Relationship between the lattice parameter and superconductivity in the 2-1-4 series n-type cuprates

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The superconductivity of $R_{2-x-y}La_yCe_xCuO_{4-\delta}$ (R=Nd, Gd, y=0, 0.2, 0.5,..., 1.4. x=0.10,..., 0.15,..., 0.25) series are studied. The solubility limit of La^{3+} in $Nd_{1.85-y}La_yCe_{0.15}CuO_{4-\delta}$ is determined to be y_{lim}=1.3, while the Ce-solubility limit increases to X_{lim}=0.25 in $Nd_{0.7-x}La_{1.3}Ce_xCuO_{4-\delta}$ with the maximum lattice parameter a=3.995 Å. The T_c^{on} and the bulk superconducting fraction are found to decrease with increasing La content. However, the reduction of superconductivity induced by increasing lattice constant a can be compensated by a proper decrease of Ce content irrespective of the lattice parameter a up to 3.982 Å. These results indicate that the lattice parameters are not directly related to the superconductivity. Actually, both the change of the a parameter and the Ce content x induce a variation in oxygen vacancies δ and result in the change of the charge-carrier density. Taking these facts into account, we give a simplified formula to calculate the charge-carrier density n_0 as $n_0=x+2\delta=x+2(Aa+Bx+C_0)$. In order to keep an optimum charge-carrier density for superconductivity, the variations in oxygen vacancies induced by the change of lattice parameter a must be compensated by an appropriate decrease of Ce dopant. This implies that the a parameter, doping concentration, oxygen vacancy, and the charge-carrier density can be taken into unified consideration, in which the charge-carrier density is considered to be a determining factor for superconductivity. [S0163-1829(97)06106-7]

I. INTRODUCTION

In the lanthanide series of $L_{2-x}Ce_xCuO_{4-\delta}$ compounds, n-type superconductivity is obtained for L=Pr, Nd, Sm, Eu, and diminishes up to L=Gd with L=La the only exception. All $L_2CuO_{4-\delta}$ compounds have a distorted K_2NiF_4 tetragonal structure, but the p-type superconductors have a T or T^* structure, whereas the n-type superconductors have a T' structure. The stabilization of such an intergrowth structure requires bond-length match across the intergrow interface. The degree of bond-length match between the intergrowth layers is expressed generally in terms of the Goldschmidt tolerance factor:[1]

$$t=(r_{Ln^{3+}}+r_{O^{2-}})/\sqrt{2}(r_{Cu^{2+}}+r_{O^{2-}}),$$

where $r_{Ln^{3+}}$, $r_{Cu^{2+}}$, and $r_{O^{2-}}$ refer to room-temperature ionic radii. A deviation from unity of the t value produces a bond-length mismatch between the intergrowth layers and results in a buildup of internal stresses in the layers. For example,[1] a room-temperature tolerance factor t=0.87 in La_2CuO_4 results in a compressive stress in the Cu-O bonds and a tensile

stress in the La-O bonds. On the other hand, the direct electrostatic repulsion between the negatively charged O^{2-} ions of the fluorite L-O_2-L layers in the L_2CuO_4 T' structure increases the lattice parameter a, which results in a tensile stress in the Cu-O bonds and a compressive stress in the L-O bonds. The presence of compressive vs tensile stress in the Cu-O bonds of the T and T' structure determines the p- vs n-type doping. So, the lattice parameter a of the T' structure is longer than that of the T structure. Whangbo *et al.*[2] have shown that the Cu-O bonds have antibonding character in the CuO_2 layer x^2-y^2 bands. The substitution of La^{3+} by Sr^{2+} corresponds to adding a hole or equivalently removing an electron from the x^2-y^2 bands. Thus, the removal of an electron from the antibonding band orbit would shorten the in-plane Cu-O bonds. In contrast, the Ce doping corresponds to adding electrons into the antibonding band orbit and thereby lengthening the in-plane Cu-O bond. Therefore, the variation of the lattice parameters is quite consistent with the fact that the T phase is doped by holes with a shortened a (p type) and the T' phase is doped by electron with a lengthened a (n type).

On the other hand, in the lanthanide series of $L_{2-x}Ce_xCuO_4$, from $L = La^{3+}$ to Gd^{3+}, the lattice constants of the tetragonal cell gradually decrease and $Gd_{2-x}Ce_xCuO_4$ ceases to be a superconductor. This leads to a hypothesis that sufficiently small in-plane Cu-O bonds inhibit electron-doped superconductivity. The compounds with $r_{L^{3+}} \leq r_{Gd^{3+}}$ fail to superconduct because the lattice spacing is too small to introduce electrons into the antibonding band orbit in CuO_2 plane. Kuklewicz and Markert[3] reported the steric effects on superconductivity in $(Nd_{1-y}Y_y)_{2-x}Ce_xCuO_{4-\delta}$ and found that lattice constants were reduced as more yttrium was substituted, and superconductivity was diminished when the lattice spacing decreased to nearly the same size ($a = 3.923$ Å when $y = 0.3$) as that of $Gd_{2-x}Ce_xCuO_{4-\delta}$ ($a = 3.902$ Å when $x = 0.15$). This seems to indicate that a small lattice spacing was the primary reason for the failure of $Gd_{2-x}Ce_xCuO_{4-\delta}$ to be a superconductor in literature.[3] Wang et $al.$[4] reported on the $R_{1.85-x}R'_xM_{0.15}CuO_z$ ($R = $Nd, Eu, $R' = $La, Y, $M = $Ce, Th, $z = 4$) series and thought that the a parameter for the optimum T_c ($T_c = 25$ K) for the lanthanum Ce-doped samples is between 3.945 and 3.955 Å. A dramatic decrease in T_c was observed when the lattice parameter a became either ≥ 3.96 Å or ≤ 3.94 Å, and in the $Nd_{1.85-x}Y_xCe_{0.15}CuO_{4-\delta}$ series, superconductivity was observed only for a≥ 3.94 Å. Therefore, they concluded that there is an optimum bond length (1.888 and 1.95 Å) for the maximum T_c in the La-Sr-Cu-O system and Nd-Ce-Cu-O system, respectively. Literature[5] reports that the substitution of a nonmagnetic Y for R in $(R_{1-x}R'_x)_{1.85}Ce_{0.15}CuO_4$ ($R = $Pr, Nd, Sm, Eu, $R' = $Gd, Y) has a stronger effect on the suppression of T_c than the substitution with magnetic Gd, suggesting that the effect of ionic size plays a much more important role than the magnetic pair breaking. They also considered that the suppression of superconductivity in $(R_{1-x}Y_x)_{1.85}Ce_{0.15}CuO_4$ ($R = $Pr, Nd, Sm, Eu) was strongly related to the structural distortion/instability and the value of x_c for the maximum T_c depended on the ionic size of R and was close to their solubility limit in those corresponding compounds. Michihito Muroi[6] investigated the whole p-type superconducting cuprates and thought that T_c increases either with the decrease of ΔV_M or with the decrease of d_p, in which d_p is the Cu-O bond length within the CuO_2 plane and ΔV_M is the difference between the Madelung site potential for a hole on a Cu site and that on an O site.

In summary, many authors considered that the Cu-O bond length in the CuO_2 plane is very important or crucial to induce superconductivity. Nevertheless, in spite of these suggestions mentioned above, there are still some controversies. So (Nd,La,Ce)-Cu-O, (Gd,La,Ce)-Cu-O and related compounds are studied to determine whether the steric effect is the truly main factor for superconductivity. Based on our experimental results, we suggest that the steric effect is not the main reason in nature for the great influence on superconductivity, and that the charge-carrier density might be a more fundamental factor.

II. EXPERIMENT

Our samples were prepared by a solid-state reaction using the related oxides as the starting materials. The mixtures were repeatedly ground with an Agate mortar, sintered in a box furnace at 1000 °C in air, and finally pelletized into thin sheets. After the procedure was repeated 3–4 times, these samples were sintered at a temperature of 1050 °C for 24 h in a box furnace in air, followed by sintering at 1050 °C for 12 h in a tube furnace containing slowly flowing dry N_2 to reduce the samples. The rates of rising and lowering furnace temperature were 2 and 4 °C/min, respectively.

X-ray-diffraction analysis was performed on a M18AHF x-ray diffractometer with Cu Kα radiation (50 kV $\times$ 200 mA). High-purity Si was added to the samples as an internal standard to correct the 2θ position of diffraction peaks.

The magnetic susceptibility and electrical resistance are measured by a superconducting quantum interference device (SQUID) and the standard four-probe technique, respectively. The superconducting critical temperature is measured down to 4.2 K.

III. RESULTS AND DISCUSSION

A. Effects of lattice parameter variation

The samples of $Nd_{2-x-y}La_yCe_xCuO_{4-\delta}$ ($y = 0$, 0.2, 0.5, 0.7, 0.9, 0.95, 1.0, 1.1, 1.2, 1.3, 1.4, $x = 0.12$, 0.15, 0.17, 0.20, 0.25) series are first prepared. The pure T' phase can be obtained up to $y = 1.3$. Therefore, the solubility limit of La^{3+} in $Nd_{1.85-y}La_yCe_{0.15}CuO_{4-\delta}$ is $y_{lim} = 1.3$ with the lattice parameter $a = 3.994$ Å. On the other hand, the Ce solubility limit increases to $X_{lim} = 0.25$ in $Nd_{0.7-x}La_{1.3}Ce_xCuO_{4-\delta}$ with the maximum lattice parameter $a = 3.995$ Å as shown in Table I. Figure 1 gives the variations of the lattice parameters a, c, V with increasing La content. It can be seen that the lattice parameters a, c, V increase linearly with increasing La content up to $y = 1.3$. The ratio of $\Delta a / \Delta y$ is approximatly 2.6%. The ratio of c/a increases with increasing La content and decreases with increasing Ce content between 3.05 and 3.09. Manthiram[8] considered that the larger the size of L^{3+} in the L_2CuO_4 series, the easier it is to stretch the Cu-O bonds by the addition of antibonding electrons into the CuO_2 sheets. Therefore, as the size of L^{3+} increases from $L = $Nd to $L = Nd_{0.7-x}La_{1.3}$, the extent to which the Cu-O bonds can be stretched by the substitution of Ce^{4+} for L^{3+} increases, i.e., the solubility of Ce increases with increasing size of L^{3+} or the a parameter. In the $Nd_{2-x}La_xCuO_{4-\delta}$ series, literature[7,8] reported that the T' structure remained only when $x \leq 0.8$–0.9. However, the doping of Ce^{4+} improved the stability of the T' structure and increased the solubility of La^{3+} in the $Nd_{2-x-y}La_yCe_xCuO_{4-\delta}$ T' structure from $y = 0.8$ to $y = 1.2$–1.3,[1] vice versa, the doping of La^{3+} improved the solubility of Ce^{4+} in the T' structure from $X_{lim} = 0.15$ when $L = $Gd to $X_{lim} = 0.25$ when $L = Nd_{0.45}La_{1.3}$. Zhu and Manthiram[1] improved the Ce solubility limit to $x_{lim} = 0.25$ in $Nd_{0.45}La_{1.3}Ce_{0.25}CuO_{4-\delta}$ which was considered to be the maximum Ce solubility and the longest a parameter (3.993 Å) that one can achieve in the T' structure.

The T_c^{on} and the bulk superconducting contents are found to decrease with increasing La content by the measurement of SQUID for $Nd_{1.85-y}La_yCe_{0.15}CuO_{4-\delta}$, whereas the T_c^{on} remains constant by the standard four-probe resistant technique, as is shown in Table I. We know that the four-probe

TABLE I. The results of the lattice parameters and superconductivity of $Nd_{2-x-y}La_yCe_xCuO_{4-\delta}$.

x	y	a (Å)	c (Å)	V (Å^3)	c/a	T_c^{on}	T_c^0	Mag. suscept.
0.15	0.0	3.9552(5)	12.124(1)	189.68	3.0653	26 K	17 K	24 K
0.15	0.2	3.9632(6)	12.157(2)	190.46	3.0675	26 K	12 K	23 K
0.15	0.5	3.9703(3)	12.209(1)	192.47	3.0753	26 K		18 K
0.15	0.7	3.9786(4)	12.249(1)	193.90	3.0787	26 K		18 K
0.15	0.95	3.9791(6)	12.267(2)	194.23	3.0829	26 K		
0.15	1.0	3.9828(5)	12.300(1)	195.12	3.0880	26 K		15 K
0.15	1.1	3.983(1)	12.303(7)	195.22	3.089	26 K		10 K
0.10	1.1	3.9821(7)	12.317(6)	195.31	3.093	27 K	15 K	23 K
0.12	1.1	3.987(2)	12.299(6)	195.60	3.085	26 K	10 K	17 K
0.25	1.1	3.9871(9)	12.234(5)	194.50	3.068			
0.15	1.2	3.9876(9)	12.283(6)	195.33	3.081	26 K		
0.15	1.3	3.9947(6)	12.307(5)	196.40	3.081			
0.20	1.3	3.994(1)	12.289(4)	196.08	3.0769			
0.25	1.3	3.995(1)	12.271(3)	195.58	3.071			
0.15	1.4	3.9935(5)	12.286(4)	195.95	3.076			

resistance measurement might give a surface or filamentary effect of superconductivity and the measurement of SQUID means a bulk effect of superconductivity. The samples of $Nd_{1.85-y}La_yCe_{0.15}CuO_{4-\delta}$ maybe contain a little amount of the $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ contents, and so remain superconducting with $T_C^{on}=26$ K but cannot reach zero resistance. As an example, the curve of ρ-T and the signal of

FIG. 1. Variations of the lattice parameters a, c, V with increasing La content in $Nd_{1.85-y}La_yCe_{0.15}CuO_{4-\delta}$.

ac magnetic susceptibility for $Nd_{1.15}La_{0.7}Ce_{0.15}CuO_{4-\delta}$ is given in Fig. 2. On the other hand, the measurement of SQUID truly reflects the bulk superconductivity of $Nd_{1.85-y}La_yCe_{0.15}CuO_{4-\delta}$. Then, could we make a conclusion that the lattice parameters are the crucial factor for superconductivity? This has been broadly emphasized in many papers.[3,5,6] However, when the Ce content is decreased from $x=0.15$ to $x=0.10$ in $Nd_{0.9-x}La_{1.1}Ce_xCuO_{4-\delta}$, the optimum T_c is found to be recovered again with $T_c=23$ K and a superconducting fraction of 23.5% by the SQUID measurement in a field of 10 G s as seen in Fig. 3. Similar results have been reported by others.[1] In other words, the superconductivity with a superconducting fraction of 23.5% and $T_c^{on}=23$ K is found in the $Nd_{0.8}La_{1.1}Ce_{0.1}CuO_{4-\delta}$ sample with the lattice parameters $a=3.982$ Å, $c=12.317$ Å. This indicates that the same superconductivity with different lattice parameters can be achieved in $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ and $Nd_{0.8}La_{1.1}Ce_{0.10}CuO_{4-\delta}$ as is shown in Table II for a comparison.

Why does the same superconductivity exist in $Nd_{0.8}La_{1.1}Ce_{0.10}CuO_{4-\delta}$ as in $Nd_{1.85}La_{0.15}CuO_{4-\delta}$, but not in $Nd_{0.75}La_{1.1}Ce_{0.15}CuO_{4-\delta}$? In other words, with the radii of L^{3+} ion or a parameter increasing, the optimum Ce content for the superconductivity in $Nd_{0.9-x}La_{1.1}Ce_xCuO_{4-\delta}$ decreases irrespective of the increase of the Ce solubility. This means that the superconductivity is not closely related to the relief of the internal stress, moreover, it is opposite to it. Manthiram[8] considered that as the Cu-O bond length in the undoped L_2CuO_4 decreased from $LaNdCuO_4$ to Gd_2CuO_4, a large amount of Ce content is necessary to decrease E_M-E_I to the critical limit $E_M=E_I$ that can give a critical covalence λ_c in the CuO_2 sheets and induce superconductivity, in which the E_M is the electrostatic Madelung energy gained by allowing the point charges Cu^{2+} and O^{2-} to order themselves in a crystalline lattice, and E_i is the total energy required to transfer an electron from a Cu^+ ion to an O^- ion at infinite separation. Finally, they concluded that the change of Ce content for T_c^{max} is only for shortening or lengthening the a parameter so as to adjust E_M to a proper
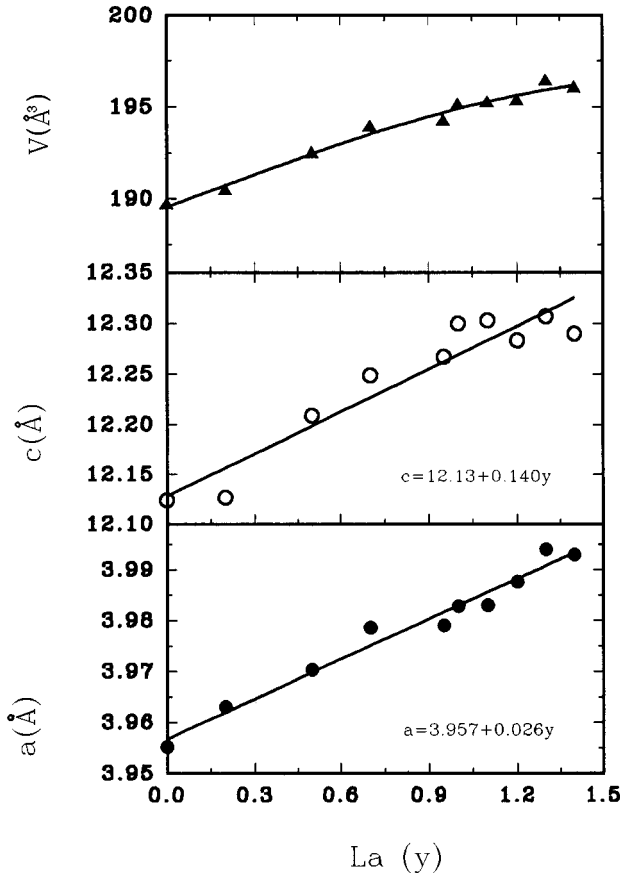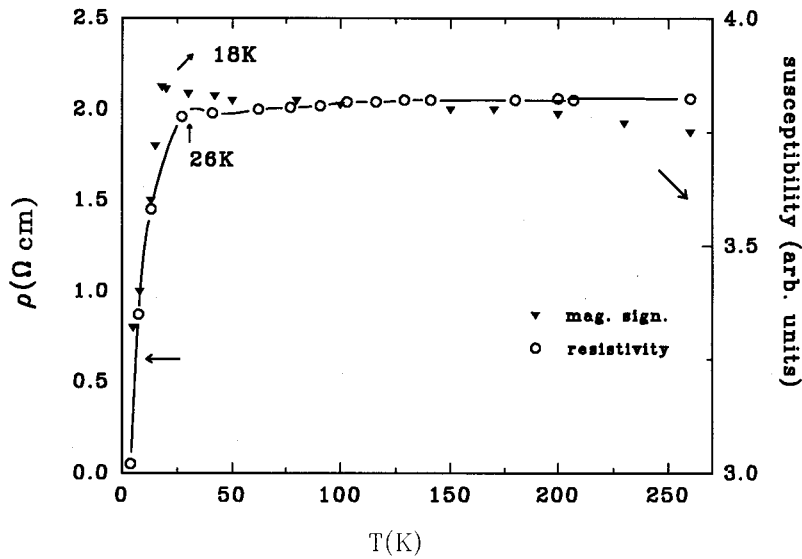
FIG. 2. The curves of ρ-T and the signal of ac magnetic susceptibility for $Nd_{1.15}La_{0.7}Ce_{0.15}CuO_{4-\delta}$.

value. But, why is the change of the a parameter by only changing La content not enough to adjust E_M or λ_c ($\lambda = b^{ca}/\Delta E, \Delta E = E_M - E_I$) (Ref. 8) for the optimum superconductivity? Why is the Ce doping necessary for superconductivity? Furthermore, for an unchanged T_c, the change of lattice parameter a needs a corresponding inverse change of Ce content. This means that the reduction of superconductivity induced by the increase of lattice constant a can be compensated by a proper decrease of Ce content irrespective of the lattice parameter a up to 3.982 Å. If we assume that the Madelung energy is sensitive to the a parameter, could the great decrease of the Madelung energy introduced by such a big lattice parameter $a = 3.982$ Å be compensated by the decrease of Ce content from 0.15 to 0.10? This is puzzling to us. Although the variation of Ce doping also changes the lattice constant a, it is much smaller than that induced by La doping.

B. Correlations of oxygen vacancy, lattice parameter a, and Ce content

Zhu and Manthiram[1] and Zhou et al.[9] found that the variation of the a parameter could result in a change of oxygen vacancies δ. The magnitude of δ increases with the increasing lattice parameter a, i.e., with the stretching of the Cu-O bond. This observation is consistent with the great internal stress to be relieved by such a self-doping.[9] The literature[17] also indicates that there is a general trend of a decrease in oxygen content as the lattice parameter increases, which is common to many cuprates. This can be explained in terms of the Goldschmidt tolerance factor. Creation of oxygen vacancies by increasing the a parameter in $L_{2-x}Ce_xCuO_{4-\delta}$ introduces antibonding electrons into the CuO_2 sheets, which can relieve the tensile stress in the Cu-O bonds. Also, oxygen vacancies in the $(L, Ce)_2O_2$ fluorite layer can reduce the electrostatic repulsion between the O^{2-} ions and the compressive stress in the (L, Ce)-O bonds.[1] This prompts us to pay attention to oxygen vacancies. The oxygen vacancies might play an important role in superconductivity by affecting the charge-carrier density. It is the change of the lattice parameter which induces the variation in oxygen vacancies and furthermore results in the change of charge-carrier density. For the n-type 2-1-4 series of cuprate superconductors, Zhu and Manthiram[1] also ascertained that creation of oxygen vacancies in
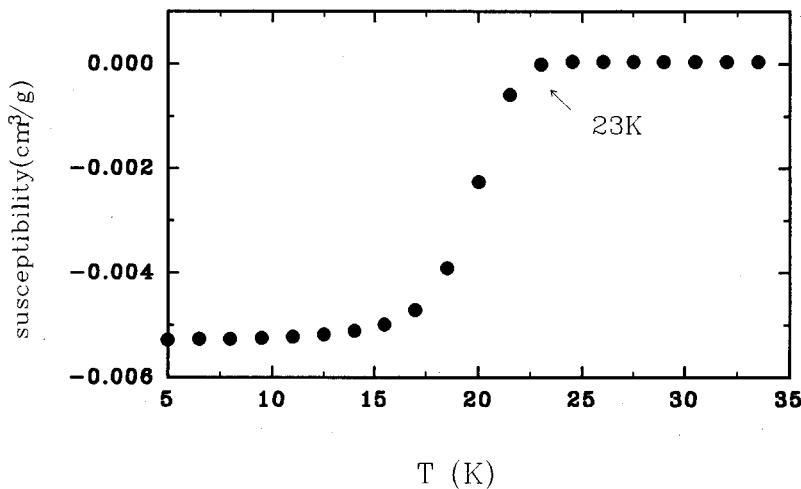

FIG. 3. Temperature dependence of magnetic susceptibility for $Nd_{0.8}La_{1.1}Ce_{0.1}CuO_{4-\delta}$ with $T_c = 23$ K and a superconducting phase content of 23.5% by the SQUID measurement in a field of 10 G s.

TABLE II. A comparison of the lattice parameters and superconductivity of $Nd_{2-x-y}La_yCe_xCuO_{4-\delta}$.

x	y	a (Å)	c (Å)	V (Å^3)	T_c^{on} (SQUID)	Superc. fract.
0.15	0.0	3.9552(5)	12.124(1)	189.68	24 K	20.4%
0.15	1.1	3.983 (1)	12.303(7)	195.22	14.5 K	6.0%
0.10	1.1	3.982 (7)	12.317(3)	195.31	23 K	23.5%

$L_{2-x}Ce_xCuO_{4+\delta}$ was an essential factor to achieve super-conductivity, as has been broadly suggested in the literature.[10,11] Likewise, for La-series p-type superconductors, La_2CuO_4 is not superconducting, but the system of $La_2CuO_{4+\delta}$ is a single phase superconductor for $0.05 < \delta \leqslant 0.09$,[9,12] with T_c above 30 K by annealing powders or single crystals at high oxygen pressure.[13] As we know, in $RBa_2Cu_3O_{7-\delta}$, the superconductivity is independent of R^{3+} except for Pr^{3+}, but closely depends on δ. The critical temperature T_c in $RBa_2Cu_3O_{7-\delta}$ is strongly dependent on the sample history as well as oxygen content.[5,7,8,14–16] In addition, many authors[12,13] have shown that the physical properties are extremely sensitive to $\leqslant 1\%$ change in the oxygen content. For example, resistivity, Neél temperature (T_N), the Cu-Cu exchange coupling, and the transition temperature (T_0) from the tetragonal to orthorhombic structure all increase with decreasing oxygen content. A consistent interpretation of these facts is that the oxygen stoichiometry is always richer than that corresponding to a Mott-Hubbard insulator with an exactly half-filled band.[13] All suggestions apparently emphasized the important role of oxygen content, oxygen valence state or copper valence state on superconductivity. We know that n-type superconductivity can be greatly influenced by four important conditions as described below: (i) necessary annealing process in an inert atmosphere; (ii) the change of annealing temperature; (iii) a certain amount of Ce (Th) doping; (iv) variation of lattice parameter a.

All four factors are found to be closely correlated with the oxygen content. Annealing of $L_{2-x}Ce_xCuO_{4-\delta}$ in an inert atmosphere at a certain temperature range is essential to induce the superconductivity. Wang et al.[4] concluded that the role of the nitrogen treatment is twofold: (i) to remove extra oxygen (either "apical" or fluorite type) within the structure and (ii) to increase the number of carriers (electrons) through the reduction of Cu^{2+} to Cu^{1+}. In addition, three types of oxygen (oxygen in the CuO_2 plane, fluorite type, and apical $4d$ sites) were considered to exist in the $Nd_{2-x}Ce_xCuO_{4-\delta}$ compounds, but we cannot presently distinguish between these two possibilities (apical versus fluorite-type oxygen) and only further neutron work may resolve this issue. They[4] also considered that a critical parameter which affects T_c in the T' phase was the oxygen content. In summary, the superconducting properties can be varied by changing the oxygen content (thereby the Cu oxidation state) through processing conditions.[4]

Regarding the Nd-La-Ce-Cu-O series, Zhu and Manthiram[1] reported that the synthesis of $Nd_{2-x-y}La_yCe_xCuO_{4-\delta}$ for $0 \leqslant y \leqslant 1.0$ had also enabled them to monitor the variation of oxygen content by changing the size of L^{3+} for a fixed Ce content $x = 0.12$ and a given

N_2-annealing temperature (950 °C). They[1] give the variation of oxygen vacancies with the lattice parameter a, so this may be linearly fitted as:

$$\delta_a = 0.31a - 1.20. \tag{1}$$

This means that the change of oxygen vacancies $\Delta\delta$ is proportional to the change of lattice parameter Δa by the ratio of 0.3 as a first-order approximation.

On the other hand, a quite interesting result is that the δ increased with decreasing Ce-doped content. This implies that the insertion of Ce reduces the ability of these materials to change reversibly oxygen stoichiometry. Independent of the Ce content, the oxygen content in the as-grown material was always greater than four. Upon nitrogen reduction, the extra oxygen (occupying the $4d$ position, i.e., apical position) and fluorite-type oxygen were partially removed and became superconducting. So both annealing in N_2 and Ce doping are necessary for superconductivity and are correlated with the gain or loss of oxygen content in n-type superconductors, i.e., formation of the oxygen vacancies.[4] For a certain L^{3+} ion and a given N_2-annealing temperature, the total oxygen content increases with increasing Ce content. Using the data in $LaNd_{1-x}Ce_xCuO_{4-\delta}$, from Ref. 1, we can obtain the following formula by linear fitting:

$$\delta_x = -0.33x + 0.05. \tag{2}$$

Equations (1) and (2) give us a clear expression of the correlations between oxygen vacancy δ, Ce-doped content x, and lattice parameter a, although these expressions are only first-order approximations. The change of a parameter and Ce doping all independently induce the change of oxygen vacancies and change the charge-carrier density. For our samples of $Nd_{2-x-y}La_yCe_xCuO_{4-\delta}$, the charge-carrier density is improved by increasing the lattice parameter and also by decreasing the Ce content through increasing the oxygen vacancies. For this reason, it may be necessary to reduce the Ce content so as to keep the carrier density to an optimum value for superconductivity.

C. Charge-carrier density—one of the determining factors for superconductivity

As we know, for the $L_{2-x}Ce_xCuO_{4-\delta}$ series, the substitution of one Ce^{4+} ion for one L^{3+} ion can give one extra electron as the conducting charge carrier, and the creation of one oxygen vacancy can give equivalently two electrons. So, the charge-carrier density can be written as: $n = x + 2\delta$, where x is the Ce-doped mole concentration and δ is the oxygen vacancy density. Meantime, the δ is determined by

two factors: the Ce doping and a parameter in our experimental conditions. So, Eqs. (1) and (2) are introduced into the n formula:

$$n = x + 2(\delta_a + \delta_x)$$
$$= x + 2(0.3a - 1.0) + 2(-0.33x + 0.05)$$
$$= 0.34x + 0.62a - 2.30$$

then,

$$\Delta n = 0.34\Delta x + 0.62\Delta a.$$

We assume that the charge-carrier density has an optimum constant n_0 for the optimum superconductivity, i.e., to keep $\Delta n_{(n=n_0)} = 0$. So, we obtain that

$$\Delta x / \Delta a \approx -0.62/0.34 \approx -1.82 (\text{mol}/\text{Å}). \quad (3)$$

This means that the increase of the a parameter induces the increase of oxygen vacancies and thus increases the charge-carrier density. In order to keep the charge-carrier density unchanged for the optimum superconductivity, the optimum Ce content must be decreased by the ratio of "-1.83" to reduce the charge-carrier density. In other words, the charge-carrier density is intrinsically crucial to the superconductivity, which is jointly affected by the variations of the a parameter and Ce doping by changing the oxygen vacancies and adding electrons.

If this conclusion is common, we can derive from Eq. (3) that the Ce content in $Nd_{2-x}Ce_xCuO_{4-\delta}$ is $x = 0.15$ for the optimum superconductivity with $a = 3.955$ Å, and then, the Ce content in $Nd_{0.9-x}La_{1.1}Ce_xCuO_{4-\delta}$ should be $x = 0.10$ with $a \approx 3.983$ Å, which is very consistent with our results as seen in Table II. Therefore, a conclusion is made: the change of the a parameter can result in a change of oxygen vacancies and change the charge-carrier density, the optimum superconductivity can be obtained again as long as the adjustment to Ce content properly compensates the change of charge-carrier density. Goldschmidt et al.[17] also pointed out that the magnitude of the lattice parameter had no direct effect on T_c which becomes more evident when comparing samples having the same T_c but with different lattice parameters. This suggests that the changes in T_c and the variation

TABLE III. Relation among T_c. Ce doping and lattice parameters (La doping) of $Nd_{2-x-y}La_yCe_xCuO_{4-\delta}$.

x	y	a (Å)	c (Å)	T_c^{on}	T_c^0	$T_{magnet.}$
0.15	0.0	3.955	12.124	26 K	17 K	23 K
0.14	0.2	3.961	12.162	26 K	13 K	23 K
0.13	0.4	3.965	12.179	26 K	13 K	22 K
0.12	0.6	3.969	12.212	26 K	14 K	23 K
0.11	0.8	3.974	12.268	26 K	13 K	24 K
0.10	1.0	3.980	12.311	26 K	15 K	23 K

in lattice parameters that occur concurrently under pressure are not directly related to one another. Also, Zhu and Manthiram[1] finally concluded that the apparent increase in the value of x_c (the Ce content in $L_{2-x}Ce_xCuO_{4-\delta}$ for the best superconductivity) with decreasing L^{3+} ion size was due to the decreasing number of oxygen vacancies and that the influence of Madelung energy or charge-transfer gap Δ was less significant in determining the critical amount of doping necessary to induce a transition from antiferromagnetic semiconductor to superconductor.

To testify further the relationship between the lattice parameter a and the doped Ce content, samples of the $Nd_{2-x-y}La_yCe_xCuO_{4-\delta}$ series are prepared as ascribed in Table III. The measurements of electrical resistance and magnetic susceptibility indicate a good and similar superconductivity. Figure 4 gives the curve of ρ-T and the ac magnetic susceptibility signal for $Nd_{1.28}La_{0.6}Ce_{0.12}CuO_{4-\delta}$, for instance. The same T_c are obtained but the lattice parameters change from 3.95 to 3.98 Å, which further testifies that the critical temperature T_c is not directly related to the a parameter, and the decrease of Ce content can recover the damage of superconductivity induced by the increasing a parameter. Figure 5 gives the relation between a parameter and Ce content by the ratio of -2.03 for keeping the unchanging optimum superconductivity. These results have little difference from "-1.8 ratio," which is obtained only from $Nd_{2-y-0.12}La_yCe_{0.12}CuO_4$.[1] The exact ratio needs more common experimental data.

Furthermore, we extrapolate the conclusion to a smaller L^{3+} ion than Nd^{3+} in $L_{2-x}Ce_xCuO_{4-\delta}$. For example, the samples of the $Nd_{2-x-y}Y_yCe_xCuO_{4-\delta}$ series are prepared with the fixed sample-prepared procedure. Kuklewicz and

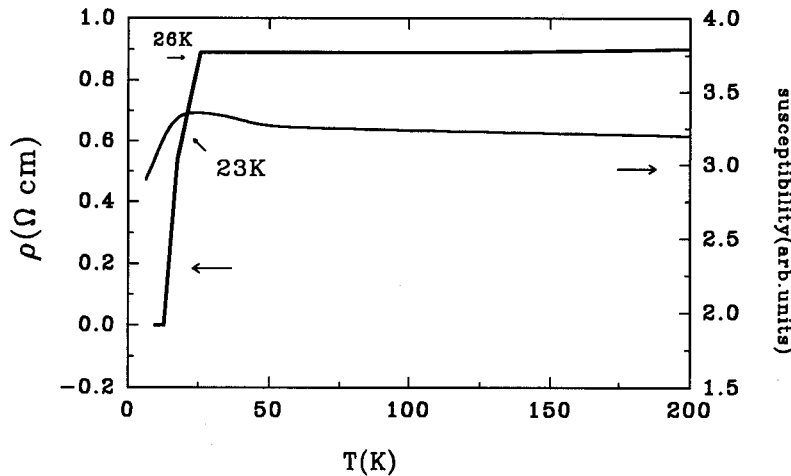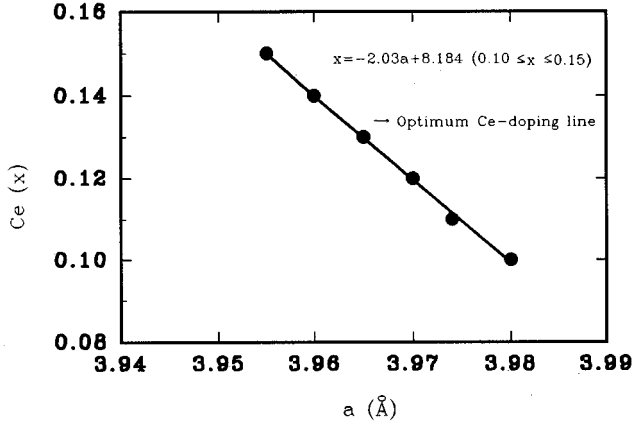FIG. 4. The curves of ρ-T and the ac magnetic susceptibility signal for $Nd_{1.28}La_{0.6}Ce_{0.12}CuO_4$.

FIG. 5. Relation between the a parameter and the optimum Ce content (x) for keeping the unchanging optimum superconductivity of $Nd_{2-x-y}La_yCe_xCuO_{4-\delta}$.

Markert[3] reported that $Nd_{1.85-y}Y_yCe_{0.15}CuO_{4-\delta}$ ceased to be superconducting as the lattice parameter a decreased to 3.925 Å when $y=0.555$. Could we recover its superconductivity by adding the Ce content according to the -1.8 ratio? We prepared the samples of the $Nd_{1.445-x}Y_{0.555}Ce_xCuO_{4-\delta}$ ($x=0.18$, 0.20) series and found that it fails to recover its superconductivity. This may be due to the smaller Ce solubility limit (< 0.15) which cannot dope enough Ce content in this system.

D. Attempting superconductivity in $Gd_{2-x-y}La_yCe_xCuO_{4-\delta}$

On the other hand, Kuklewicz and Markert[3] considered that the $Gd_{1.85}Ce_{0.15}CuO_{4-\delta}$ samples failed to be a superconductor due to steric effects, which resulted in an insufficient electron concentration or apical-oxygen-induced electron localization. In addition, Zhu and Manthiram[1] suggested that the smaller Gd^{3+} ion limited the Ce solubility to $X_{lim}=0.15$. The electron concentration $n=0.15$ at $x_{lim}=0.15$, was much less than the n_c value of 0.175 ± 0.005 required to induce superconductivity. Although n can further be increased in other systems with large L^{3+} ions via the creation of oxygen vacancies, such a mechanism does not seem to work with the smaller $L=Gd$. A stronger bond-

TABLE IV. The results of the composition and lattice parameters of $Gd_{2-x-y}La_yCe_xCuO_{4-\delta}$.

| x	y	a (Å)	c (Å)	V (Å^3)	c/a
0.15	0.3	3.9194(3)	11.917(1)	183.06	3.0408
0.15	0.5	3.9295(8)	11.974(3)	184.89	3.0476
0.15	0.8	3.9435(8)	12.063(3)	187.59	3.0593
0.15	0.9	3.9558(7)	12.117(3)	189.63	3.0637
0.15	1.0	3.957(7)	12.130(6)	189.93	3.0650
0.15	1.1	3.9645(4)	12.182(2)	191.48	3.0734
0.15	1.2	3.976(3)	12.256(3)	193.79	3.0825
0.12	1.0	3.952(1)	12.134(6)	189.60	3.0703
0.17	1.0	3.9581(6)	12.118(2)	189.85	3.0598
0.19	1.0	3.9606(3)	12.099(6)	189.80	3.0545
0.20	1.0	3.968(2)	12.110(3)	190.70	3.0519
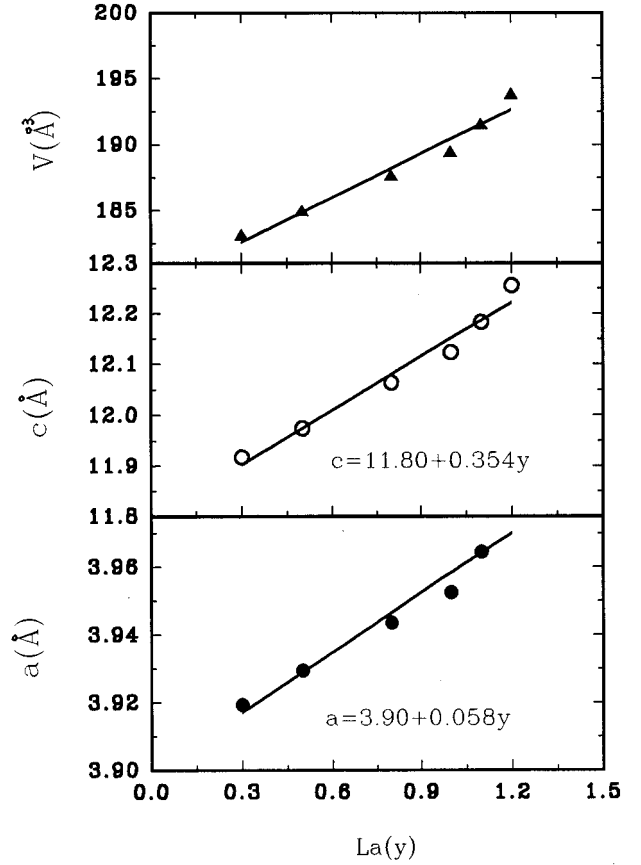
FIG. 6. Variation of the lattice parameters a, c, V with increasing La content in $Gd_{1.85-y}La_yCe_{0.15}CuO_{4-\delta}$.

ing between smaller Gd^{3+} and O^{2-} ions and a nearly complete relief of the internal stresses near the Ce solubility limit $x_{lim}=0.15$ in $Gd_{1.85}Ce_{0.15}CuO_{4-\delta}$ make it difficult to create oxygen vacancies in the compound.[1] Manthiram[8] suggested that probably it would become a superconductor if one could increase the solubility limit of Ce in $Gd_{2-x}Ce_xCuO_{4-\delta}$ beyond 0.15. Also according to our result of the -1.8 ratio, the Ce content for the best superconductivity should be more than $x=0.15$ in $Gd_{2-x}Ce_xCuO_{4-\delta}$ because the size of Gd^{3+} ion is smaller than that of Nd^{3+}, but the $x=0.15$ in $Gd_{2-x}Ce_xCuO_{4-\delta}$ is the highest Ce solubility limit. Therefore, we try to lengthen the lattice parameter a to induce more Ce content or oxygen vacancies into $Gd_{2-x}Ce_xCuO_4$ by the substitution of La^{3+} for Gd^{3+}, i.e., $Gd_{2-x-y}La_yCe_xCuO_{4-\delta}$ samples are prepared. Table IV and Fig. 6 give the results of the composition and lattice parameters of $Gd_{2-x-y}La_yCe_xCuO_{4-\delta}$ samples.

The lattice parameters a, c increase linearly with increasing La content with the ratio (Å/mole) of 5.8 and 35.4 %, respectively. Unfortunately, superconductivity is not found in the Gd-containing series. In other words, this also testifies that the lattice parameters a, c are not the crucial factor to induce superconductivity, because the $a=3.957$ Å, $c=12.130$ Å in $Gd_{0.85}LaCe_{0.15}CuO_{4-\delta}$ is the same as that of $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$. In addition, we change the Ce content from $x=0.12$ to $x=0.17$, 0.19, 0.20 and find that the a parameter increases and the c parameter decreases with increasing Ce content, which means that the increasing of Ce

content does introduce antibonding electrons into the CuO_2 plane, but still does not find any superconductivity. Maybe the N_2-annealing temperature is too high (1050 °C) to induce superconductivity. So, we prepare again the $Gd_{0.88}LaCe_{0.12}CuO_{4-\delta}$ and $Gd_{0.83}LaCe_{0.17}CuO_{4-\delta}$ samples with a N_2-annealing temperature of 800 °C, but no superconductivity is observed. Why is there such a big difference in superconductivity between $Gd_{0.85}LaCe_{0.15}CuO_{4-\delta}$ and $Nd_{0.85}LaCe_{0.15}CuO_{4-\delta}$? Are there other important factors for inducing superconductivity between Gd^{3+} and Nd^{3+} except for the difference of ion radii? As to the influence of the magnet in Gd^{3+} on superconductivity, many authors[3,10,13] had negated the opinion. More recently, Braden and co-workers[18,19] reported that a long-range lattice deformation characterized by the rotation of the CuO_2 squares around the c axis was observed in Gd_2CuO_4 and $(Nd_{1-x}Tb_x)_{1.85}Ce_{0.15}CuO_4$ by neutron-diffraction structural analysis. They suggested that this structural distortion might help to explain the nonexistence of superconductivity in $Gd_{2-x}Ce_xCuO_4$. This needs further experiment to clarify the problem, especially, whether there does exist the same structural distortion in $Gd_{1-x}LaCe_xCuO_{4-\delta}$.

In summary, superconductivity in the cuprate oxides is not directly or intrinsically correlated with the lattice parameters a. The charge-carrier density is one of the crucial factors that influences intrinsically the superconductivity. Of course, $Gd_{2-x}Ce_xCuO_4$ fails to be a superconductor perhaps because the CuO_2 planes are not integrated according to Refs. 18 and 19.

IV. CONCLUSION

The superconductivity of the $R_{2-x-y}La_yCe_xCuO_{4-\delta}$ (R = Nd, Gd, y = 0, 0.2, 0.5, . . . , 1.4. x = 0.10, . . . , 0.15, . . . , 0.25) series are studied and the solubility limit of La^{3+} in $Nd_{1.85-y}La_yCe_{0.15}CuO_{4-\delta}$ is y_{lim} = 1.3 with the maximum lattice parameter a = 3.994 Å. The Ce solubility limit increases to X_{lim} = 0.25 in $Nd_{0.7-x}La_{1.3}Ce_xCuO_{4-\delta}$ with the maximum lattice parameter a = 3.995 Å. The T_c^{on} and the bulk superconducting content are found to decrease with increasing La content. However, the reduction of superconductivity caused by the increase of lattice constant a (up to 3.982 Å) can be compensated by the decrease of Ce content by a certain ratio.

The lattice parameters are not directly and intrinsically related to the superconductivity. The charge-carrier density is suggested to be intrinsically the crucial factor for superconductivity. The effects of lattice parameter and oxygen vacancy on superconductivity are made through changing the charge-carrier density. The influence of lattice parameter and Ce doping on superconductivity can be compensated by each other.

$Gd_{0.85}LaCe_{0.15}CuO_{4-\delta}$ is prepared with the lattice parameters of a = 3.957 Å, c = 12.130 Å, which are the same as that of $Nd_{0.85}Ce_{0.15}CuO_{4-\delta}$. But it fails to superconduct which further indicates that the a parameter is not intrinsically the crucial factor for its superconductivity. In addition, no superconductivity is found with the change of Ce content and sintering temperature in $Gd_{1-x}LaCe_xCuO_{4-\delta}$.

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