749 (1991).

⁶B. Büchner *et al.*, Physica C **185-189**, 903 (1991).

⁷T. Fukase *et al.*, Jpn. J. Appl. Phys. **7**, 213 (1992).

⁸B. Büchner *et al.*, Phys. Rev. Lett. **73**, 1841 (1994).

⁹T. Suzuki *et al.*, Phys. Rev. B **49**, 12 392 (1994).

¹⁰J. Yamada *et al.*, J. Phys. Soc. Jpn. **63**, 2314 (1994).

¹¹T. R. Thurston *et al.*, Phys. Rev. B **39**, 4327 (1989).

¹²M. Sera *et al.* (unpublished).

¹³J. Rodriguez-Carvajal *et al.*, J. Phys. Condens. Matter **3**, 3215 (1991).

¹⁴K. Yamada *et al.*, Phys. Rev. B **39**, 2336 (1989).

¹⁵G. H. Lander *et al.*, Phys. Rev. B **40**, 4463 (1989).

¹⁶S. J. L. Billinge *et al.*, Phys. Rev. Lett. **72**, 2282 (1994).

¹⁷B. Büchner *et al.*, Europhys. Lett. **21**, 953 (1993).

¹⁸K. Kumagai *et al.*, J. Phys. Soc. Jpn. **60**, 1448 (1991).

¹⁹S. J. L. Billinge *et al.*, Phys. Rev. Lett. **71**, 1903 (1993).

²⁰W. Schafer *et al.*, Phys. Rev. B **49**, 9248 (1994).

²¹E. Takayama-Muromachi and D. E. Rice, Physica C **177**, 195 (1991).

²²H. Fujishita and M. Sato, Solid State Commun. **72**, 529 (1989).

²³M. Sera *et al.*, J. Phys. Soc. Jpn. **62**, 281 (1993).

²⁴G. Xiao *et al.*, Phys. Rev. B **42**, 8752 (1990).

²⁵M. Sera *et al.*, Solid State Commun. **90**, 803 (1994).

²⁶M. Sera *et al.*, Solid State Commun. **92**, 289 (1994).

²⁷M. Hiroi *et al.*, Solid State Commun. **92**, 579 (1994).